Nanoparticle Assembly

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Synthesis and Assembly of Dipolar Heterostructured Tetrapods: Colloidal Polymers with "Giant *tert-butyl*" Groups

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Abstract: *We report on the first synthesis of a heterostructured semiconductor tetrapod from CdSe@CdS that carries a single dipolar nanoparticle tip from a core–shell colloid of Au@Co. A four-step colloidal total synthesis was developed, where the key step in the synthesis was the selective deposition of a single AuNP tip onto a CdSe@CdS tetrapod under UV-irradiation. Synthetic accessibility to this dipolar heterostructured tetrapod enabled the use of these as colloidal monomers to form colloidal polymers that carry the semiconductor tetrapod as a side chain group attached to the CoNP colloidal polymer main chain. The current report details a number of novel discoveries on the selective synthesis of an asymmetric heterostructured tetrapod that is capable of 1D dipolar assembly into colloidal polymers that carry tetrapods as side chain groups that mimic "giant tert-butyl groups".*

The synthesis of complex nanoparticles (NPs) composed of discrete, disparate components and their subsequent assembly into well-defined, asymmetric hybrid colloids has garnered significant interest as an approach to create novel materials with modular properties.[1] In particular, the construction of "colloidal molecules" has recently been explored via total synthesis approaches where well-defined nanoparticles are used as the chemical precursors to prepare the desired multi-component colloidal material.[2]

Colloidal heterostructured materials based on metal NP tipped semiconductor nanorods (NRs) are an intriguing class of multi-component NPs that were pioneered by Banin et al. where the composition and asymmetry of the NR can be precisely controlled.[3,4] In particular, the development of precise synthetic methods have enabled metal NP deposition onto either one, or both NR termini to control NR topology, allowing access to either "dumbbell", or "matchstick" NRs by careful control of reaction conditions, or harnessing of electrochemical ripening processes.[5] Alternatively, the use of photo-irradiation has been demonstrated as a means to promote selective deposition of a single AuNP tip onto the semiconductor NR has been demonstrated.[6] We have also demonstrated kinetic control over the deposition of metallic platinum (Pt) NP tips onto CdSe@CdS NRs by control of reagent stoichiometry and reaction time to afford either matchstick, or dumbbell tipped NRs.[7] To date, the ability to selectively control the number of NP tips onto more architecturally complex semiconductor nanocrystals remains a synthetic challenge. The semiconductor tetrapod construct (e.g., CdSe@CdS TPs) is particularly challenging to selectively functionalize with metal NP tips, due to the symmetry and comparable reactivity of the four CdS "arms", generally affording distributions of multi-tipped TP products. A notable exception was the controlled AuNP deposition onto CdSe@CdS TPs by Chan et al., where careful control of conditions promoted the growth of a single AuNP tipped TP, along with asymmetric TPs with NP tips of different compositions (i.e., Au, Ag_2S).[8] These challenges were most notably illustrated when we attempted to control the deposition of a single PtNP tip onto a CdSe@CdS TP using conditions that were successful for CdSe@CdS NRs, which actually afforded multiple PtNP tips per TP (see Supporting Information). Hence, there also remain opportunities to explore new synthetic methods to promote selective metal deposition onto semiconductor TPs, in particular for use as key precursors in colloidal total synthesis routes to prepare multi-component NP materials.

Colloidal heterostructured materials have also been used as monomeric building blocks for assembly into 1D or network assemblies that have been referred to as colloidal polymers.[9–13] Earlier work from our group has focused on preparing colloidal polymers from dipolar cobalt nanoparticles (CoNPs) and heterostructured dipolar NPs that introduce noble metal NPs, or CdSe@CdS NRs as inclusions, or side chain groups into the colloidal polymer material.[7,14] The key to preparing these complex colloidal polymers has been the development of selective synthetic methods to prepare multi-component colloids that combine dipolar CoNPs with disparate colloidal materials. However, to date the preparation of heterostructured semiconductor tetrapods capable of dipolar assembly for "colloidal polymerization" has not been conducted.

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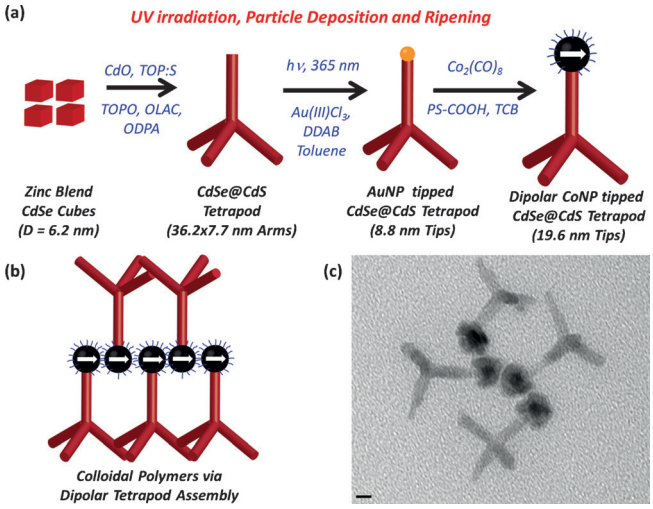

Scheme 1. a) Total synthesis scheme of heterostructured Au@Co-CdSe@CdS TPs. b) Schematic view and c) TEM image of colloidal polymers from tetrapod assembly. Scale bar is 10 nm.

Herein, we report on a four-step colloidal total synthesis of CdSe@CdS tetrapods that carry a single NP tip composed of a dipolar, core/shell Au@Co colloid (Scheme 1). Synthetic accessibility to this dipolar heterostructured tetrapod enabled the use of these as colloidal monomers to form colloidal polymers that carry the semiconductor tetrapod as a side chain group attached to the CoNP colloidal polymer main chain. The key step in the synthesis of these heterostructured tetrapods and colloidal polymers was the selective deposition of a single AuNP tip onto a CdSe@CdS tetrapod under UV-irradiation using a modified method from Banin et al. developed for NR systems.[6] To our knowledge the current report details a number of novel discoveries on the selective synthesis of an asymmetric heterostructured tetrapod that is capable of 1D dipolar assembly into colloidal polymers that carry tetrapods as side chain groups that mimic "giant *tert*-butyl groups".

The general strategy for the preparation of dipolar tetrapods comprised of a four-step synthesis that was enabled by a new method for the synthesis of CdSe@CdS tetrapods and the use of UV-irradiation during the AuNP deposition step to promote electrochemical ripening and formation of CdSe@CdS tetrapods with a single AuNP tip. Synthetic accessibility to this highly asymmetric tetrapod enabled selective deposition of the dipolar CoNP around the AuNP tip using our earlier methods for the preparation of dipolar CoNPs.

In the first step of this synthesis, CdSe@CdS tetrapods were prepared using a modified seeded growth approach utilizing for the first time zinc blend (ZB) CdSe nanocubes (effective diameter, $D_{eff} = 6.2 \pm 0.9$ nm) which were prepared using the method of Li et al.[15] While a number of methods have been developed to prepare CdSe, or CdSe@CdS tetrapods,[16] we were surprised to find that these ZB CdSe nanocubes reproducibly seeded the growth of CdSe@CdS tetrapods without nanorod side products. By varying the concentration of quantum dot seeds (3.6–0.5 μM) while keeping all other parameters constant, it was found that the length of CdS arms grown could be tuned between 20 nm to 100 nm (Figure S2 in the Supporting Information (SI)), similar to what has been shown for CdSe@CdS nanorods.[7,17] It is also important to note that when ZB CdSe seeds of spherical, or other non-cubic geometries were employed using identical conditions the formation of CdSe@CdS nanorods of broad size distributions was observed.

As alluded to earlier, the key step in the total synthesis of the dipolar tetrapod was the selective deposition of a single AuNP tip onto a CdSe@CdS tetrapod. Due to the symmetry and identical chemical nature of the termini of the tetrapod, conventional solution deposition methods used in the past to obtain single PtNP tipped nanorods in our group afforded multiple tipping (see SI, Figure S8). The key literature precedence to enable our total synthesis strategy was demonstrated by Banin et al. for the selective deposition of a single AuNP tip onto the terminus of a CdSe@CdS NR.[6] However, we postulate that the photo-deposition process can proceed when using CdSe@CdS tetrapods devoid of amine reducing agents due to the ability of the non-tipped tetrapod arms to undergo slight sacrificial photo-corrosion to enable reductive deposition of the AuNP tip. These photo-deposition experiments were conducted with argon sealed vessels in air, however, transfer of the reagents in this synthesis into reaction vessels were done in a Ar-filled dry box using degassed, anhydrous solvents which otherwise afforded uncontrolled deposition of AuNPs. Furthermore, to compensate for light induced heating of the reaction vessel during irradiation, reaction mixtures were pre-cooled ($T \approx -4$ °C), which otherwise, also resulted in poor control of AuNP deposition. As alluded to earlier, when we attempted control experiments to deposit a single PtNP tip onto CdSe@CdS TPs in the dark using low concentrations of the Pt^{II} salt precursor and short reaction times, we observed almost exclusive formation of TPs with four Pt NP tips (see SI, Figure S8). These same conditions in our earlier study afforded primarily single PtNP tipped CdSe@CdS NRs.[7] These critical control experiments further confirmed the need for the photo-irradiation step to impart selective Au NP deposition.

To investigate the mechanistic aspects of the AuNP photodeposition, TEM imaging of aliquots removed from the reaction mixture at varying times was conducted (Figure 1 a). Early reaction times (within 5 min) revealed the formation of very small AuNPs ($D \approx 1.6 \pm 0.4$ nm) laterally deposited along tetrapod arms, along with terminal deposition onto a teterapod arm of a larger single AuNP tip (4.2 ± 1.0 nm). However, after irradiation of the tetrapod in the presence of Au^{III} salts for 1 h (Figure 1 b,c), complete dissolution of these smaller AuNPs was observed, along with significant growth of a single AuNP tip (8.8 ± 1.4 nm) on a single tetrapod arm, which was indicative of the electrochemical Ostwald ripening mechanism posited by Banin et al for singly tipped Au-CdSe@CdS NRs.[6] Both bright field TEM, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and EDX elemental mapping confirmed the selective growth of a single AuNP tip onto CdSe@CdS tetrapods without residual AuNPs (either free in solution, or laterally deposited along the tetrapod). To

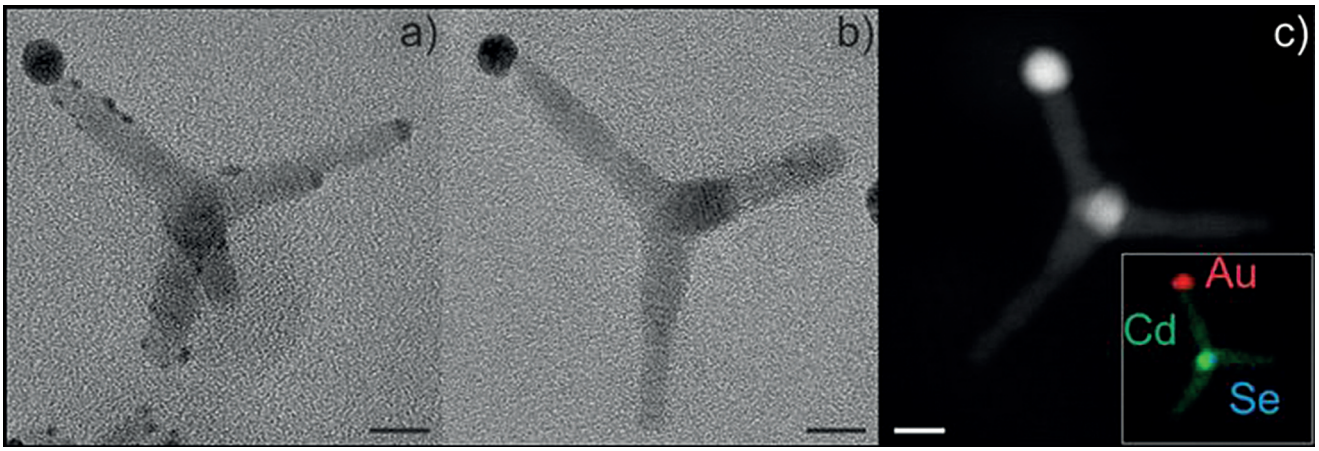

Figure 1. Au-CdSe@CdS TP: a) Representative HRTEM image of an Au-CdSe@CdS TP after 5 min of reaction time, showing a large, single AuNP and laterally deposited AuNPs. b) HRTEM image of a single Au-CdSe@CdS TP after 1 h of reaction time. c) HAADF-STEM image of a single Au-CdSe@CdS TP after 1 h of reaction time; inset: Au, Cd and Se EDX elemental map of a similar tetrapod (Se map proves the presence of the seed particle in the center of the tetrapod). Scale bars are 10 nm.

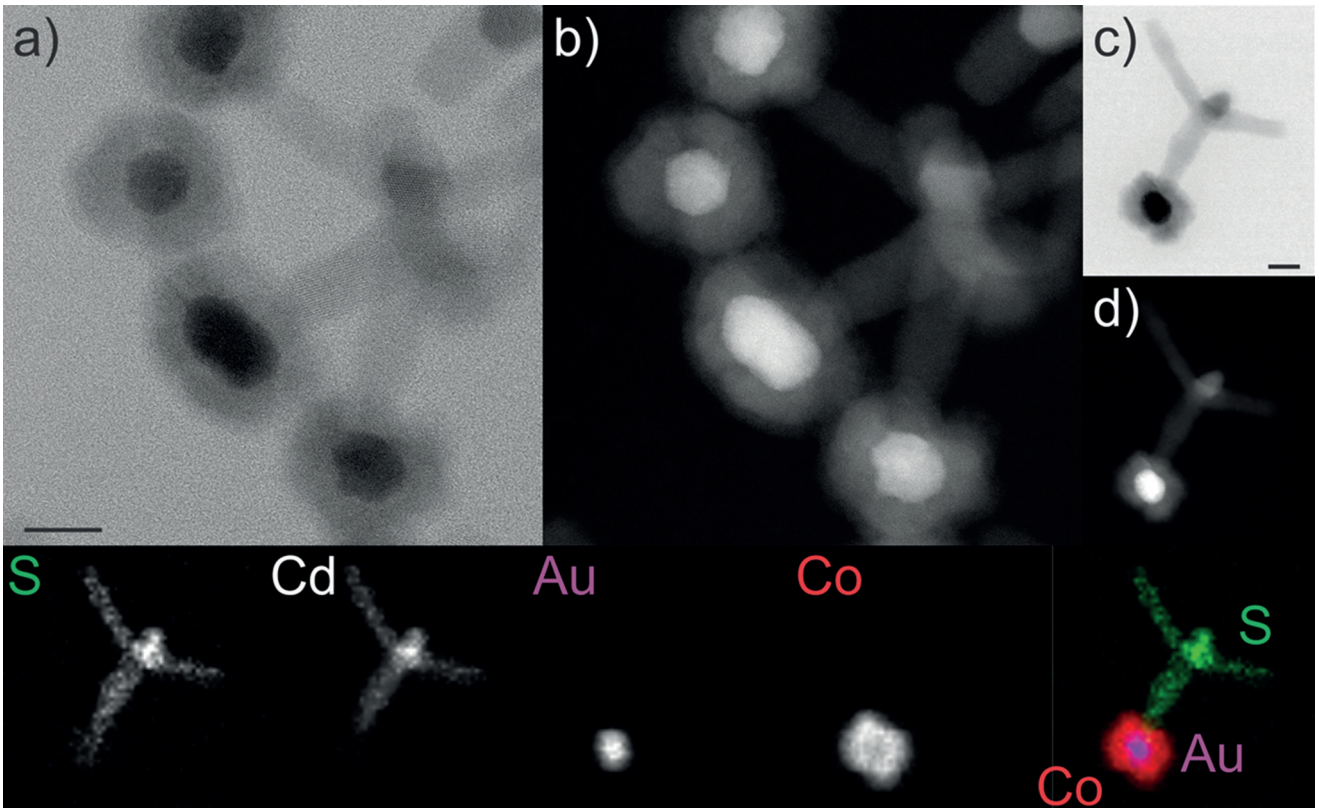

Figure 2. Au@Co-CdSe@CdS TP: a,b) Representative bright field (BF) and HAADF-STEM images of an assembly of Au@Co-CdSe@CdS TP, and c,d) BF and HAADF-STEM images of a single heterostructure. Scale bars are 10 nm. Lower part: corresponding elemental maps for S, Cd, Au, Co, and the superimposed S, Au, and Co maps.

our knowledge this is the first example of a photoelectrochemically driven Ostwald ripening process being utilized to selectively functionalize a semiconductor tetrapod with a noble metal tip with a high degree of selectivity (96% single tipped, 4% unmodified, $n = 200$).

Synthetic accessibility to CdSe@CdS tetrapods with a single AuNP tip enabled the preparation of dipolar heterostructured tetrapods by direct overcoating of the AuNP with a ferromagnetic CoNP outer shell. We previously demonstrated that both noble metal NPs, or noble metal NP tipped CdSe@CdS NRs, were able to seed the selective deposition of dipolar CoNPs,[7,18,19] which was the strategy also applied in this total synthesis. In the CoNP deposition reaction, the thermolysis of dicobaltoctacarbonyl ($Co_2(CO)_8$)

with carboxylic acid terminated polystyrene ligands (PS-COOH) was conducted in 1,2,4-trichlorobenzene at elevated temperatures ($T = 140\,°C$) to form the desired dipolar tetrapod. The diameter of the CoNP tips was found to be tunable in the range of 10–20 nm by variation of PS-COOH ligand concentrations (0.510–1.99 mM) (see SI, Figure S3). High resolution bright field and HAADF-STEM images confirmed the connectivity of the desired heterostructured tetrapod (Figure 2 a,b). The successful incorporation of tetrapods was noted by the imaging of intact CdS tetrapod arms for these materials. Furthermore, the preparation of the desired core–shell NP tip was confirmed by the presence of a high contrast, high Z colloidal core ($D \approx 9$ nm), which corresponded to the AuNP tip, along with the formation of an outer shell of polycrystalline cobalt. To further confirm the composition of this complex nanocomposite material, elemental mapping of the target dipolar tetrapod shown in Figure 2 c,d was conducted and also correlated precisely with the anticipated synthetic transformations in the colloidal total synthesis. As shown in Figure 2, spatial and elemental mapping of Cd and S was observed to be localized to only the regions of the tetrapod arms, while both Au and Co were observed at only one terminus of a tetrapod arm.

The ability to tune the size of the CoNP outer shell on AuNP tipped CdSe@CdS nanorods (typically CoNP shells ≥ 5 nm) enabled the incorporation of inherently dipolar NP tips onto tetrapods, which promoted their spontaneous 1D assembly (at room temperature and under zero-field conditions) into colloidal polymers carrying tetrapod side chain groups in every repeating unit.

An attractive feature of this synthetic methodology was the ability to control the grafting density of tetrapod side groups by variation of conditions in the total synthesis of the dipolar tetrapod. The preparation of CdSe@CdS tetrapods with a single core–shell Au@CoNP tip was initially pursued as an approach to prepare colloidal copolymers that carried a single CdSe@CdS tetrapod per CoNP repeating unit (Figure 3 b,d). However, the grafting density of tetrapods in these colloidal polymers could be lowered by the addition of free dodecylamine reducing agent (9.68 mM) in the photo-

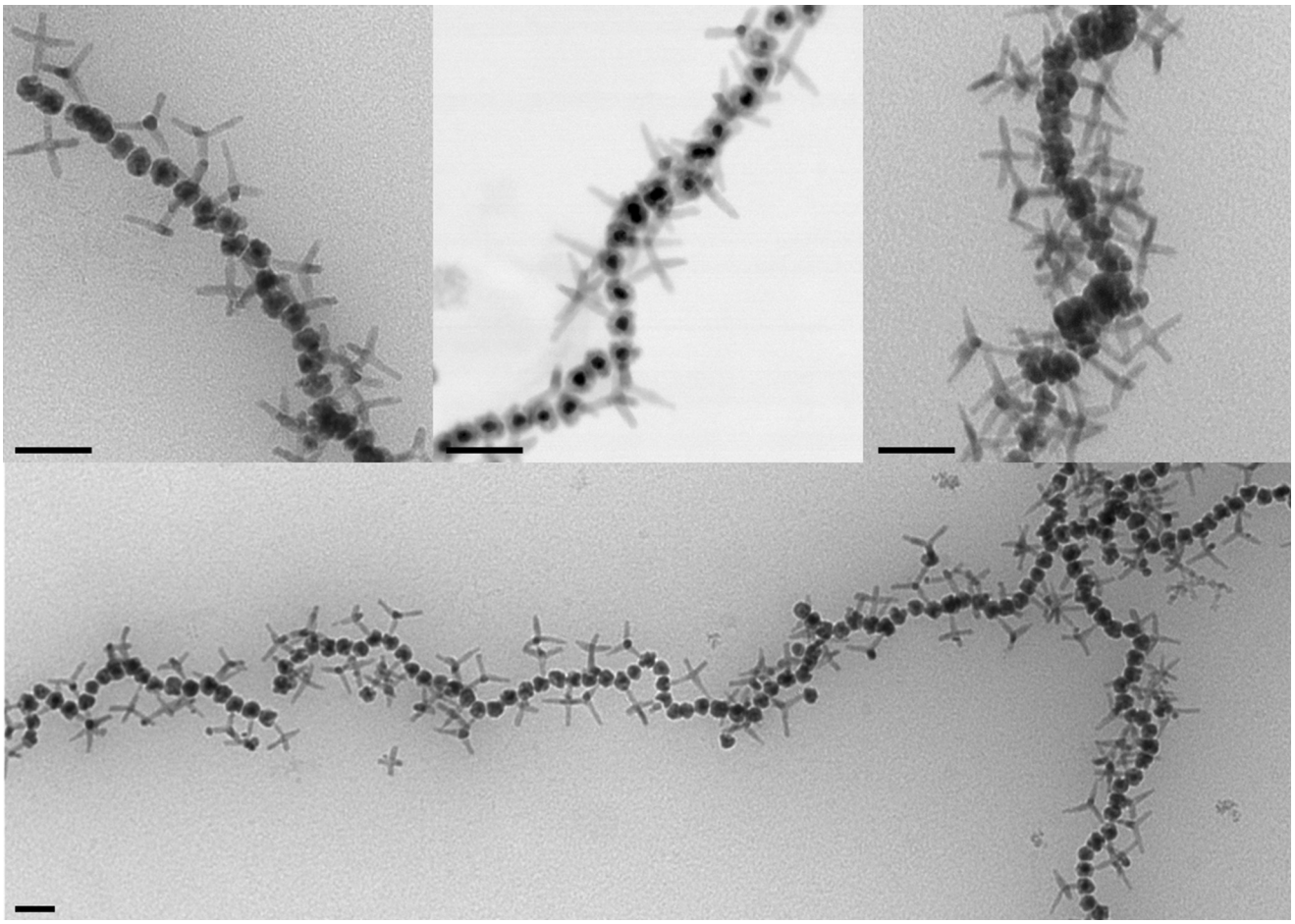

Figure 3. Self-assembly of Au@Co-CdSe@CdS TPs: a) Dipolar self-assembly resulting from treating a blend of free AuNPs and Au-TPs under Co deposition conditions, resulting in low grafting density. b) Dipolar assembly with a grafting density of 1 TP per Au@Co NP as a consequence of Co deposition onto pure Au-TPs synthesized without reducing agent. c) Highly grafted colloidal polymer chains resulting from a low concentration of stabilizing ligand in the Co deposition. d) Long range dipolar assembly resulting from conditions identical to those in (b) (1 TP per Au@CoNP). All scale bars are 50 nm.

deposition step of AuNP tips onto CdSe@CdS tetrapods (Figure 3a). The addition of the excess reducing agent in solution resulted in both the deposition of a single AuNP tip onto tetrapods and the formation of unbound AuNPs in solution. When this mixture was subsequently overcoated with dipolar CoNP shells, both dipolar tetrapods and free dipolar core–shell Au@CoNPs were concurrently formed resulting in random colloidal copolymers composed of "bare" and tetrapod carrying NP units. Conversely, increasing the grafting density to more than one tetrapod per CoNP unit was achieved by reducing the PS-COOH ligand concentration in the CoNP deposition step onto singly AuNP tipped CdSe@CdS tetrapod (which were devoid of free unbound AuNPs) (Figure 3c). The lowered PS-COOH ligand concentration likely promoted slight agglomeration of CoNP tipped tetrapods resulting in a high concentration of tetrapods around the CoNP main chain. This precise tuning of the colloidal (co)polymer composition and architecture were direct results of the synthetic parameters in the discrete reactions compiled to complete the total synthesis of these heterostructured tetrapods.

In conclusion, the synthesis of heterostructured CdSe@CdS tetrapods that carry a single dipolar Au@CoNP tip has been achieved using a colloidal total synthesis approach. The key step in the synthesis was the selective deposition of a single AuNP tip onto the CdSe@CdS tetrapod which required UV-irradiation in a photodeposition step. This further enabled selective deposition of a dipolar CoNP shell onto the tetrapod, where the intrinsic ferromagnetic nature of the NP tip promoted spontaneous 1D assembly into colloidal polymers, where CdSe@CdS tetrapods were carried as side chain groups to the CoNP main chain and the tetrapod grafting density could be precisely controlled. To our knowledge, this is the first example of an asymmetrically functionalized CdSe@CdS tetrapod architecture being synthesized via a photoexcitation-induced metal deposition process and subsequent electrochemical ripening of the deposited nanoparticle tips. Furthermore, this system is the first example of such a structure being utilized to form controlled self-assembled colloidal polymers of more complex architecture and composition.

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