

# Biomimetic Hierarchical Assembly of Helical Supraparticles from Chiral Nanoparticles

Yunlong Zhou,<sup>†,‡</sup> Ryan L. Marson,<sup>§,||</sup> Greg van Anders,<sup>†,§</sup> Jian Zhu,<sup>†</sup> Guanxiang Ma,<sup>†</sup> Peter Ercius,<sup>#</sup> Kai Sun,<sup>||</sup> Bongjun Yeom,<sup>†,¶</sup> Sharon C. Glotzer,<sup>\*,†,§,||</sup> and Nicholas A. Kotov<sup>\*,†,§,||,⊥</sup>

<sup>†</sup>Department of Chemical Engineering, <sup>§</sup>Biointerfaces Institute, <sup>||</sup>Department of Materials Science and Engineering, <sup>⊥</sup>Department of Biomedical Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States

<sup>‡</sup>Wenzhou Institute of Biomaterials and Engineering, CNITECH.CAS-Wenzhou Medical University, Wenzhou, Zhejiang 325011, People's Republic of China

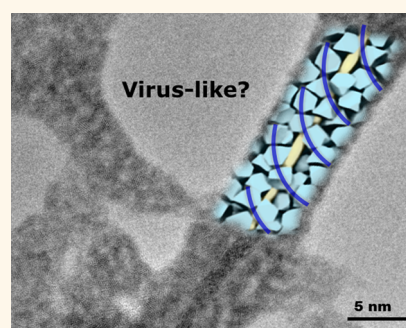
<sup>#</sup>National Center for Electron Microscopy, the Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

<sup>¶</sup>Department of Chemical Engineering, Myongji University, Yongin, Gyeonggi-do 17058, South Korea

**S** Supporting Information

**ABSTRACT:** Chiroptical materials found in butterflies, beetles, and other creatures are attributed to biocomposites with helical motifs and multiscale hierarchical organization. These structurally sophisticated materials self-assemble from primitive nanoscale building blocks, a process that is simpler and more energy efficient than many top-down methods currently used to produce similarly sized three-dimensional materials. Here, we report that molecular-scale chirality of a CdTe nanoparticle surface can be translated to nanoscale helical assemblies, leading to chiroptical activity in the visible electromagnetic range. Chiral CdTe nanoparticles coated with cysteine self-organize around Te cores to produce helical supraparticles. D-/L-Form of the amino acid determines the dominant left/right helicity of the supraparticles. The small energy difference between the chiral asymmetry of the amino acid interactions at the surface of the nanoparticles is amplified by their collective behavior. Coarse-grained molecular dynamics simulations with a helical pair-potential confirm the assembly mechanism and the origin of its enantioselectivity, providing a framework for engineering three-dimensional chiral materials by self-assembly. The helical supraparticles further self-organize into lamellar crystals with liquid crystalline order, demonstrating the possibility of hierarchical organization and with multiple structural motifs and length scales determined by molecular-scale asymmetry of nanoparticle interactions.

**KEYWORDS:** biomimetic nanoparticles, self-assembly, chirality, supraparticles, helices, virus-like nanostructures



Examples of astounding structural complexity of nature's materials raise the challenges of translating biological mechanisms of their synthesis to the industrial scale.<sup>1–4</sup> Inorganic nanoscale components are particularly attractive for many emerging and established technologies due to their special optical and electronic properties and their greater environmental robustness compared to many organic molecules.<sup>4–6</sup> Nature's method to fabricate and diversify its materials is based on the structural hierarchy utilizing a spectrum of small structural units that hierarchically self-organize across multiple scales into ever more sophisticated systems.<sup>7,8</sup> Therefore, one can ask a question: *Can the assembly of small inorganic building blocks with some biomimetic characteristics self-organize into hierarchical systems with a degree of complexity rivaling that found in nature?* Answer to this question will also help us understand better the limits of stunning analogies between nanoparticles and globular biomolecules, such as proteins.<sup>4</sup>

Inorganic nanoparticles modified with an amino acid represent one of the simplest biomimetic inorganic building blocks.<sup>9–12</sup> Notably, such particles can also be chiral; that is, their mirror image would not be superimposable with the original.<sup>13</sup> Chirality is ubiquitous in living systems and important in virtually all biological functions.<sup>14</sup> Its role in structural diversification can also be seen in the rapidly expanding spectrum of chiral metal and semiconductor nanomaterials with multiple functionalities.<sup>15–17</sup> Also important, mathematical relationships between the symmetries of structural units and assemblies as well as their optical manifestations can complement the experimental discovery tools available for evaluation of assembly mechanisms.<sup>18–22</sup>

**Received:** September 22, 2015

**Accepted:** February 22, 2016

## 62 RESULTS AND DISCUSSION

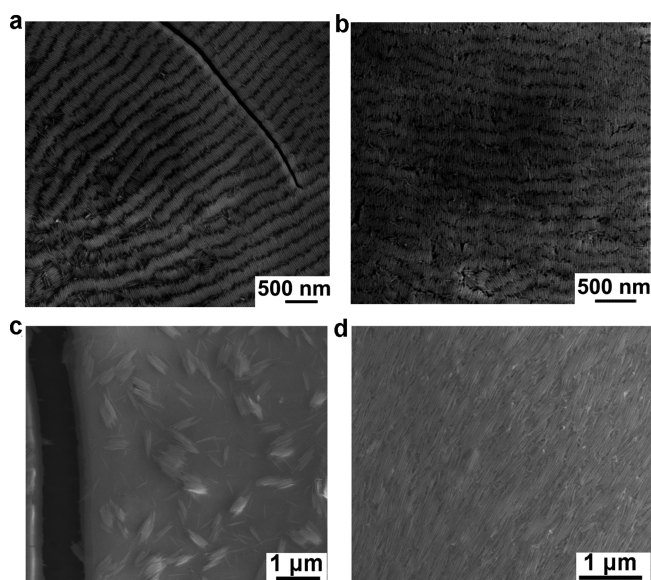
63 Here, we systematically investigate the self-organization of  
 64 CdTe nanoparticles (NPs) modified with L- or D-cysteine  
 65 (CYS) as the basic biomimetic building block. Despite a  
 66 relatively small difference in the energy of interactions  
 67 associated with chiral asymmetry,<sup>23</sup> it was found that these  
 68 NPs assemble into helical supraparticles with enantiomeric  
 69 preference.

70 D- and L-CYS-stabilized CdTe NPs (denoted as D-NPs and L-  
 71 NPs, respectively) were synthesized by the arrested precip-  
 72 itation method following a standard protocol (see [Methods](#)).<sup>24</sup>  
 73 Note that notation D and L with respect to NPs denotes only  
 74 the method of synthesis but not the chiral symmetry of the  
 75 particles. Tetrahedral CdTe NPs could have symmetry that is  
 76 similar to chiral D or L centers in amino acids when all the four  
 77 corners have different truncation.<sup>25</sup> Alternatively, the atoms in  
 78 the apexes of the NPs could also follow the familiar chiral  
 79 pattern of tetrahedra with four different substituents.<sup>26</sup> In this  
 80 work, however, we study the effect of chiral surface ligands on  
 81 the surfaces of the four sides of tetrahedral NPs.

82 To observe self-organization, the CdTe NPs were  
 83 precipitated by addition of 2-propanol and centrifuged for 5  
 84 min, followed by redispersion in deionized water with pH 9.0 in  
 85 a nitrogen atmosphere (see [Methods](#)). The solution of NPs  
 86 changed color from orange to dark red when left in the dark at  
 87 room temperature for 8 h, indicating that self-assembly of NPs  
 88 has occurred. It should be noted that the assembly conditions  
 89 here are different from previous studies, in which the self-  
 90 assembly was induced by light or different inter-particle  
 91 forces.<sup>27–30</sup> The conditions here enable the self-limiting  
 92 assembly at the NP–NP interfaces capped with CYS surface  
 93 ligands. The assembly process of CYS-stabilized NPs described  
 94 here was critically influenced by the efficiency of oxygen  
 95 removal and control over pH value, which are both key factors  
 96 for successful helical assembly controlled by small anisotropy in  
 97 NP interactions. When the assembly process was carried out  
 98 under a high value of pH, *i.e.*, pH 11.0, the final assemblies  
 99 displayed a morphology of dense NP chains irregularly attached  
 100 on the surface of Te nanowires. If assembly occurred in an open  
 101 atmosphere, NPs transitioned to a deeper oxidation state, a  
 102 greater number of Te nanowires formed, and only a few NPs  
 103 remained to assemble around them ([Figure S1](#)).

104 Scanning electron microscopy (SEM) showed the formation  
 105 of nanorods (NRs) as the primary product of the self-assembly  
 106 process. The lengths of the NRs were  $\sim 250$  nm for assembly of  
 107 D-NPs and  $\sim 300$  nm for L-NPs ([Figure 1a,b](#)). The length of  
 108 NRs can be controlled by the assembly conditions and can be  
 109 as long as  $5 \mu\text{m}$  using NPs synthesized with a molar ratio of  
 110 CYS/Cd of 1.7:1 in a pH 10.0 solution, indicated in [Figure](#)  
 111 [1c,d](#). The diameters of NRs assembled from D- and L-NPs are  
 112  $\sim 20$  and  $\sim 23$  nm, respectively, and reveal high uniformity.  
 113 Both D- and L-NRs self-organize into even higher order lamellar  
 114 assemblies. Similarly to liquid crystals, the self-organized  
 115 structures from chiral NRs may also reveal a chiral, for  
 116 instance, cholesteric, pattern of three-dimensional organization.  
 117 [Figure 1a](#) and [b](#), however, display only a two-dimensional  
 118 representation of the higher order structures from NRs and are  
 119 not sufficient to elaborate on the micrometer-scale chirality of  
 120 the lamellae or potential twist in the mutual orientation of  
 121 adjacent NRs.

122 Scanning transmission electron microscopy (STEM) high  
 123 angle annular dark-field (HAADF) images ([Figure 2a,b,d, e](#)) and

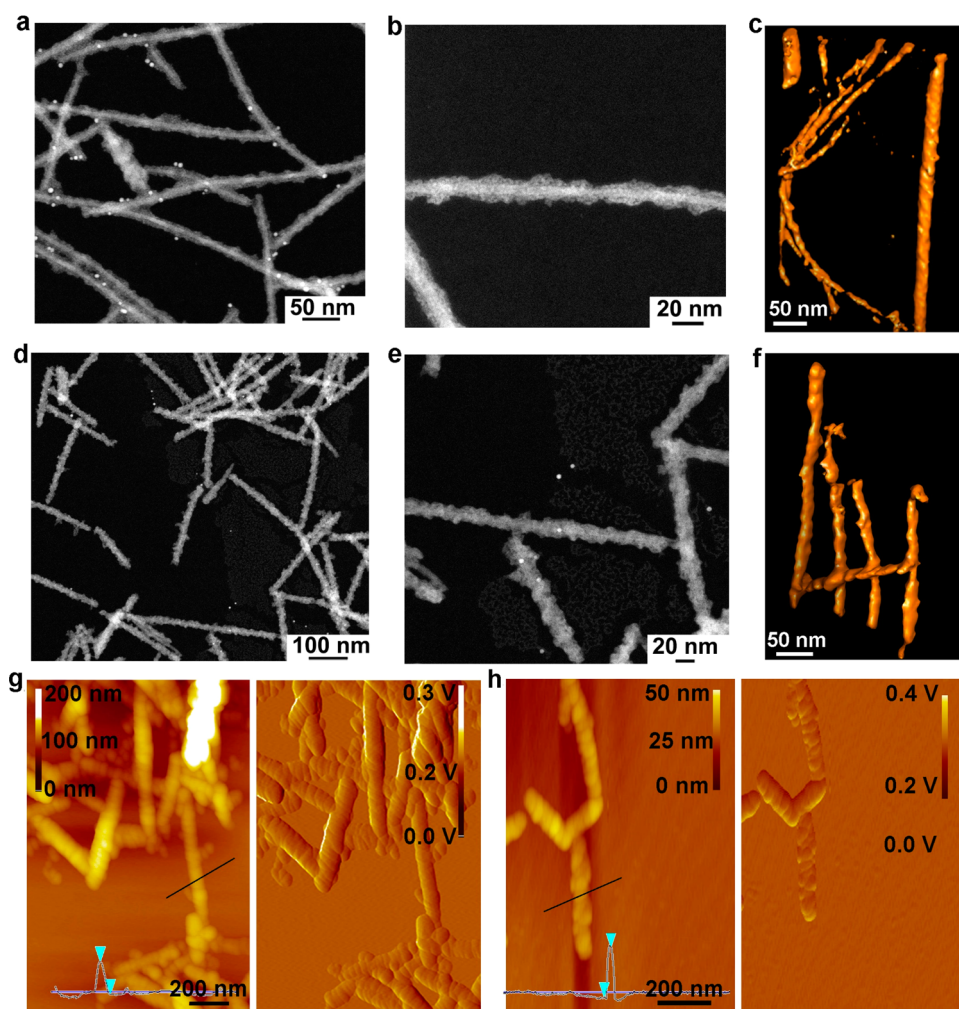


**Figure 1.** SEM images of NP assemblies from D-NPs (a, c) and L-NPs (b, d).

STEM tomography ([Figure 2c,f](#)) showed that NRs have  
 124 pronounced twist although not as regular as in DNA or some  
 125 viruses.<sup>6,31</sup> Comparing the organization of the biological and  
 126 NP systems, we note that the outer shell of viruses also reveals  
 127 a considerable amount of disorder and may not be perfectly  
 128 packed especially under room-temperature imaging conditions.  
 129 On the other hand, the size/shape distribution of NPs does  
 130 decrease the perfection in the NR packing. Importantly, the  
 131 self-assembly of NRs is enantioselective, with the twist  
 132 directions dictated by the starting NPs' chirality. The NRs  
 133 from D-NPs are *left-handed*, whereas those from L-NPs are  
 134 *right-handed* helices that are easily distinguishable in tomo-  
 135 graphically reconstructed 3D images from tilt-series STEM–  
 136 HAADF images ([Figure 2c,f](#)). AFM images also reveal their  
 137 helical geometry in periodic topographical features typical for  
 138 helices ([Figure 2g,h](#)). We evaluated the handedness of 100  
 139 samples by AFM images of helical NRs and found consistent  
 140 dominance of a specific handedness of the helices. The overall  
 141 yield of left-handed and right-handed helices from D-NPs and L-  
 142 NPs is  $\sim 70\%$  and  $\sim 74\%$ , respectively. The average pitch of  
 143 helices seen in the TEM images is  $\sim 10$  nm, which is further  
 144 confirmed by SAXS data, revealing distinct peaks for both D-  
 145 and L-NRs with  $q = 0.05\text{Å}^{-1}$ , characteristic of a repetitive  
 146 structural distance of 12.6 nm ([Figure S2](#)).  
 147

Nanoscale X-ray energy dispersive spectroscopy (XEDS)  
 148 ([Figure 3a–c](#)) showed a Te/Cd atomic ratio of  $\sim 2:1$  in the  
 149 central part of the chiral helical structures; however, the Te to  
 150 Cd ratio converges to 1:1 for the outside layer. High-resolution  
 151 TEM (HRTEM) images ([Figure 3d,e](#), [Figure S3](#)) indicate the  
 152 CdTe NPs reside on the outside of the helical NRs; the center  
 153 part is a single crystal nanowire with a diameter of  $\sim 5$  nm. The  
 154 thickness of the twisted CdTe layer is about 10–15 nm. The  
 155 Electron diffraction for the helical NRs reveals the presence of  
 156 two phases: cubic CdTe and hexagonal Te. The diffraction  
 157 spots for the CdTe phase correspond to (111) ( $d = 0.39$  nm),  
 158 (220) ( $d = 0.22$  nm), and (311) ( $d = 0.19$  nm) lattice planes.  
 159 The diffraction patterns for the central Te-rich part show the  
 160 maxima from (101) ( $d = 0.32$  nm), (012) ( $d = 0.23$  nm), and  
 161 (110) ( $d = 0.20$  nm) lattice planes. These data indicate that the  
 162 helical NRs have unusually complex core–shell morphology, 163





**Figure 2.** Nanoscale geometry of left- and right-handed helical NP assemblies. STEM–HAADF (a,b) and STEM (c) tomography images of *left*-NRs assembled from D-NPs. STEM–HAADF (a,b) and STEM (f) tomography images of *right*-NRs assembled from L-NPs. (g, h) AFM images of NRs obtained from D-NPs and L-NPs, left: height images, right: amplitude images. Note: In panels a, d, and e, the bright points are gold NPs added as markers for STEM tomography.

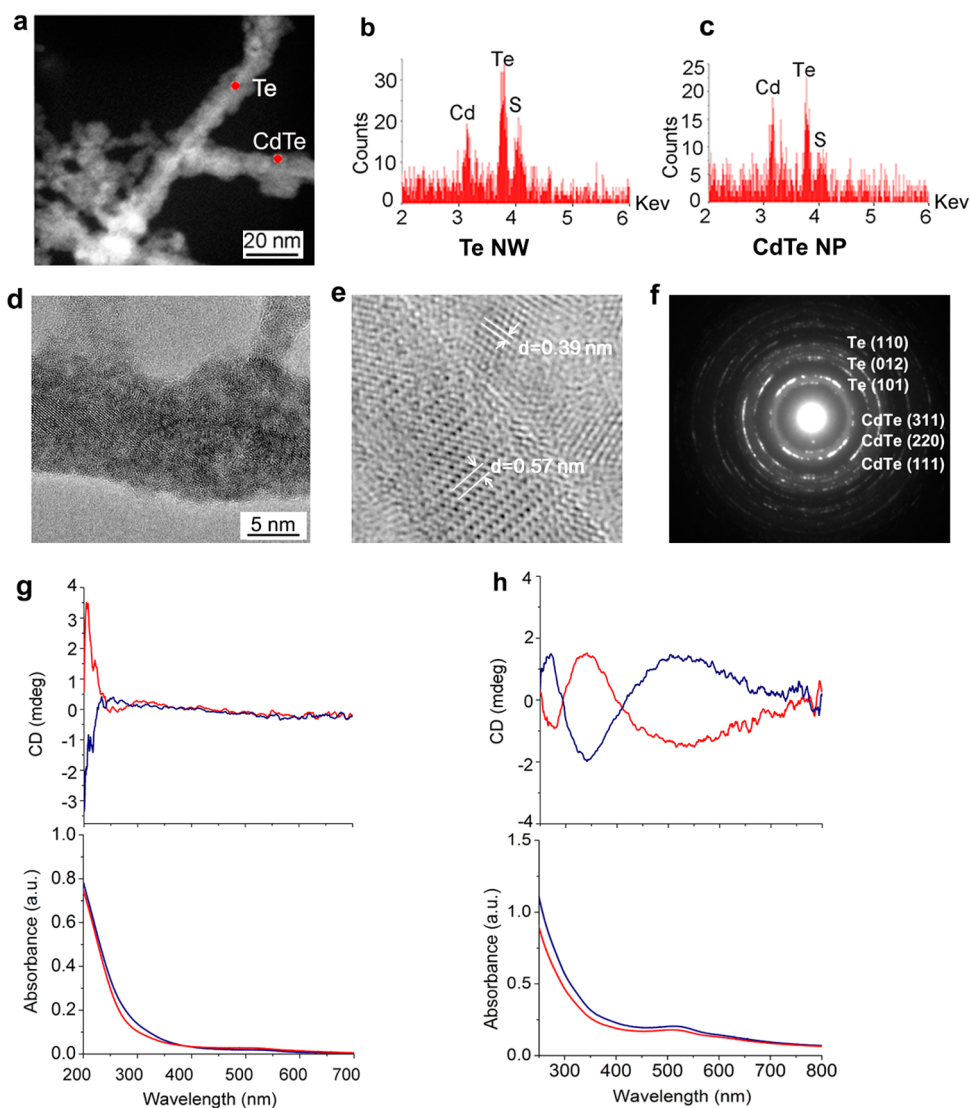
164 more sophisticated than what was observed before by Yeom *et*  
 165 *al.*,<sup>27</sup> with a solid crystalline Te rod in the center and a  
 166 polycrystalline NP shell on the outside. A gradual growth of the  
 167 central  $\sim 5$  nm Te rods/nanowires along the (001) direction is  
 168 due to the slow oxidation process of CdTe (Figure 3a–f),<sup>32</sup> and  
 169 thus the control of the oxygen content in the media during the  
 170 assembly is essential.

171 From the circular dichroism (CD) spectra (Figure 3h) one  
 172 can see that the helical NRs have distinct chiroptical activity in  
 173 the region from 300 to 800 nm, confirming enantioselectivity of  
 174 the assembly process. Importantly, D- and L-NPs produce  
 175 helical NRs with mirror-image CD spectra, whereas the  
 176 precursors to the supraparticles, *i.e.*, NPs, and their early  
 177 assemblies appearing as NP chains (Figure 4a, Figure S4) show  
 178 no chiroptical activity in the visible range (Figure 3g). Only CD  
 179 peaks associated with individual D- and L-CYS moieties in the  
 180 UV spectral region between 200 and 300 nm appear.<sup>24</sup>

181 To further understand the mechanism of the assembly  
 182 process and the driving forces responsible for the enantioselective  
 183 transition of D/L-NPs to NRs, we examined the  
 184 dispersions using different spectroscopy and microscopy  
 185 techniques at the time points of 8, 24, 48, and 72 h (Figure  
 186 4, Figures S4–S8). In the first 8 h, TEM bright-field (BF)

images revealed transformation of short NP chains for both  
 187 enantiomers of CdTe particles (Figure 4, Figure S4). The L-NP  
 188 assemblies show a broad and weak positive CD peak at  $\sim 430$   
 189 nm compared with the NP solution and D-NP assemblies  
 190 (Figure S6b,d). By 24 h, the chains transformed into short NRs  
 191 that display chiroptical activity (Figure 4, Figure S6). Neither  
 192 morphology nor CD spectra for mixed D/L-NP assemblies  
 193 could show the same changes in 48 h. After 48 and 72 h, both  
 194 D-NP and L-NP assemblies show self-organization into short  
 195 helical rods, for which the corresponding CD spectra display  
 196 peaks and Cotton effects of opposite signs (Figure S6).<sup>24</sup> Note  
 197 that the intermediate stages *en route* from single NPs to helical  
 198 NRs are markedly different from previous observations for  
 199 assemblies of organic and inorganic helical systems.<sup>18,33–35</sup> The  
 200 growth of Te cores takes place concurrently with the  
 201 attachment of CdTe.  
 202

The zeta potential decreased with time for both D-NP and L-  
 203 NP assemblies (Figure S7), indicating the continuously  
 204 decreasing repulsive interactions between the NPs and the  
 205 NRs. Such a temporal trend in  $\zeta$  is conducive to the self-  
 206 limiting aggregation of NPs into supraparticles.<sup>36,37</sup> The  
 207 uniformity of NR diameters leading to their hierarchical  
 208 organization into the lamellar phase (Figure 1a,b) is also 209



**Figure 3.** Nanoscale structure and chirality of helical NP assemblies. (a–c) XEDS analysis of peripheral and core parts of *left-* handed helical NRs. (d, e) HRTEM image of peripheral CdTe NPs and Te core. (f) Electron diffraction of the *right-* handed NRs. (g) CD/UV-vis spectra of supraparticle precursors: NP chains obtained after 8 h of assembly of D- (red) and L-NPs (blue). (h) CD spectra of *left-* (red) and *right-* handed (blue) helical NRs obtained after 2 weeks of assembly. Complementary CD/UV-vis spectra of L/D-cysteine are given in Figure S5.

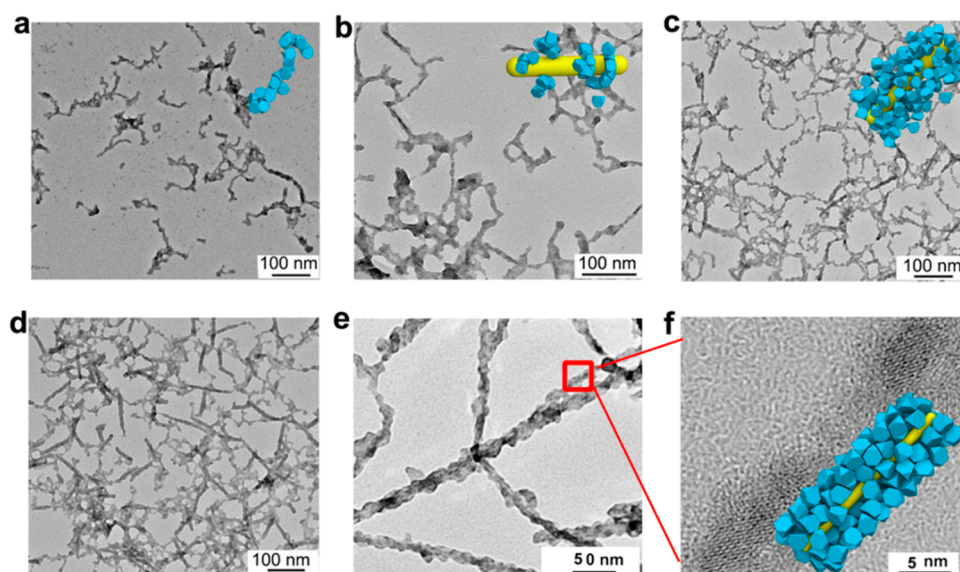
210 indicative of the self-limiting terminal assembly pattern.  
 211 Photoluminescence (PL) and UV-vis spectra remain essentially  
 212 unchanged (Figures S8, Figure S6c,d); the red-shift of the  
 213 luminescence due to aggregation is (over)compensated by the  
 214 blue-shift due to oxidation, leading to the formation of Te  
 215 cores. PL lifetimes increased from 22 ns for D-NPs to 52 ns for  
 216 the left-handed helix and from 19 ns for L-NPs to 35 ns for the  
 217 right-handed helix (Figure S9). There could be several reasons  
 218 for such a noticeable change in PL dynamics. One of them is  
 219 the decrease of the spatial confinement of the electrons and  
 220 holes. Another could be the formation of a thin layer of CdS  
 221 on the surface of CdTe NPs from the decomposition of cysteine  
 222 surface ligands. The CdS layer can elongate the lifetime of the  
 223 electron–hole pair by temporary localization of some of the  
 224 charge carriers.<sup>38,39</sup>

225 Previous reports indicated that the self-organization of  
 226 helices from organic building blocks arises mainly from the  
 227 concerted action of multiple types of short-range and long-  
 228 range interactions.<sup>37</sup> Hydrogen bonding and hydrophobic  
 229 interactions are some of the most important forces in the

self-organization of chiral biotic assemblies, *e.g.*, the DNA  
 230 double-helical structure and chiral peptides–amphiphile nano-  
 231 fibers.<sup>40,41</sup> Biomolecule-stabilized inorganic NPs can interact *via*  
 232 a similar set of intermolecular interactions as biological species  
 233 of the same size, although the van der Waals attraction between  
 234 them is typically stronger due to higher values of pairwise  
 235 Hamaker constants.<sup>42</sup> Therefore, we hypothesize that the  
 236 formation of helical NRs is due to the chirality of interactions at  
 237 the NP–NP interfaces capped with CYS moieties as opposed  
 238 to chiral preference of the packing of NP cores,<sup>43</sup> NR  
 239 twisting,<sup>44</sup> oriented attachment,<sup>45</sup> or screw axis dislocation.<sup>46</sup> 240

Compared to other types of inter-NP interactions,<sup>47</sup> which  
 241 include van der Waals forces, dipole–dipole, charge–charge,  
 242 and charge–dipole interactions, hydrogen bonds, and other  
 243 interactions between NPs, this chiral contribution may appear  
 244 to be small, but it is actually appreciable, especially for chiral  
 245 molecules on the surface of NPs. The energy difference  
 246 between intermolecular bonds binding two homochiral CYS  
 247 molecules or two heterochiral CYS molecules is comparable to  
 248 other forces. According to Kühnle *et al.*, the heterochiral dimer 249





**Figure 4.** Intermediate stages of self-organization of helical hierarchical assemblies from D-NPs. (a–d) TEM BF images of the formation process of *left-handed* NRs by assembly of D-NPs in 8 h (a), 24 h (b), 48 h (c), and 72 h (d). TEM BF (e) and HREM (f) images of helical NRs obtained after 72 h of assembly. Inset images are the simulated assembly of helical NRs from a CdTe NP; the central Te core is yellow, and the surrounding CdTe NPs are blue.

250 of gold-bound CYS was found to be energetically less favorable  
 251 than the homochiral dimers by *ca.* 0.2 eV, *i.e.*, 20 kJ/mol at 295  
 252 K.<sup>23</sup> The three-point bonding involving carboxyl groups and  
 253 amine–gold interactions give an LL pair advantage over an LD  
 254 pair. CYS molecules in our system are bound to the surface of  
 255 CdTe, and the same three-point intermolecular interactions  
 256 involving the carboxylic group and amino group coordination  
 257 to the cadmium atoms on the CdTe surface are likely to take  
 258 place.<sup>48</sup> The energy cost for breaking the cysteine–Cd<sup>2+</sup>  
 259 tetrahedral coordination bond affected by the rotation of the  
 260 amino acid segments and/or its chirality can be as high as 117.3  
 261 kcal/mol (490.8 kJ/mol);<sup>49</sup> thus its deformation depending on  
 262 the even seemingly minor alteration of the atomic structures  
 263 can easily amount to 20 kJ/mol.

264 For comparison, the energy of dipolar attraction, known to  
 265 be a significant factor determining the geometry of self-  
 266 assembled structures for 3.2 nm CdTe NPs, can be estimated to  
 267 be *ca.* 9.7 kJ/mol using, for instance, the classical formula for  
 268 aligned dipoles (Supporting Information, Part I).<sup>30</sup> This  
 269 juxtaposition with dipole–dipole interactions shows the  
 270 importance of the chiral interactions as a determinant of the  
 271 assembly geometry, especially considering their cooperative  
 272 nature for the face-to-face contact between NPs.

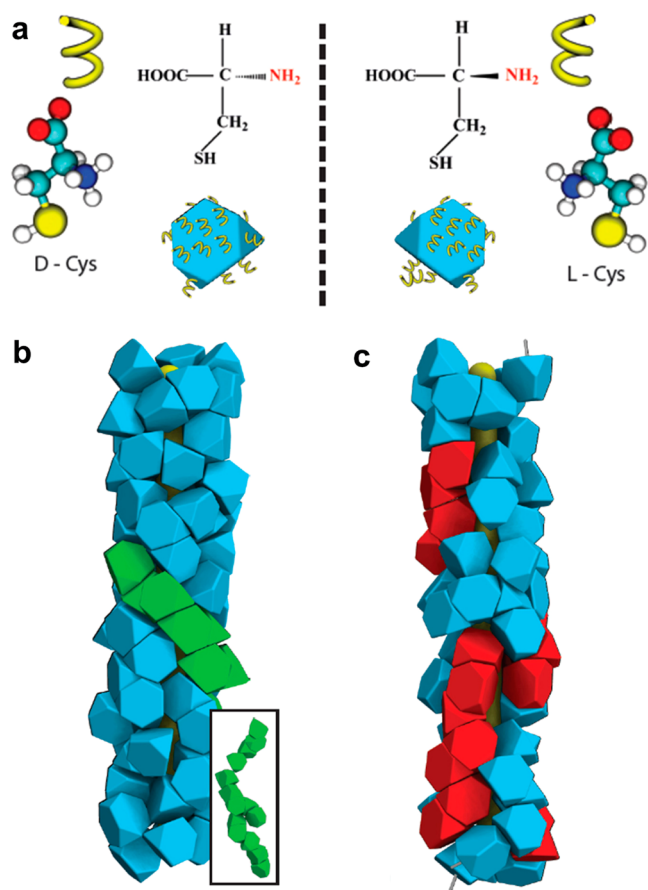
273 To confirm that the molecular-scale chirality of CYS surface  
 274 ligands can indeed translate into the nanoscale chirality of the  
 275 NRs, we performed coarse-grained molecular dynamics (MD)  
 276 simulations of NP self-assembly (Supporting Information Part  
 277 II). Four primary features of the experimental system, *i.e.*, the  
 278 excluded volume effects due to the NP shape, the attraction of  
 279 the NPs to the surface of the Te core, dipolar interactions, and  
 280 the chiral asymmetry of NP–NP interactions originating from  
 281 the CYS layer on the NP surface (Figure Sa), included in the  
 282 simulations. Among others, excluded volume effects are  
 283 captured *via* a purely repulsive Weeks–Chandler–Andersen  
 284 potential from the NP surface.<sup>50</sup> To model the axial form of the  
 285 Te core, we confine particles using a cylindrical harmonic well

$$U = \frac{1}{2}kx^2 \quad (\text{where } x \text{ denotes the radial distance from the } z\text{-axis})$$

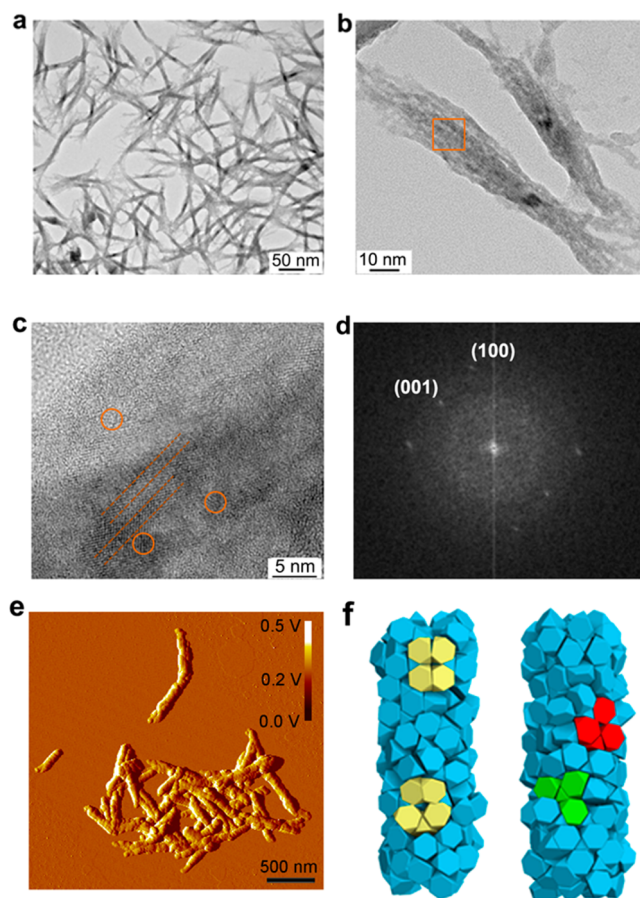
at the center of the simulation box. To account for the twisting  
 preference induced by the amino acid surface ligand, we include  
 a specially developed chiral potential that acts between  
 interacting faces of the particles. The potential describes the  
 cumulative torque from collective interactions of chiral surface  
 ligands on the NP surfaces; it changes signs for the clockwise  
 and counterclockwise direction of rotation, as can be seen in  
 the description of the potential with respect to face normals  
 given in the SI (Figure S12). For the entire NP the total energy  
 of chiral interactions affecting its motion in the simulations was  
 $\pm 1, 10,$  and  $100 k_B T$  (0.41, 4.1, and 41.0 kJ/mol at 295 K), the  
 lower values of which are an underestimate considering the 20  
 kJ/mol at 295 K difference stemming from the chiral  
 asymmetry of CYS.<sup>23</sup>

Simulated assemblies without the D/L asymmetry of CYS–  
 CYS interactions resulted in chiral structures, but without  
 preferred handedness. The chirality of these terminal  
 assemblies is the result of the confinement of multiparticle  
 assemblies to a cylindrical surface. The pitch and geometry of  
 such structures can be described analytically and strongly  
 depend on the ratio of diameters between the NP and the  
 structure-directing cylinder.<sup>51</sup> In contrast, when we included  
 the chiral interaction between NPs, the assembly of the  
 supraparticular NRs was enantioselective for interaction  
 energies of  $10 k_B T$  (4.1 kJ/mol) and above (Figure Sb,c).  
 This value is noticeably smaller than the estimated 20 kJ/mol  
 energy difference for surface–bound homo- and heterochiral  
 CYS dimers made above. Multiple and cooperative CYS–CYS  
 interactions can occur for face-to-face contacts between  
 tetrahedral NPs, thereby further increasing the energy  
 preference and enantiomeric bias.

Structures with predictable chirality were observed in  
 simulations of particles between 100 and 300 particles and  
 for rod diameters of 1 and 2 NP widths; the effects are  
 particularly pronounced in simulations where the particle  
 number, rod thickness, and box length were commensurate  
 with a close packing of tetrahedra around the rod.



**Figure 5.** Simulated helical hierarchical assemblies of D- and L-NPs. (a) Schematics of the NP surfaces coated with D- and L-CYS. Chemical structures are related to a “steric coil”. Structures produce a predetermined twist based upon the chirality of the stabilizer by biasing local NP motifs. Either *left* (b) or *right* (c) handed structures are produced, depending upon the choice of “twist”, as determined by a chiral interaction between NP faces. The Te core is shown in yellow, with an outer layer of NPs removed. Insets show the unaltered wire (top) and centers of mass of the NPs connected with bonds along closest neighbors (bottom).



**Figure 6.** Supraparticle NRs resulting from self-assembly of *rac*-NPs. (a, b) TEM BF images of the NR formed from the *rac*-NPs. HRTEM (c) and its corresponding FFT pattern (d) characterizations of twinning structures of Te attached with CdTe NPs and corresponding fast Fourier transform pattern of Te nanowires. The fast Fourier transform pattern of the hexagonal Te phase corresponds to (100) (0.38 nm) and (001) (0.6 nm).<sup>32</sup> (e) AFM amplitude image of self-assembled supraparticle NRs from *rac*-NPs. (f) Simulations of assemblies of tetrahedral *rac*-NPs (left: front, right: back).

323 The data described so far show that molecular chirality of  
 324 stabilizers induces the formation of chiral superstructures. To  
 325 confirm the finding that molecular-scale chirality is reflected in  
 326 the nanoscale geometry of the assemblies, we also need to test  
 327 the case of racemic stabilizer-capped NPs. Therefore, we carried  
 328 out a complementary experimental and computational study of  
 329 self-assembly processes from *rac*-NPs taken in the same amount  
 330 and assembled under the same conditions. The *in-silico*  
 331 assemblies driven by an achiral interparticle pair-potential  
 332 demonstrated (Figure 6f) no distinct handedness, as opposed  
 333 to the helical assemblies in Figure 5b,c. Concomitant TEM and  
 334 AFM results of the experimental supraparticle NRs made from  
 335 *rac*-NPs show intertwined rod-like assemblies with a diameter  
 336 of ~40 nm, which is almost double the diameter (Figure 6 and  
 337 Figure S10a) of helical NRs in Figure 1. The experimental  
 338 terminal assemblies of *rac*-NPs are composed of many  
 339 intertwined thin, ~2 nm nanowires attached with CdTe NPs  
 340 according to HRTEM image and XEDS analysis (Figure 6c,  
 341 Figure S11), in which the presence of the hexagonal Te phase  
 342 can be discerned from the fast Fourier transform pattern  
 343 (Figure 6d). CD spectra show a weak band around 350–550  
 344 nm, which may be surprising (Figure S10b). This CD band

observed for *rac*-NP assemblies is broader than the CD bands  
 345 obtained for NPs with homochiral surface ligands. At the same  
 346 time, we see no evidence of helical or other assemblies of NPs  
 347 with specific chiral preference in TEM and AFM data. The  
 348 small chiral bias visible in CD spectroscopy for NP mixtures  
 349 with expected racemic behavior can be attributed to  
 350 stochastically assembled small NP clusters and should be  
 351 investigated further. 352

## CONCLUSIONS

Overall, our findings in this study demonstrate that a small  
 354 biomimetic unit can drive hierarchical self-assemblies across  
 355 several scales. The self-assembly of NPs with atomic-scale  
 356 chirality imparted by the surface ligands results in the formation  
 357 of helical supraparticles structurally resembling biological  
 358 prototypes exemplified by the tobacco mosaic virus. The  
 359 nanoscale twists of helical supraparticles are deterministically  
 360 controlled by the molecular-scale chirality of the constitutive  
 361 NPs, which lays the groundwork for understanding the  
 362 collective behavior of nanoscale biomimetic units. The resulting  
 363 helical NRs can further self-organize into lamellar liquid 364



365 crystals, which expand the family of hierarchical assemblies of  
366 anisotropic inorganic particles.<sup>27,37</sup> Although possible, chiral  
367 order in the lamellar assemblies at the micrometer scale was not  
368 observed in this work, and further studies regarding potential  
369 chiral hierarchy in these superstructures need to be undertaken.  
370 The self-assembly phenomena reported here present multiple  
371 venues for further research toward biologically inspired  
372 assembly processes and optoelectronic technologies.<sup>52,53</sup>

## 373 MATERIALS AND METHODS

374 **Materials.** Cadmium perchlorate hexahydrate was purchased from  
375 Alfa-Aesar. Aluminum telluride powder was purchased from Materion  
376 Advanced Chemicals. L-cysteine (L-CYS) hydrochloride and D-cysteine  
377 (D-CYS) hydrochloride were purchased from Sigma-Aldrich. All  
378 chemicals are used as received.

379 **Synthesis and Assembly of (D, L, and rac)-cysteine-Stabilized**  
380 **CdTe NPs (D-NPs, L-NPs, and rac-NPs).** The molar ratio of CYS to  
381 Cd<sup>2+</sup> used in the synthesis of the NPs was 2.2:1, and the synthesis  
382 concentration of Cd<sup>2+</sup> was 0.01 mol/L. In order to reduce the  
383 possibility of decomposition of cysteine in highly basic solutions, the  
384 solution of cadmium perchloride and cysteine was taken at pH 9.6. We  
385 briefly dissolved 0.373 g of cadmium perchloride hexahydrate and  
386 0.343 g of D-CYS, L-CYS, or rac-CYS in 80 mL of 18 MΩ pure water,  
387 subsequently adjusting the pH value to 9.6. The solution was purged  
388 with nitrogen for 1.0 h to remove oxygen. CdTe NPs nucleate after  
389 subsequent purging of H<sub>2</sub>Te generated separately by mixing 0.5 M  
390 H<sub>2</sub>SO<sub>4</sub> and 0.08 g of Al<sub>2</sub>Te<sub>3</sub>. The CdTe NPs' growth was conducted at  
391 90 °C for 4 h and then cooling to room temperature with nitrogen  
392 bubbling. The assembly procedure can be summarized as follows: We  
393 added a 1:1 volume ratio of 2-propanol to the freshly prepared CdTe  
394 solution and centrifuged the mixture solution at 6000 rpm/min for 10  
395 min. After removing the supernatant containing free cadmium  
396 complexes and other salts, we immediately dissolved CdTe in pH  
397 9.0 ultrapure water and bubbled with nitrogen for 5 min. Solutions  
398 were kept in 20 mL glass vials sealed with Parafilm at room  
399 temperature. It can be found that the solution of nanoparticles changes  
400 in color from orange to dark red when left in a dark place at room  
401 temperature for 8 h, giving a visual indication that the self-assembly of  
402 NPs has occurred.

403 **Characterization.** Samples for characterizations were first  
404 centrifuged at 5000 rpm/min for 5 min, and then the precipitates  
405 were redispersed in water in order to remove the random network  
406 assemblies in the precursors. In order to get the real-time morphology  
407 in the process of self-assembly, the CD spectra and other data about  
408 intermediate states were obtained with samples without separation of  
409 NP chains and supraparticles NRs. Circular dichroism spectra were  
410 collected on a JASCO-815. Fluorescence spectra were carried on a  
411 Horiba Fluoro MAX-3. AFM images were taken using the tapping  
412 model on a Bruker Multimode-II. TEM images were taken by a JEM-  
413 3011 transmission electron microscope. Annular dark-field STEM  
414 images and XEDS analysis were taken using a JEOL 2010F scanning  
415 transmission electron microscope at 200 kV. SEM images were  
416 conducted on a FEI Nova NanoLab scanning electron microscope.  
417 STEM tomography images were collected on a FEI Titan in annular  
418 dark-field mode at 200 kV at the Molecular Foundry, Lawrence  
419 Berkeley National Lab. The collection angle was from -70° to +70°.  
420 Tomographic alignment of a tilt series and 3D reconstruction were  
421 performed using IMOD software. This is achieved by first tracking the  
422 small movement of fiducial gold markers with a diameter of 10 nm.  
423 Then, the reconstructed volume was filtered using a Gaussian (width,  
424 1) for noise reduction in UCSF Chimera software. SAXS were  
425 conducted on a Bruker NanoStar small-angle X-ray scattering (SAXS)  
426 system.

## 427 ASSOCIATED CONTENT

### 428 **S** Supporting Information

429 The Supporting Information is available free of charge on the  
430 ACS Publications website at DOI: 10.1021/acsnano.5b05983.

Addition electron microscopy images, optical character- 431  
izations, zeta potential, SAXS data, and simulations 432  
(PDF) 433

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: sglotzer@umich.edu. 436

\*E-mail: kotov@umich.edu. 437

### Notes

The authors declare no competing financial interest. 439

## ACKNOWLEDGMENTS

This material is based upon work supported by the U.S. Army 441  
Research Office under Grant Award No. ARO MURI 442  
W911NF-10-1-0518. Y.L.Z. acknowledges support from Na- 443  
tional Natural Science Foundation of China (NSFC-21573162) 444  
and WIBEZD2014001-02. R.L.M. and N.A.K. were supported 445  
in part by the National Science Foundation, Division of 446  
Materials Research Award # DMR 1120923. N.A.K. also wishes 447  
to acknowledge support from NSF under grants ECS-0601345; 448  
CBET 0933384; CBET 0932823; and CBET 1036672. We 449  
thank the University of Michigan's Electron Microscopy and 450  
Analysis Laboratory (EMAL) for its assistance with electron 451  
microscopy and for NSF grants (numbers DMR-0320740 and 452  
DMR-9871177), for funding the FEI Nova Nanolab Dualbeam 453  
focused ion beam workstation and scanning electron micro- 454  
scope and the JEM-2010F analytical electron microscope used 455  
in this work. Y.L.Z. thanks Jinyan Chen and Hailin Qiu for the 456  
assistance with the PL lifetime experiment. R.L.M. is grateful to 457  
Matthew Spellings for numerous fruitful discussions. Simu- 458  
lations were carried out using computational resources and 459  
services supported by Advanced Research Computing at the 460  
University of Michigan, Ann Arbor. The experiments 461  
performed at the Molecular Foundry, Lawrence Berkeley 462  
National Laboratory were supported by the U.S. Department 463  
of Energy under contract no. DE-AC02-05SCH11231. We also 464  
thank EMAL and the College of Engineering for assistance with 465  
the Bruker NanoStar small-angle X-ray scattering. The 466  
experiments performed at the Molecular Foundry, Lawrence 467  
Berkeley National Laboratory were supported by the U.S. 468  
Department of Energy under contract #DE-AC02-05SCH11231. 469

## REFERENCES

- (1) Vukusic, P.; Sambles, J. R. Photonic Structures in Biology. *Nature* 2003, 424, 852–855. 471
- (2) Shopsowitz, K. E.; Qi, H.; Hamad, W. Y.; MacLachlan, M. J. Free- 472  
Standing Mesoporous Silica Films with Tunable Chiral Nematic 473  
Structures. *Nature* 2010, 468, 422–425. 474
- (3) Whitesides, G. M.; Grzybowski, B. Self-Assembly at All Scales. 475  
*Science* 2002, 295, 2418–2421. 476
- (4) Kotov, N. A. Inorganic Nanoparticles as Protein Mimics. *Science* 477  
2010, 330 (6001), 188–189. 478
- (5) Liu, S.; Han, L.; Duan, Y.; Asahina, S.; Terasaki, O.; Cao, Y.; Liu, 480  
B.; Ma, L.; Zhang, J.; Che, S. Synthesis of Chiral TiO<sub>2</sub> Nanofibre with 481  
Electron Transition-Based Optical Activity. *Nat. Commun.* 2012, 3, 482  
1215. 483
- (6) Kuzyk, A.; Schreiber, R.; Fan, Z.; Pardatscher, G.; Roller, E. M.; 484  
Hogele, A.; Simmel, F. C.; Govorov, A. O.; Liedl, T. DNA-Based Self- 485  
Assembly of Chiral Plasmonic Nanostructures with Tailored Optical 486  
Response. *Nature* 2012, 483, 311–314. 487
- (7) Aggeli, A.; Nyrkova, I. A.; Bell, M.; Harding, R.; Carrick, L.; 488  
McLeish, T. C. B.; Semenov, A. N.; Boden, N. Hierarchical Self- 489  
Assembly of Chiral Rod-Like Molecules as a Model for Peptide β-sheet 490



- 491 Tapes, Ribbons, Fibrils, and Fibers. *Proc. Natl. Acad. Sci. U. S. A.* **2001**,  
492 98, 11857–11862.
- 493 (8) Pokroy, B.; Kang, S. H.; Mahadevan, L.; Aizenberg, J. Self-  
494 Organization of A Mesoscale Bristle into Ordered, Hierarchical Helical  
495 Assemblies. *Science* **2009**, 323, 237–240.
- 496 (9) Schaaff, T. G.; Knight, G.; Shafiqullin, M. N.; Borkman, R. F.;  
497 Whetten, R. L. Isolation and Selected Properties of a 10.4 kDa  
498 Gold:Glutathione Cluster Compound. *J. Phys. Chem. B* **1998**, 102,  
499 10643–10646.
- 500 (10) Govorov, A. O.; Gun'ko, Y. K.; Slocik, J. M.; Gerard, V. A.; Fan,  
501 Z.; Naik, R. R. Chiral Nanoparticle Assemblies: Circular Dichroism,  
502 Plasmonic Interactions, and Exciton Effects. *J. Mater. Chem.* **2011**, 21,  
503 16806–16818.
- 504 (11) Gautier, C.; Burgi, T. Vibrational Circular Dichroism of N-  
505 acetyl-L-cysteine Protected Gold Nanoparticles. *Chem. Commun.* **2005**,  
506 43, 5393–5395.
- 507 (12) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.;  
508 Kornberg, R. D. Structure of a Thiol Monolayer-Protected Gold  
509 Nanoparticle at 1.1 Å Resolution. *Science* **2007**, 318, 430–433.
- 510 (13) Liu, Y.; Zhang, X. Metamaterials: A New Frontier of Science  
511 and Technology. *Chem. Soc. Rev.* **2011**, 40, 2494–2507.
- 512 (14) Zhang, M.; Qing, G.; Sun, T. Chiral Biointerface Materials.  
513 *Chem. Soc. Rev.* **2012**, 41, 1972–1984.
- 514 (15) Shemer, G.; Krichevski, O.; Markovich, G.; Molotsky, T.;  
515 Lubitz, I.; Kotlyar, A. B. Chirality of Silver Nanoparticles Synthesized  
516 on DNA. *J. Am. Chem. Soc.* **2006**, 128, 11006–11007.
- 517 (16) Moloney, M. P.; Gun'ko, Y. K.; Kelly, J. M. Chiral Highly  
518 Luminescent CdS Quantum Dots. *Chem. Commun.* **2007**, 38, 3900–  
519 3902.
- 520 (17) Garzón, I.; Beltrán, M.; González, G.; Gutierrez-González, I.;  
521 Michaelian, K.; Reyes-Nava, J.; Rodríguez-Hernández, J. Chirality,  
522 Defects, and Disorder in Gold Clusters. *Eur. Phys. J. D* **2003**, 24, 105–  
523 109.
- 524 (18) Song, C.; Blaber, M. G.; Zhao, G.; Zhang, P.; Fry, H. C.; Schatz,  
525 G. C.; Rosi, N. L. Tailorable Plasmonic Circular Dichroism Properties  
526 of Helical Nanoparticle Superstructures. *Nano Lett.* **2013**, 13, 3256–  
527 3261.
- 528 (19) Hendry, E.; Carpy, T.; Johnston, J.; Popland, M.; Mikhaylovskiy,  
529 R. V.; Laphorn, A. J.; Kelly, S. M.; Barron, L. D.; Gadegaard, N.;  
530 Kadodwala, M. Ultrasensitive Detection and Characterization of  
531 Biomolecules using Superchiral Fields. *Nat. Nanotechnol.* **2010**, 5,  
532 783–787.
- 533 (20) Hentschel, M.; Schaferling, M.; Weiss, T.; Liu, N.; Giessen, H.  
534 Three-Dimensional Chiral Plasmonic Oligomers. *Nano Lett.* **2012**, 12,  
535 2542–2547.
- 536 (21) Guerrero-Martínez, A.; Alonso-Gómez, J. L.; AuguÍ, B.; Cid, M.  
537 M.; Liz-Marzán, L. M. From Individual to Collective chirality in Metal  
538 Nanoparticles. *Nano Today* **2011**, 6, 381.
- 539 (22) Baimuratov, A. S.; Rukhlenko, I. D.; Gun'ko, Y. K.; Baranov, A.  
540 V.; Fedorov, A. V. Dislocation-Induced Chirality of Semiconductor  
541 Nanocrystals. *Nano Lett.* **2015**, 15, 1710–1715.
- 542 (23) Kuhnle, A.; Linderth, T. R.; Hammer, B.; Besenbacher, F.  
543 Chiral Recognition in Dimerization of Adsorbed Cysteine Observed  
544 by Scanning Tunneling Microscopy. *Nature* **2002**, 415, 891–893.
- 545 (24) Zhou, Y. L.; Zhu, Z. N.; Huang, W. X.; Liu, W. J.; Wu, S. J.; Liu,  
546 X. F.; Gao, Y.; Zhang, W.; Tang, Z. Y. Optical Coupling Between  
547 Chiral Biomolecules and Semiconductor Nanoparticles: Size-Depend-  
548 ent Circular Dichroism Absorption. *Angew. Chem., Int. Ed.* **2011**, 50,  
549 11456–11459.
- 550 (25) Yan, W.; Xu, L.; Xu, C.; Ma, W.; Kuang, H.; Wang, L.; Kotov, N.  
551 A. Self-Assembly of Chiral Nanoparticle Pyramids with Strong R/S  
552 Optical Activity. *J. Am. Chem. Soc.* **2012**, 134, 15114–15121.
- 553 (26) Zhou, Y. L.; Yang, M.; Sun, K.; Tang, Z. Y.; Kotov, N. A. Similar  
554 Topological Origin of Chiral Centers in Organic and Nanoscale  
555 Inorganic Structures: Effect of Stabilizer Chirality on Optical  
556 Isomerism and Growth of CdTe Nanocrystals. *J. Am. Chem. Soc.*  
557 **2010**, 132, 6006–6013.
- 558 (27) Yeom, J.; Yeom, B.; Chan, H.; Smith, K. W.; Dominguez-  
559 Medina, S.; Bahng, Joong, H.; Zhao, G.; Chang, W.-S.; Chang, S.-J.;  
Chuvilin, A.; Melnikau, D.; Rogach, A. L.; Zhang, P.; Link, S.; Král, P.;  
Kotov, N. A. Chiral Templating of Self-Assembling Nanostructures by  
Circularly Polarized Light. *Nat. Mater.* **2015**, 14, 66–72.
- (28) Hu, T.; Isaacoff, B. P.; Bahng, J. H.; Hao, C.; Zhou, Y.; Zhu, J.;  
Li, X.; Wang, Z.; Liu, S.; Xu, C.; Biteen, J. S.; Kotov, N. A. Self-  
Organization of Plasmonic and Excitonic Nanoparticles into Resonant  
Chiral Supraparticle Assemblies. *Nano Lett.* **2014**, 14, 6799–6810.
- (29) Srivastava, S.; Santos, A.; Critchley, K.; Kim, K.-S.; Podsiadlo, P.;  
Sun, K.; Lee, J.; Xu, C.; Lilly, G. D.; Glotzer, S. C.; Kotov, N. A. Light-  
Controlled Self-Assembly of Semiconductor Nanoparticles into  
Twisted Ribbons. *Science* **2010**, 327, 1355–1359.
- (30) Tang, Z.; Kotov, N. A.; Giersig, M. Spontaneous Organization  
of Single CdTe Nanoparticles into Luminescent Nanowires. *Science*  
**2002**, 297, 237–240.
- (31) Klug, A. The Tobacco Mosaic Virus Particle: Structure and  
Assembly. *Philos. Trans. R. Soc., B* **1999**, 354, 531–535.
- (32) Tang, Z.; Wang, Y.; Sun, K.; Kotov, N. A. Spontaneous  
Transformation of Stabilizer-Depleted Binary Semiconductor Nano-  
particles into Selenium and Tellurium Nanowires. *Adv. Mater.* **2005**,  
17, 358–363.
- (33) Prins, L. J.; Huskens, J.; de Jong, F.; Timmerman, P.; Reinhoudt,  
D. N. Complete Asymmetric Induction of Supramolecular Chirality in  
A Hydrogen-Bonded Assembly. *Nature* **1999**, 398, 498–502.
- (34) Bierman, M. J.; Lau, Y. K. A.; Kvit, A. V.; Schmitt, A. L.; Jin, S.  
Dislocation-Driven Nanowire Growth and Eshelby Twist. *Science*  
**2008**, 320, 1060–1063.
- (35) Govorov, A. O.; Gun'ko, Y. K.; Slocik, J. M.; Gerard, V. A.; Fan,  
Z.; Naik, R. R. Chiral Nanoparticle Assemblies: Circular Dichroism,  
Plasmonic Interactions, and Exciton Effects. *J. Mater. Chem.* **2011**, 21,  
16806–16818.
- (36) Xia, Y.; Nguyen, T. D.; Yang, M.; Lee, B.; Santos, A.; Podsiadlo,  
P.; Tang, Z.; Glotzer, S. C.; Kotov, N. A. Self-assembly of Self-limiting  
Monodisperse Supraparticles from Polydisperse Nanoparticles. *Nat.*  
*Nanotechnol.* **2011**, 6, 580–587.
- (37) Nguyen, T. D.; Schultz, B. A.; Kotov, N. A.; Glotzer, S. C.  
Generic, Phenomenological, On-The-Fly Renormalized Repulsion  
Model for Self-Limited Organization of Terminal Supraparticle  
Assemblies. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, 112, 3161–3168.
- (38) Dai, M.-Q.; Zheng, W.; Huang, Z.; Lanry Yung, L.-Y. Aqueous  
Phase Synthesis of Widely Tunable Photoluminescence Emission  
CdTe/CdS Core/Shell Quantum Dots under A Totally Ambient  
Atmosphere. *J. Mater. Chem.* **2012**, 22, 16336–16345.
- (39) Zeng, Q.; Kong, X.; Sun, Y.; Zhang, Y.; Tu, L.; Zhao, J.; Zhang,  
H. Synthesis and Optical Properties of Type II CdTe/CdS Core/Shell  
Quantum Dots in Aqueous Solution via Successive Ion Layer  
Adsorption and Reaction. *J. Phys. Chem. C* **2008**, 112, 8587–8593.
- (40) Paramonov, S. E.; Jun, H.-W.; Hartgerink, J. D. Self-Assembly of  
Peptide–Amphiphile Nanofibers: The Roles of Hydrogen Bonding  
and Amphiphilic Packing. *J. Am. Chem. Soc.* **2006**, 128, 7291–7298.
- (41) Zhang, S. Fabrication of Novel Biomaterials Through Molecular  
Self-assembly. *Nat. Biotechnol.* **2003**, 21, 1171–1178.
- (42) Kotov, N. A. *Terminal and Extended Assemblies of Nanoparticles*,  
*MPL Lecture*; California Institute of Technology, Pasadena, CA, March  
26, 2014.
- (43) Damasceno, P. F.; Engel, M.; Glotzer, S. C. Predictive Self-  
Assembly of Polyhedra into Complex Structures. *Science* **2012**, 337,  
453–457.
- (44) Ma, W.; Kuang, H.; Wang, L.; Xu, L.; Chang, W.-S.; Zhang, H.;  
Sun, M.; Zhu, Y.; Zhao, Y.; Liu, L.; Xu, C.; Link, S.; Kotov, N. A.  
Chiral Plasmonics of Self-assembled Nanorod Dimers. *Sci. Rep.* **2013**,  
3, 1934.
- (45) Cho, K.-S.; Talapin, D. V.; Gaschler, W.; Murray, C. B.  
Designing PbSe Nanowires and Nanorings Through Oriented  
Attachment of Nanoparticles. *J. Am. Chem. Soc.* **2005**, 127, 7140–  
7147.
- (46) Han, X. D.; Zhang, Y. F.; Zheng, K.; Zhang, X. N.; Zhang, Z.;  
Hao, Y. J.; Guo, X. Y.; Yuan, J.; Wang, Z. L. Low-Temperature *in situ*  
Large Strain Plasticity of Ceramic SiC Nanowires and Its Atomic-Scale  
Mechanism. *Nano Lett.* **2007**, 7, 452–457.

- 629 (47) Bishop, K. J.; Wilmer, C. E.; Soh, S.; Grzybowski, B. A.  
630 Nanoscale Forces and Their Uses in Self-Assembly. *Small* **2009**, *5*,  
631 1600–1630.
- 632 (48) Mah, V.; Jalilehvand, F. Cadmium(II) Complex Formation with  
633 Glutathione. *JBIC, J. Biol. Inorg. Chem.* **2010**, *15*, 441–458.
- 634 (49) Rulišek, L.; Havlas, Z. Theoretical Studies of Metal Ion  
635 Selectivity. I. DFT Calculations of Interaction Energies of Amino Acid  
636 Side Chains with Selected Transition Metal Ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  
637  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$ ). *J. Am. Chem. Soc.* **2000**, *122*, 10428–10439.
- 638 (50) Chandler, D.; Weeks, J. D.; Andersen, H. C. Van der Waals  
639 Picture of Liquids, Solids, and Phase Transformations. *Science* **1983**,  
640 *220*, 787–794.
- 641 (51) Erickson, R. O. Tubular Packing of Spheres in Biological Fine  
642 Structure. *Science* **1973**, *181*, 705–716.
- 643 (52) Sharma, A.; Mori, T.; Lee, H.-C.; Worden, M.; Bidwell, E.;  
644 Hegmann, T. Detecting, Visualizing, and Measuring Gold Nano-  
645 particle Chirality Using Helical Pitch Measurements in Nematic Liquid  
646 Crystal Phases. *ACS Nano* **2014**, *8*, 11966–11976.
- 647 (53) Kumar, S. Discotic Liquid Crystal-Nanoparticle Hybrid Systems.  
648 *NPG Asia Mater.* **2014**, *6*, e82.