Supporting information for “Imaging Nanoscale Heterogeneity in Ultrathin Biomimetic and Biological Crystals”

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Table S1. Fit parameters of the triple Gaussian fit to the catalase spectra shown in Figure 3b.

<table>
<thead>
<tr>
<th>Region</th>
<th>1643 cm(^{-1})</th>
<th>1666 cm(^{-1})</th>
<th>1684 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(p_0)</td>
<td>(\Delta\nu) (cm(^{-1}))</td>
<td>(p_0)</td>
</tr>
<tr>
<td>1 (blue)</td>
<td>0.12</td>
<td>22</td>
<td>0.11</td>
</tr>
<tr>
<td>2 (red)</td>
<td>0.13</td>
<td>28</td>
<td>0.1</td>
</tr>
<tr>
<td>3 (orange)</td>
<td>0.15</td>
<td>22</td>
<td>0.14</td>
</tr>
</tbody>
</table>

See corresponding regions indicated by red, blue, and orange markers in Figure 3a and spectra in Figure 3b.

Peptoid synthesis

Methods for the automated solid-phase synthesis

Lipid-like peptoids were synthesized on a commercial Aaptec Apex 396 robotic synthesizer using a modified solid-phase submonomer synthesis method. Rink amide resin (0.09 mmol) was
used to generate C-terminal amide peptoids. In this method, the Fmoc group on the resin was
deprotected by adding 2 mL of 20% (v/v) 4-Methylpiperidine/N,N-dimethylformamide (DMF),
agitating for 20 min, draining, and washing with DMF. All DMF washes consisted of the
addition of 1.5 mL of DMF, followed by agitation for 1 min (repeated five times). An acylation
reaction was then performed on the amino resin by the addition of 1.6 mL of 0.6 M bromoacetic
acid in DMF, followed by 0.35 mL of 50% (v/v) N,N-diisopropylcarbodiimide (DIC)/DMF.
The mixture was agitated for 30 minutes at room temperature, drained, and washed with
DMF for 5 times. Nucleophilic displacement of the bromide with various primary amines
occurred by a 1.6 mL addition of the primary amine monomer as a 0.6 M solution in N-methyl-2-pyrrolidone (NMP), followed by agitation for 60 minutes at room temperature. The monomer
solution was drained from the resin, and the resin was washed with DMF for 5 times. The
acylation and displacement steps were repeated until a lipid-like peptoid of the desired length
was synthesized.

Pep-1

Figure S2. a) Structural of peptoid composing the nanosheets investigated in this study. b) Representative AFM image of a ~4 nm peptoid layer.
Figure S3. a) Ultra performance liquid chromatography characterization of Pep-1 with the gradient of 5% - 95% CH₃CN in H₂O. b) MS characterization of Pep-1.

**Assembly of Pep-1:**

1 μmol of lyophilized Pep-1 powder was dissolved in 200 μL of water and acetonitrile (v/v=1:1) mixture to make 5.0 mM clear solution. The mixture was then put in the 4 °C refrigerator for slow evaporation. Over four days’ generation, gel-like materials including a large number of 2D nanosheets was obtained.