

Open Channel Metal Particle Superlattices

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21 **Summary Paragraph**

22 **Although tremendous advances have been made in preparing porous crystals from**
23 **molecular precursors^{1,2}, there are no general ways of designing and making topologically**
24 **diversified porous colloidal crystals over the 10-1000 nm length scale. Control over porosity**
25 **in this size range would enable the tailoring of molecular absorption and storage, separation,**
26 **chemical sensing, catalytic and optical properties of such materials. Here, a universal**
27 **approach for synthesizing metallic open channel superlattices with 10 to 1000 nm pores from**
28 **DNA-modified hollow colloidal nanoparticles (NPs) is reported. By tuning hollow NP**
29 **geometry and DNA design, one can adjust crystal pore geometry (pore size and shape) and**
30 **channel topology (the way in which pores are interconnected). The assembly of hollow NPs**
31 **is driven by edge-to-edge rather than face-to-face DNA-DNA interactions. Two new design**
32 **rules describing this assembly regime emerge from these studies and are then used to**
33 **synthesize 12 open channel superlattices with control over crystal symmetry, channel**
34 **geometry and topology. The open channels can be selectively occupied by guests of the**
35 **appropriate size and that are modified with complementary DNA (e.g., Au NPs).**

36

37 **Main Text**

38 **Introduction**

39 Porous crystals are a class of materials with extraordinary properties, including high surface
40 areas and low densities, that can be engineered to physically absorb and chemically interact with
41 guest species of known size, shape, and chemical functionality^{2–15}. Porous colloidal materials are
42 a particularly interesting class of such structures, as they provide access to inverse photonic
43 structures that can be used for optics, energy storage, and biological applications¹⁶. These
44 structures are typically made by templating processes¹⁷, a strategy that often relies on face-centered
45 cubic crystals made from spherical particles as templates; this limits the possible pore topologies
46 and distribution of pore volumes.

47 Although reticular chemical synthesis based upon metal ions and bridging ligand building
48 blocks has led to significant advances in the realization of porous materials (pore apertures < 10
49 nm), and design rules now exist for the construction of such materials at the molecular scale^{18–20},
50 it is still remarkably difficult to prepare porous crystals with customized pore topologies and pore
51 sizes in the range between 10 nm and 1 μm . We hypothesized that three-dimensional (3D) metallic
52 hollow nanoparticles (NPs) [nanoframes (NFs) and nanocages (NCs)] could be assembled into
53 open channel superlattices using colloidal crystal engineering with DNA, an approach that thus far
54 yields access to over 70 different crystal symmetries via well-established design rules based upon
55 the complementary contact model (CCM, the notion that DNA-modified building blocks will
56 arrange themselves in space to maximize complementary interactions)^{21–23}. Indeed, consistent with
57 the CCM²³, we determined that the attractive DNA hybridization interactions between the edges
58 of adjacent NFs lead to the formation of ordered superlattices. Notably, this registry-driven edge-

59 to-edge assembly mode (edge-bonding) is distinct from the canonical face-to-face interactions
60 (face-packing) that typically govern the assembly outcomes of solid NPs²⁴. It should be noted that
61 an approach that relies on the crystallization of DNA origami subunits^{25,26} has been developed,
62 and although this method enables access to certain crystal structures through vertex-to-vertex
63 bonding, it yields structures that are limited in pore dimensions (typical unit size < 50 nm).

64 Importantly, herein we introduce two new design rules that summarize this edge-bonding
65 construction strategy, through which 12 novel open channel superlattices are synthesized. These
66 structures have symmetries, pore geometries, and topologies that can be deliberately tuned through
67 the choice of hollow NP and DNA. These open channel metallic superlattices not only have the
68 potential to exhibit unnatural optical properties that make them attractive as optical metamaterials
69 but also can be useful for localizing large guests for a variety of applications, including
70 biomolecular absorption and storage, separation, chemical sensing, and catalysis.

71 **Synthesis of open channel superlattices**

72 3D hollow NPs were synthesized in two forms (Fig. 1a): NFs, which represent only the edges
73 of a polyhedron, and NCs, which have some solid faces. Au-Pt NFs were synthesized according
74 to a modified literature procedure²⁷ from polyhedral Au NPs via a three-step reaction pathway
75 (Fig. 1b-i): 1) edge-selective growth of Pt on Au NPs (Fig. 1b-e); 2) selective etching of Au (Fig.
76 1f, g), and 3) overgrowth of Au on Pt skeletons (Fig. 1h, i). Using this route, NFs with different
77 shapes (octahedra, triangular prisms, truncated octahedra, cuboctahedra, truncated cubes, and
78 cubes; Fig. 1a and Supplementary Fig.1a-e) and sizes were synthesized. In addition, a novel
79 synthetic route was developed for truncated octahedral, cuboctahedral, and truncated cubic NCs,
80 utilizing a facet-specific growth of Pt on Au NPs method (Supplementary Figs. 1f-h and 2a-d).

81 The pore sizes of the synthesized NFs and NCs were tailored by changing the growth solution
82 conditions or the sizes of the original NPs utilized (Supplementary Figs. 2e-i and 3a-c). Also, other
83 metallic elements (such as Pd, Rh, Ru, and Ag) can be incorporated into such hollow NPs, if
84 desired, for use in specific applications²⁸. For example, Au-Ag NFs were synthesized
85 (Supplementary Fig. 3e) according to literature methods²⁹.

86 To assemble these building blocks into superlattices, NFs and NCs were functionalized with
87 self-complementary oligonucleotides (anchor strand A and linker A₂) (Fig. 1j and Supplementary
88 Table 1), such that every particle can hybridize with any other particle in the system. The DNA-
89 functionalized hollow NPs were crystallized into superlattices via slow-cooling, where the
90 temperature of the system was lowered from 65 to 25 °C³⁰; this strategy allows the system to reach
91 its lowest free energy configuration (Fig. 1k). These crystals were then analyzed in solution by
92 small angle X-ray scattering (SAXS; Extended Data Fig. 6), and they were also encapsulated in
93 silica³¹ or stabilized with Ag⁺³² (Fig. 1l) to permit their analysis in the solid state by scanning
94 electron microscopy (SEM) and transmission electron microscopy (TEM). Representative
95 nanoparticle building blocks used to form the open channel superlattices were also reconstructed
96 by electron microscopy tomography (Supplementary video 4), and 3D models of the corresponding
97 superlattices were constructed based on these tomography data (Extended Data Fig. 7).

98 **Space-Filling NF Polyhedra**

99 *Design rule 1: NFs that derive from space-filling shapes assemble into the corresponding space-*
100 *filling construction via edge-to-edge assembly (edge-bonding). The CCM for the DNA-mediated*
101 *assembly of space-filling NPs dictates that the most thermodynamically stable assembly outcome*
102 *is that which maximizes DNA hybridization*²³. Analogously, we posited that for DNA-

103 functionalized NFs, edge-to-edge contact would maximize DNA hybridization and drive the
104 assembly of these particles into specific crystal structures. Based on geometric considerations, we
105 also noted that the arrangement of space-filling shapes, such as cubes, truncated octahedra, and
106 triangular prisms, into their corresponding space-filling constructions also maximizes edge-to-
107 edge contact. Therefore, we predicted that the edge-bonding-driven assembly of NFs with space-
108 filling shapes would favor the most symmetrical space-filling constructions, in which the faces of
109 the representative polyhedra are registered and completely overlapping with one another, but with
110 open channels dictated by NF voids (Extended Data Fig. 1).

111 The edge-bonding of cubic NFs serves as an illustrative example (Fig. 2a-d). Cubic NFs
112 assemble into porous simple cubic (*sc*) lattices (Fig. 2a-d), corresponding to the space-filling
113 construction, whereby rectangular channels of different sizes and triangular channels are discerned
114 along different lattice directions (Fig. 2b). This design rule is also validated by the construction of
115 body-centered cubic (*bcc*) lattices (Fig. 2e-h, and Supplementary Fig. 4) via the edge-bonding of
116 truncated octahedral NFs. Three representative channel topologies of the *bcc* lattice are shown
117 along the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ directions of the crystal, with mixtures of periodic triangular,
118 quadrilateral, and hexagonal channels in view (Fig. 2f).

119 Interestingly, triangular prism NFs assembled into two different open channel superlattices
120 depending on DNA design. When functionalized with short, rigid DNA (Supplementary Table 1,
121 anchor strand A and linker A₁), the triangular prism NFs formed one-dimensional (1D) open
122 columnar structures with a single triangular channel along the column direction (Fig. 2i-1). This
123 structure is analogous to that expected from the assembly of solid triangular nanoprisms³³. In
124 contrast, when more flexible DNA linkers were used (Supplementary Table 1, anchor strand A
125 and linker A₂), the triangular prism NFs assembled into a 3D interlocked honeycomb (*ih*) lattice

126 (Fig. 2m-p, and Supplementary Fig. 5), in which there are additional in-plane interactions between
127 the sides of adjacent columns. This observation is consistent with studies from our laboratory that
128 elucidate the influence of linker flexibility on NP assembly³⁴. Briefly, when DNA flexibility is
129 increased via the incorporation of polyethylene glycol (PEG) units, the stress of contact between
130 the NPs decreases and intracolumnar side-to-side interactions occur. Moreover, DNA surface
131 functionalization renders the outlined shape of a triangular prism NF similar to that of a truncated
132 bitetrahedral frame (Supplementary Fig. 5), a space-filling shape that corresponds to the *ih* lattice.
133 This example shows that the chemical modularity of oligonucleotides enriches the diversity of
134 open channel superlattices that can be prepared via edge-bonding.

135 **Non-Space-Filling NF Polyhedra**

136 *Design rule 2: NFs that outline one shape of a convex space-filling pair can assemble into the*
137 *corresponding space-filling cocrystal lattice via edge-bonding.* There are several pairs of solid
138 polyhedra that co-assemble to fill 3D space. If only one solid polyhedron of these space-filling
139 pairs is assembled into the space-filling construction, the structure is not well-stabilized; the
140 system cannot maximize face-to-face interactions and contains voids and unregistered facets^{24,35}.
141 In contrast, edge-bonding of non-space-filling NF polyhedra provides a means to facilitate a stable
142 assembly of colloidal particles into highly porous structures, in which NFs tile along their edges
143 (edge-tiling) and edge-to-edge interactions are maximized. For example, NFs that derive from one
144 shape of a space-filling pair can assemble into the corresponding, stable, space-filling lattice, but
145 with structural voids representing the missing shape of the pair. And, unlike with solid polyhedra,
146 these structural voids, which are geometrically complementary to the shape of the NF building
147 blocks, are uniquely stabilized by maximizing the edge-to-edge interactions between the building
148 blocks (Extended Data Fig. 2).

149 Octahedra and tetrahedra represent one space-filling pair and co-assemble into a cubic close-
150 packed (*ccp*) structure (Extended Data Fig. 2a). The edge-bonding assembly of only octahedral
151 NFs gives the corresponding dual-shape lattice, the *ccp* structure (Fig. 3a-d, and Extended Data
152 Fig. 2b). This *ccp* lattice with an octahedral habit exhibits triangular channels of different sizes
153 (Fig. 3b), and two sets of tetrahedral voids in alternating orientations (shown in yellow and orange
154 in Fig. 3a). In this lattice, the DNA on every edge of the octahedral NFs is hybridized to the DNA
155 on at least one other edge, maximizing overall edge-to-edge interactions and stabilizing the porous
156 structure as well as its void spaces. This result shows that edge-bonding can give rise to new highly
157 porous and non-dense packed (they have voids in addition to the pores) structures that are
158 nonetheless stable. For example, in terms of symmetry, face-packing of solid octahedra (which
159 favor *bcc* symmetry) and vertex-bonding of octahedral origami subunits (which favor *sc*
160 symmetry) do not result in crystals with *ccp* symmetry^{24,36}.

161 This design rule can also be applied to cuboctahedra and square pyramids, which form a space-
162 filling pair with body-centered tetragonal (*bct*) symmetry (Extended Data Fig. 2c). We assembled
163 cuboctahedral NFs into an open-channel, low-symmetry lattice with *bct* symmetry (Fig. 3e-h,
164 Extended Data Fig. 2d, and Supplementary Fig. 7). Compared with cubic lattices (*sc*, *bcc*, and
165 *ccp*), the lower symmetry of the *bct* lattice means that there are two types of $\langle 100 \rangle$ and $\langle 110 \rangle$
166 directions with distinct projections that contain triangular and quadrilateral channels (Fig. 3f). In
167 addition to these porous channels, there are two sets of square pyramidal voids with alternating
168 orientations (highlighted in yellow and orange in Fig. 3e).

169 The generality of this rule also allows the structural outcome of NF assembly to be predicted.
170 Finally, noting that truncated cubes and octahedra also form a complementary space-filling pair
171 (Extended Data Fig. 2e), we hypothesized that the assembly of truncated cubic NFs would yield a

172 lattice with octahedral voids. Indeed, we observed a *sc* structure with a cubic habit and octahedral
173 voids (Fig. 3i-l, Extended Data Fig. 2f, and Supplementary Fig. 8). In this *sc* lattice, channels
174 viewed along different crystal directions exhibit triangular, hexagonal, or octagonal shapes (Fig.
175 3j). Both the channels and structural voids within the lattice define the pore topology of the
176 assembled crystals. Taken together, these three examples of superlattices assembled via the edge-
177 bonding of a single NF from a space-filling pair support Design Rule 2, and also markedly increase
178 the number and diversity of open channel superlattice symmetries and topologies that can be
179 accessed.

180 **Programming Pore Geometry and Topology**

181 Pore geometry and topology are two important characteristics that determine potential
182 applications. These parameters can be deliberately adjusted by changing the dimensions of the
183 hollow NPs. First, the channel size can be tuned by changing the size and thickness of the NFs
184 (Supplementary Figs. 2, 3a-c, and Extended Data Fig. 3). As a proof-of-concept, we synthesized
185 octahedral NFs with edge lengths of 70, 130, 175, and 250 nm with triangular pores of 30, 75, 90
186 and 160 nm, respectively. Each of these NFs assembled into superlattices with *ccp* symmetry but
187 with substantially different channel sizes (Fig. 3d, and Extended Data Fig. 3). Note that, in the *ccp*
188 lattice, one of the channel sizes is the same as the particle pore size, but several channels of
189 different sizes exist (Fig. 3b). To illustrate the broad range of pore size tunability through choice
190 of NF building block, we also synthesized octahedral NFs with pores spanning the meso- and
191 macroporous range, specifically, 8, 285 and 1020 nm pores on NFs (Supplementary Fig. 3a-c). In
192 principle, the channel sizes can be readily tuned in the 10 nm to 1 μ m range by using particles with
193 different edge lengths and pore sizes.

194 Second, we show that pore topology can be changed by assembling NFs with specific faces
195 retained, that is, the corresponding NCs (Extended Data Fig. 4). To help visualize the channel
196 topologies of different porous crystals, models of crystals are constructed, in which the volumes
197 occupied by all the pores and channels are filled, and the solid material in the NFs and DNA are
198 removed. Truncated octahedral NFs can be assembled via edge-bonding (Fig. 2e) into crystals with
199 the same symmetry (*bcc*) as those attained when solid truncated octahedral NPs are assembled via
200 face-to-face packing. We therefore hypothesized that a *bcc* lattice with intermediate pore size and
201 different pore topology could be obtained via assembly through the specific-facet registration of
202 truncated octahedral NCs (prepared by selectively retaining the {100} facets of truncated
203 octahedral NFs) (Fig. 4a-d). Indeed, crystals with the same symmetry but with distinct pore
204 topology and dramatically reduced pore size along the <100> direction were obtained when NCs
205 (Fig. 4b) were assembled instead of truncated octahedral NFs (Fig. 2f). Similarly, the channels
206 within *sc* structures assembled from truncated cubic NCs (Fig. 4e-h, and Supplementary Fig. 9)
207 are less open than those in *sc* structures prepared using truncated cubic NFs (Fig. 3i-l).

208 A similar effect is observed for hollow cuboctahedral NPs, where cuboctahedral NCs with six
209 {100} facets assemble into a *bct* lattice (Fig. 4i-l, and Supplementary Fig. 10), the same structure
210 observed for the edge-bonding of cuboctahedral NFs, but with a different pore topology and
211 reduced pore size. Notably, increasing the flexibility of the DNA attached to the cuboctahedral
212 NCs changes the lattice symmetry (from *bct* to *sc*) with a concomitant change in pore topology
213 and size (Supplementary Fig. 11). Therefore, the pore geometry and topology of the superlattice
214 can be tuned by changing the dimensions of the NFs, by employing NCs where specific facets are
215 solid (compared to NFs), and through judicious DNA design (that also affects lattice symmetry).

216 Importantly, we can control the pore topology and crystal symmetry independently using these
217 strategies.

218 By surveying the 12 porous structures discovered here and comparing the projections of their
219 continuous channels along different directions as the crystals grow (simulation in Supplementary
220 Video 1), we see that the channel topology is a function of both the crystal symmetry and the shape
221 of the constituent building block (Extended Data Fig. 5). For example, the four *sc* structures
222 (Extended Data Fig. 5d,f,h,j) obtained via assembly of cubic NFs, truncated cubic NFs, truncated
223 cubic NCs, and cuboctahedral NCs have substantially different channel topologies even though
224 their crystal symmetries are identical. Furthermore, the three *bcc* structures (Extended Data Fig.
225 5e,g,i) assembled from truncated octahedral NFs and truncated octahedral NCs, and the two *bct*
226 structures (Extended Data Fig. 5k,l) assembled from cuboctahedral NFs and cuboctahedral NCs,
227 all display significantly different channel topologies. Note that even within a single crystal, there
228 are often channels of different shapes and sizes that are highly tailorable. Therefore, building block
229 shape and lattice symmetry provide two design handles for defining the channel topology in
230 nanoscale porous crystals.

231 **Encapsulation of Guests in Open Lattices**

232 As a proof-of-concept test of the open channels inside the assembled crystals, we co-assembled
233 Au nanospheres of different sizes (core diameters of 30 and 20 nm with DNA shell thickness of
234 approximately 7.5 nm) with truncated cubic NFs (edge length of ~100 nm). NFs were
235 functionalized with anchor A/linker A₃ or anchor B/linker B (Fig. 4m, Supplementary Table 1),
236 whereby complementary linkers A₃ and B hybridize to form a *sc* superlattice. Spheres were
237 functionalized with strand B* and thus can hybridize with half of the NFs (those with linker A₃,

238 Fig. 4n). Both SEM and cross-section TEM images reveal that spheres interact with the assembled
239 truncated cubic NFs and localize selectively in alternating pores of the resulting *sc* lattice (Fig.
240 4o,p). This selective localization is signified by a characteristic checkerboard pattern for co-
241 crystals with 30 nm spheres (Fig. 4o and Supplementary Fig. 13) and 20 nm spheres (Fig. 4p and
242 Supplementary Fig. 14). These results suggest that one can achieve selective guest localization in
243 the periodic, continuous pores of open channel superlattices through DNA-programmed
244 interactions. Furthermore, assembled superlattices are able to act as host structures, encapsulating
245 guests via post-synthesis diffusion (Supplementary Fig. 15). This capability provides opportunities
246 to design the loading and transport of large guest species that could yield material behaviors not
247 yet achievable in existing porous crystals.

248 **Negative Refractive Index Metamaterials**

249 The controllable and tunable pore topologies and periodicities of open channel superlattices
250 make them promising candidates to realize optical phenomena that are not observed in natural
251 materials. Indeed, negative refractive index materials, structures aggressively pursued by the
252 materials science and physics communities, could become important for super-resolution imaging,
253 cloaking, and other applications³⁷. Since these open channel superlattices are reminiscent of split
254 ring resonators, metamaterials known to exhibit negative refractive indices³⁸, we were curious if
255 this new class of structures could also exhibit negative refraction. Interestingly, optical simulations
256 of a *ccp* crystal (Extended Data Fig. 8, see also Supplementary Information) indeed confirm that
257 it is possible to realize negative refraction with open channel superlattice architectures. Although
258 promising, there are two practical challenges that must be overcome before open channel
259 superlattices can be developed practically as functional negative refractive materials: (a) new
260 fabrication techniques that potentially take advantage of colloidal crystal engineering coupled with

261 top-down lithography methods would be required to mold the open channel superlattices into
262 large-area, single-crystalline films with desired shapes³⁹, and (b) new NF synthesis strategies for
263 preparing colloidal building blocks consisting of low-loss metals such as aluminum, would
264 increase the transmission of the open channel superlattices, thereby increasing the performance of
265 devices based upon them.

266 **Conclusion**

267 We have presented a new edge-bonding approach to design and synthesize open channel
268 superlattices using hollow NPs with pore sizes over the 10-1000 nm length scale. The DNA-
269 mediated assembly of hollow NPs offers a potential opportunity to construct negative-refractive-
270 index metamaterials from the bottom-up. Looking forward, functional materials (such as quantum
271 dots, proteins, and viruses) can be strategically localized in the open channels, potentially offering
272 routes to composite architectures that could impact a broad range of fields, spanning catalysis,
273 plasmonics, electronics, and biology.

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Figure Legends

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Fig. 1| Reaction pathway for the synthesis of hollow NPs (NFs and NCs) and open channel superlattices. **a**, Models of hollow NPs of different shapes. **b-i**, SEM images and corresponding models of intermediates in the synthesis of Au octahedral NFs, including **(b-e)** octahedral NPs with edge-selective Pt growth, **(f, g)** Pt octahedral NFs where the Au content has been selectively etched, and **(h, i)** Au-Pt octahedral NFs where Au has been grown on the Pt skeleton. **j-l**, Scheme of the DNA-mediated crystallization and stabilization of open channel superlattices. Octahedral NFs are **(j)** functionalized with DNA, **(k)** slowly annealed from high to low temperature to form crystals, and **(l)** stabilized by encapsulation in silica or by soaking with Ag^+ ions. Scale bars: 100 nm.

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Fig. 2| Edge-bonding of NFs that outline space-filling shapes. **a-d**, Porous crystals with *sc* symmetry assembled from cubic NFs, with models shown in **(a)** perspective view and **(b)** projected along the indicated lattice directions. **(c)** Model showing the pore topology, in which the volumes occupied by all the pores and channels are filled, and the solid material in the NFs and DNA are removed. **(d)** SEM images with different magnifications. **e-h**, Porous crystals with *bcc* symmetry assembled from truncated octahedral NFs, with models shown in **(e)** perspective view and **(f)** projected along the indicated lattice directions. **(g)** Model showing the pore topology. **(h)** SEM images with different magnifications. **i-l**, Porous open columnar structures assembled from triangular prism NFs using short, rigid DNA, with models shown in **(i)** perspective view and **(j)** projected along the indicated directions. **(k)** Model showing the pore topology. **(l)** SEM images with different magnifications. **m-p**, Porous *ih* structures assembled from triangular prism NFs using flexible DNA, with models shown in **(m)** perspective view and **(n)** projected along the indicated directions. **(o)** Model showing the pore topology. **(p)** SEM images with different magnifications. Scale bars: 2.5 μm (SEM images, left) and 500 nm (SEM images, right).

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Fig. 3| Edge-bonding of NFs that outline one shape of a space-filling pair. **a-d**, Porous crystals with *ccp* symmetry assembled from octahedral NFs, with models shown in **(a)** perspective view and **(b)** projected along the indicated lattice directions. In **(a)**, the tetrahedral voids are depicted in yellow and orange. **(c)** Model showing the pore topology. **(d)** SEM images with different magnifications. **e-h**, Porous crystals with *bct* symmetry assembled from cuboctahedral NFs, with models shown in **(e)** perspective view and **(f)** projected along the indicated lattice directions. In **(e)**, square pyramidal voids are depicted in yellow and orange. **(g)** Model showing the pore topology. **(h)** SEM images with different magnifications. **i-l**, Porous crystals with *sc* symmetry assembled from truncated cubic NFs, with models shown in **(i)** perspective view and **(j)** projected along the indicated lattice directions. In **(i)**, octahedral voids are depicted in yellow. **(k)** Model showing the pore topology. **(l)** SEM images with different magnifications. Scale bars: 2.5 μm (SEM images, left) and 500 nm (SEM images, right).

400

401

402 **Fig. 4| Adjusting pore topologies of open channel superlattices and encapsulation of guests**
403 **in open lattices. a-d**, Porous crystals with *bcc* symmetry assembled from truncated octahedral
404 NCs, with models shown in **(a)** perspective view and **(b)** projected along the indicated lattice
405 directions. **(c)** Model showing the pore topology. **(d)** SEM images. **e-h**, Porous crystals with *sc*
406 symmetry and cubic habit assembled from truncated cubic NCs, with models shown in **(e)**
407 perspective view and **(f)** projected along the indicated lattice directions. **(g)** Model showing the
408 pore topology. **(h)** SEM images. **i-l**, Porous crystals with *bct* symmetry assembled from
409 cuboctahedral NCs, with models shown in **(i)** perspective view and **(j)** projected along indicated
410 lattice directions. **(k)** Model showing the pore topology. **(l)** SEM images. **m**, Scheme showing co-
411 assembly of Au spheres and truncated cubic NFs. Color denotes DNA design: anchor A/linker A₃
412 (dark purple) or anchor B/linker B (yellow) or strand B* (light purple). **n**, Model of the co-
413 assembled crystal with *sc* symmetry and cubic habit. **o**, **p**, EM images of the resulting crystals,
414 where **(o)** 30 or **(p)** 20 nm spheres are selectively located in the pores of the open channel
415 superlattices. High-resolution SEM images (top insets) and cross-section TEM images (bottom
416 insets), showing the checkerboard pattern formed by NFs that adsorbed spheres and those that did
417 not. Unless otherwise indicated, scale bars: 2.5 μm (SEM images, left) and 500 nm (SEM images,
418 right); 100 nm (bottom insets of o, p).
419
420

421 **Methods**

422 **Synthesis of Au-Pt nanoframes and nanocages**

423 Gold triangular nanoprisms were synthesized according to Millstone *et al.*⁴⁰ The synthesis of
424 nanoprisms resulted in a significant number of pseudo-spherical nanoparticle (NP) impurities. To
425 isolate the triangular nanoprisms, a depletion force-mediated procedure reported by Young *et al.*⁴¹
426 was utilized. Briefly, the unpurified nanoprism solution was transferred to 15-ml Falcon tubes and
427 brought to 0.2 M NaCl. After 1 h, this solution was centrifuged for 10 s at 6,000 rpm. The
428 supernatant, containing the pseudo-spherical NP impurities, was removed. The pellet containing
429 triangular nanoprisms was then resuspended in 50 mM CTAB.

430 Cubic, octahedral, truncated octahedral, cuboctahedral, and truncated cubic gold NPs were
431 synthesized via a literature method^{42,43}. In this strategy, iterative oxidative dissolution and
432 reductive growth reactions were utilized to control NP seed structural uniformity. Subsequently,
433 these seeds were used to template the growth of different anisotropic NPs: cubes, octahedra,
434 truncated octahedra, cuboctahedra, and truncated cubes. NPs of larger sizes (> 400 nm) were
435 synthesized through iterative growth.

436 Gold nanoframes (NFs) of different shapes were synthesized based on a reported pathway²⁷.
437 This pathway includes three chemical reactions: 1) edge-selective growth of Pt on Au NPs of
438 different shapes; 2) selective etching of Au; and 3) overgrowth of Au on Pt skeletons to form Au
439 NFs of different shapes, including cubic, triangular prism, truncated cubic, cuboctahedral, and
440 truncated octahedral NFs (Supplementary Fig. 1). First, for the edge-selective growth process to
441 synthesize Au@Pt NPs, 7.5 ml of 50 mM CTAB, 2.5 ml of NP solution, 5 ml of 10 mM AgNO₃,
442 and 144 ml of 100 mM ascorbic acid (AA) were added to a vial in the presence of NaI (50 mM).
443 The solution was heated to 70 °C to promote the deposition of Ag layers onto the Au octahedral

444 NPs. After 1 h, 14.4 ml of 1 M HCl and 40 ml of 16 mM aqueous H_2PtCl_6 solution were injected
445 into the growth solution. The mixture was kept at 70 °C for approximately 3 h. After completion
446 of the reaction, the reaction products were purified from excess reagents via centrifugation for 5
447 min at 1,500 rcf. The supernatant was removed, and the NPs were resuspended in 10 ml of 50 mM
448 CTAB. Second, to obtain the Pt skeleton, 10 ml of 50 mM CTAB, 60 ml of 25 mM HAuCl_4 , and
449 Au@Pt NPs were combined in the presence of iodide ions (50 mM). The Au etching step took 2 h
450 at 50 °C. After etching, the products of the reactions were purified from the excess reagents by
451 centrifugation for 5 min at 2,800 rcf. The supernatant was removed, and the Pt skeletons were
452 resuspended in 50 mM CTAB. Finally, to synthesize the Au-Pt NFs, the Pt skeletons were
453 dispersed in 12 ml of CTAB with 50 mM of iodide ions and 12 ml of 1 M HCl, 120 ml of 100 mM
454 AA, 3 ml of 10 mM AgNO_3 , and 16 ml of 25 mM HAuCl_4 was added. To control the pore sizes of
455 the NFs, the volume of Au^{3+} solution was varied from 5 to 60 ml. The pore sizes decrease as more
456 gold atoms are deposited on each frame (Supplementary Fig. 2).

457 Gold nanocages (NCs) of different shapes were synthesized through a pathway similar to that
458 for the NFs above with slight modifications. The steps involved: 1) edge and specific facet-
459 selective growth of Pt on Au NPs of different shapes; 2) selective etching of Au; and 3) overgrowth
460 of Au on Pt cages to form Au NCs of different shapes, including truncated octahedral,
461 cuboctahedral, and truncated cubic NCs (Supplementary Figs. 1 and 2). Compared to the NF
462 synthesis, in the first step of the NC synthesis, the concentration of the Au NP starting material
463 was half that used for the NF synthesis, and the temperature was 75 °C. All other conditions were
464 the same.

465
466

467 **DNA synthesis and purification**

468 Oligonucleotide sequences were carefully designed for all experiments prior to synthesis
469 (Supplementary Table 1). Oligonucleotides were synthesized on a Mermade 12 (MM12) DNA
470 synthesizer. After synthesis, the oligonucleotides were cleaved from the controlled pore glass
471 (CPG) beads using a solution containing a 1:1 volume mixture of 30% ammonium hydroxide and
472 40% aqueous methylamine solution (incubation at 55 °C for 30 min). After evaporation, all of the
473 oligonucleotides were purified using reverse-phase high performance liquid chromatography (RP-
474 HPLC) on a Varian Microsorb C18 column (10 μ m, 300 \times 10 mm). Then, the oligonucleotides
475 were treated with acetic acid solution and ethyl acetate solutions to remove the DMT functional
476 groups. After synthesis and purification, all oligonucleotides were characterized by matrix-assisted
477 laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) to confirm their
478 molecular mass and purity.

479 **Synthesis of open channel superlattices**

480 All of the synthesized porous NPs, including NFs and NCs, were functionalized with anchor
481 DNA following a literature procedure²³. First, 3'-propylthiol-terminated anchor strands were
482 incubated with 100 mM dithiothreitol (DTT) for 1 h to cleave the disulfide end. Then, the DTT
483 was removed via size-exclusion chromatography with a NAP25 Column (GE Healthcare).
484 Afterwards, the anchor strands were added to the porous NP suspensions (~8 nmol DNA per ml
485 of porous NPs), and 1 wt% sodium dodecyl sulfate (SDS) and 1 M sodium phosphate (pH = 7.5)
486 were added to reach final concentrations of 0.01 wt% SDS and 10 mM sodium phosphate,
487 respectively. Next, stepwise additions of 5 M NaCl solution (with each aliquot raising the total
488 NaCl concentration by approximately 0.1 M) were added to the solution until it reached a final
489 concentration of 0.5 M NaCl; each addition was followed by 30 s of sonication. This solution was

490 shaken overnight to maximize DNA loading. Excess DNA strands were removed by three rounds
491 of centrifugation/supernatant removal/resuspension. After the final centrifugation step, the anchor-
492 coated porous NPs were redispersed in 0.5 M NaCl buffer (with 0.01 wt% SDS and 10 mM sodium
493 phosphate buffer). Then, 10 nmol of DNA linkers were added to 200 μ L of concentrated NP
494 solution. Self-complementary particles are ones with DNA that allow all particles to recognize and
495 hybridize with one another, while complementary systems involve particles with two different but
496 complementary DNA designs. The crystallization was performed through slow-cool annealing
497 with a ProFlex PCR system (Applied Biosystems)³⁰. Specifically, the temperature was slowly
498 decreased from 65 °C to 25 °C at a rate of 0.01 °C/min.

499 **Resin embedding of silica embedded crystals and ultramicrotomy**

500 The samples were embedded in a silica/resin following literature methods²⁴. Briefly, the silica
501 embedded colloidal crystals were added to 0.2 ml of 4% gelatin. The gelatin sample was
502 dehydrated upon immersion in anhydrous ethanol solutions of increasing concentration (30% \rightarrow
503 50% \rightarrow 70% \rightarrow 80% \rightarrow 90% \rightarrow 100%). Next, the sample immersed in 100% ethanol was solvent-
504 exchanged with acetone twice for 10 min. In acetone, the gelatin was embedded in EMBed-812
505 resin (Electron Microscopy Sciences) following the standard protocol provided by the
506 manufacturer. The samples were held at 65 °C for 48 h to polymerize and solidify the resin, and
507 the resin was then sectioned into 100-nm slices (Leica EM UC7).

508 **Characterization**

509 These crystals were analyzed in solution by small angle X-ray scattering (SAXS); and in the
510 solid state, after encapsulation in silica or stabilization with Ag⁺, with scanning electron
511 microscopy (SEM)^{31,32}. These two methods allow one to transfer open channel superlattices in the
512 assembled state and preserve crystal symmetry for imaging. To characterize the inner-guest

513 distribution of the crystals, the silica-stabilized crystals were subsequently embedded in a resin
514 and cross-sectioned to image the interior structure.

515 **3D reconstruction**

516 The tilt series high angle annular dark field (HAADF) images were collected using a JEOL
517 ARM 200CF microscope, operated at 200 kV. This microscope was equipped with a probe
518 corrector, and the spatial resolution in scanning transmission electron microscope (STEM) mode
519 is about 0.8 Å. The convergence angle used was 30 mrad. The collection angle of HAADF imaging
520 ranged from 90 to 250 mrad. The tilt series were collected manually from -70° to $+70^\circ$ at 2°
521 increments. All tilt series were initially aligned using the IMOD software package⁴⁴. For the final
522 3D reconstruction (Supplementary Video 4), we used the MBIR method⁴⁵.

523 **Optical simulation of open channel superlattices**

524 Full electromagnetic simulations were performed using commercial software, Ansys
525 Lumerical Finite Difference Time Domain (FDTD). The core diameter, shell diameter, and edge
526 length of the NFs, and interparticle gap between adjacent NFs were taken as 17 nm, 30 nm, 160
527 nm, and 10 nm, respectively. The NFs were embedded into SiO_2 ($n=1.45$). Johnson-and-Christy's
528 model⁴⁶ and Werner's model⁴⁷ were used as material model for Au and Pt, respectively. The
529 transverse electromagnetic polarized plane wave source was located at $(0, 0, 1700 \text{ nm})$ propagating
530 toward the $+z$ direction. The structure was located at the origin " $(0, 0, 0)$ ". The S-parameters were
531 taken from 2D/ z -normal near-field monitors located in the front ($z < 0$) and back ($z > 0$) of the
532 structure. Simulated phase propagation movies inside the porous *ccp* structure show negative phase
533 propagation inside the material (Supplementary Videos 2 and 3).

534

535

536 **Data availability**

537 All data are available in the main Article and Supplementary Information, or from the
538 corresponding authors on request.

539 **Additional References**

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576 **Conflict of interests**

577 The authors declare no competing interests.

578

579 **Author contributions**

580 Y.L. designed and performed experiments and analyzed the data. W.Z. performed experiments
581 and analyzed the data. I.T. and W.H. did the optical simulation. X.H. and J.L. performed the 3D
582 reconstruction. B.L. performed the SAXS simulations. C.A.M. and K.A. supervised the project.
583 Y.L. wrote the initial draft. Y.L., W.Z., B.E.P., H.L., I.T., W.H., X.H., B.L., J.L., V.P.D., K.A.,
584 and C.A.M. all analyzed the data, interpreted the data, and contributed to the writing of the
585 manuscript.

586 **Additional Information**

587 Supplementary Information is available for this paper. Correspondence and requests for
588 materials should be addressed to chadnano@northwestern.edu; aydin@northwestern.edu.

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590

591 **Extended Data Figure Legends**

592

593 **Extended Data Fig. 1 Edge-bonding of NFs and face-packing of solid NPs that outline space-**
594 **filling shapes. a,** Models of *sc* crystals assembled from cubic NFs. **b,** Models of *sc* crystals
595 constructed from solid cubes. **c,** Models of *bcc* crystals assembled from truncated octahedral NFs.
596 **d,** Models of *bcc* crystals constructed from solid truncated octahedra. **e,** Schematic showing that
597 when the building blocks are derived from space-filling shapes (e.g., cubic, truncated octahedral,
598 and triangular prism NFs), maximizing area sharing maximizes edge sharing at the same time,
599 which drives the thermodynamically stable structure based on CCM. Therefore, NFs that derive
600 from space-filling shapes assemble into the corresponding space-filling construction via edge-
601 bonding. Note that the solid cases are built based on the uniform tessellation of polyhedra.

602

603 **Extended Data Fig. 2 Edge-bonding of NFs that outline one shape of a space-filling pair a,**
604 Octahedra and tetrahedra represent one space-filling pair for *ccp* symmetry. **b,** The edge-bonding
605 assembly of only octahedral NFs gives the corresponding dual-shape lattice, the *ccp* structure, with
606 triangular channels of different sizes, and two sets of tetrahedral voids in alternating orientations
607 (shown in yellow and orange). **c,** Cuboctahedra and square pyramids form a space-filling pair for
608 *bct* symmetry. **d,** The edge-bonding assembly of only cuboctahedral NFs gives the corresponding
609 dual-shape lattice, the *bct* structure, with quadrilateral and triangular channels, and two sets of
610 square pyramidal voids with alternating orientations (highlighted in yellow and orange). **e,** Truncated
611 cubes and octahedra form a space-filling pair for *sc* symmetry. **f,** The edge-bonding assembly of
612 only truncated cubic NFs gives the corresponding dual-shape lattice, the *sc* structure, with
613 triangular, hexagonal, and octagonal channels, and octahedral voids (highlighted in yellow).
614 Therefore, NFs that outline one shape of a convex space-filling pair can assemble into the
615 corresponding space-filling cocrystal lattice via edge-bonding. Note that the solid cases are built based
616 on uniform tessellation of polyhedra.

617

618 **Extended Data Fig. 3 Pore sizes can be deliberately tailored by changing the dimensions of**
619 **the hollow NP building blocks. a-i,** Open channel superlattices with *ccp* symmetry and different
620 channel sizes. Models (**a, d, g**) and SEM images (**b, c, e, f, h, i**) of *ccp* crystals assembled from
621 Au-Pt octahedral NFs in different sizes. Scale bars: 200 nm (**c, f, i**); 5 μm (**b, e, h**). L: NF size; l:
622 pore size.

623

624 **Extended Data Fig. 4 The pore geometry and topology of the superlattices can be tuned by**
625 **employing NCs where specific facets are solid (compared to NFs). a,b,** Models of *bcc* crystals
626 assembled from truncated octahedral NFs and NCs, respectively. **c,d,** Models of *sc* crystals
627 assembled from truncated cubic NFs and NCs respectively. **e,f,** Models of *bct* crystals assembled
628 from cuboctahedral NFs and NCs, respectively. From left to right, each panel contains models
629 showing the building blocks, the assembled porous crystals, and the pore topologies of the
630 corresponding crystals.

631

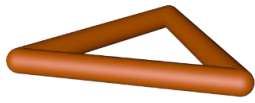
632 **Extended Data Fig. 5 Pore topologies are programmed by both the shape of the building**
633 **blocks and the crystal symmetry. a-l,** A library of open channel superlattices include: (a) 1D
634 chain assembled from triangular prism NFs; (b) *ih* crystal assembled from triangular prism NFs;
635 (c) *ccp* crystal assembled from octahedral NFs; (d) *sc* crystal assembled form cubic NFs; (e) *bcc*
636 crystal assembled from truncated cubic NCs; (f) *sc* crystal assembled from cuboctahedral NCs; (g)
637 *bcc* crystal assembled from truncated octahedral NFs; (h) *sc* crystal assembled from truncated
638 cubic NFs; (i) *bcc* crystal assembled from slightly truncated octahedral NCs; (j) *sc* crystal
639 assembled from truncated cubic NCs; (k) *bct* crystal assembled from cuboctahedral NFs; and (l)
640 *bct* crystal assembled from cuboctahedral NCs. From left to right, each panel contains models
641 shown in perspective view, projected along the indicated lattice directions [including $\langle 111 \rangle$,
642 $\langle 100 \rangle$ and $\langle 110 \rangle$ directions (c-j); $\langle 001 \rangle$, $\langle 011 \rangle$, $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ directions (k-l)], and
643 models showing the pore topologies.
644

645 **Extended Data Fig. 6 a-h, Experimental (red) and simulated (black) SAXS profiles of open**
646 **channel superlattices with different symmetries,** including (a) porous crystals with *sc*
647 symmetry assembled from cubic NFs, (b) porous crystals with *bcc* symmetry assembled from
648 truncated octahedral NFs, (c) porous crystals with *ccp* symmetry assembled from octahedral
649 NFs, (d) porous crystals with *bct* symmetry assembled from cuboctahedral NFs, (e) porous
650 crystals with *sc* symmetry assembled from cuboctahedral NCs, (f) porous crystals with *bcc*
651 symmetry assembled from truncated octahedral NCs, (g) porous crystals with *sc* symmetry
652 assembled from truncated cubic NCs, (h) porous crystals with *bct* symmetry assembled from
653 cuboctahedral NCs, and (i) porous crystals with *sc* symmetry assembled from truncated cubic
654 NFs. It is worth noting that the signal of the peaks is not strong due to the porous and anisotropic
655 nature of the crystals.

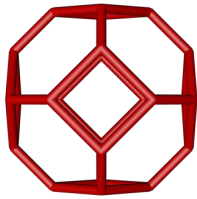
656
657 **Extended Data Fig. 7 a-b, Reconstructed 3D models of open channel superlattices from**
658 **electron microscopy tomography. (a)** Porous crystals with *ccp* symmetry assembled from
659 octahedral NFs viewed from different angles. (b) Porous crystals with *bct* symmetry assembled
660 from cuboctahedral NFs viewed from different angles. Tomographic reconstruction is consistent
661 with symmetry considerations.
662

663 **Extended Data Fig. 8 Negative effective index simulation of the porous *ccp* crystal assembled**
664 **from Au-Pt octahedral NFs. a,** Calculated effective refractive index (n , blue line) and extinction
665 coefficient (k , red line) of a porous Au-Pt *ccp* crystal. **b,** Electric field phase accumulated
666 throughout the Au-Pt *ccp* crystal at wavelengths corresponding to positive (blue line), near-zero
667 (red line), and negative index (black and purple lines) regions.
668

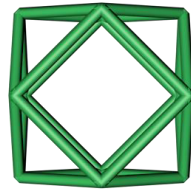
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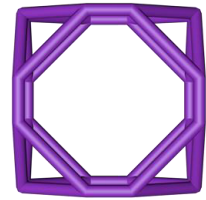
Triangular Prism NF



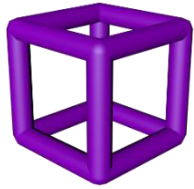
Truncated Octahedral NF



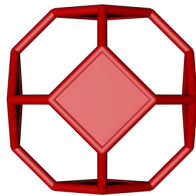
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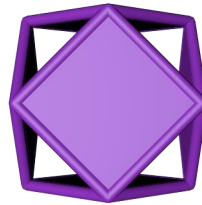
Truncated Cubic NF



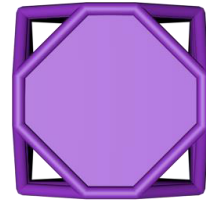
Cubic NF



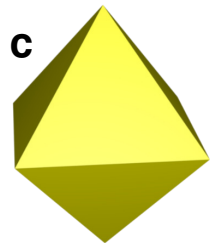
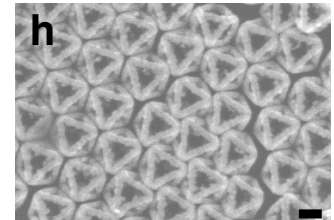
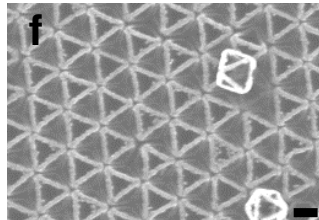
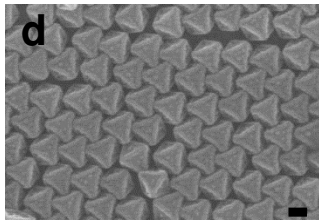
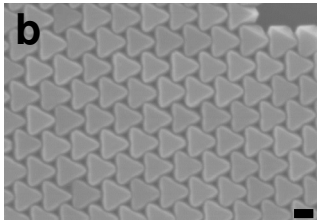
Truncated Octahedral NC



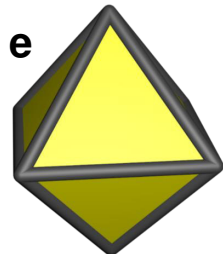
Cuboctahedral NC



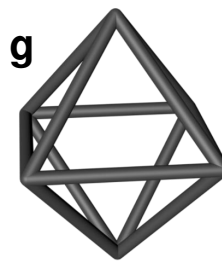
Truncated Cubic NC



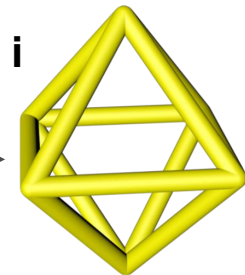
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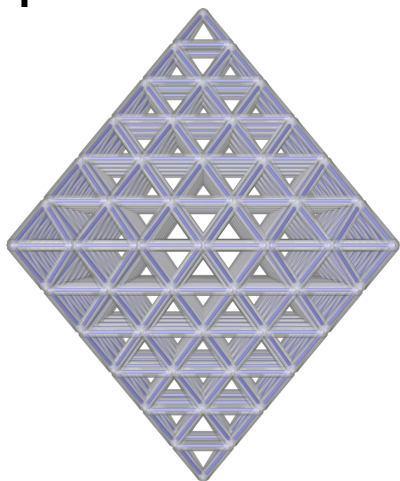
e



g

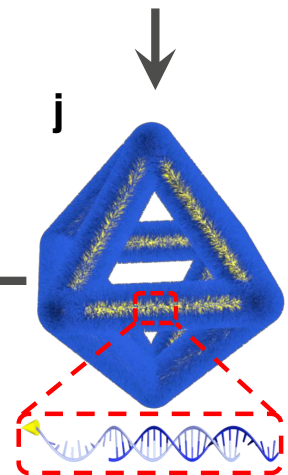
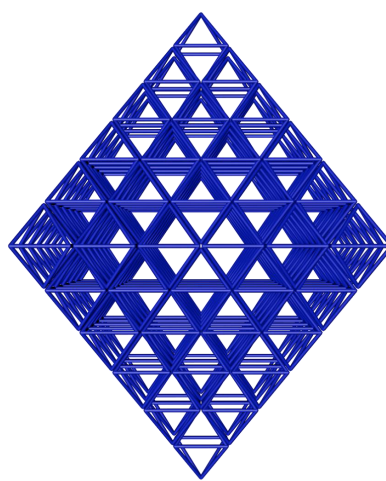


i



l

k



j

