Supporting Information

Dictating Orientation Diversity of Body-Centered Cubic Superlattices in the Self-Assembly of Polymer-Grafted Nanocubes through Heterogeneous Grafting Designs

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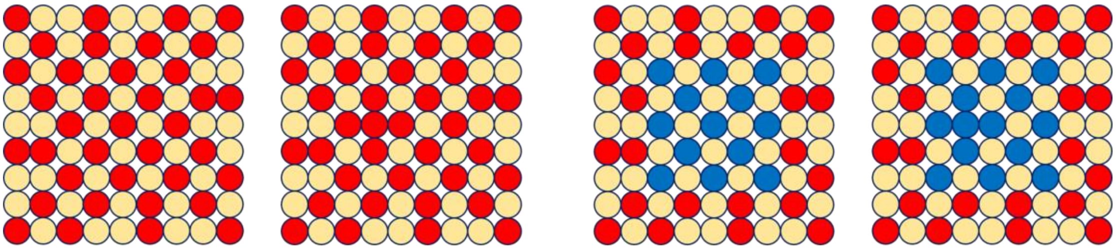
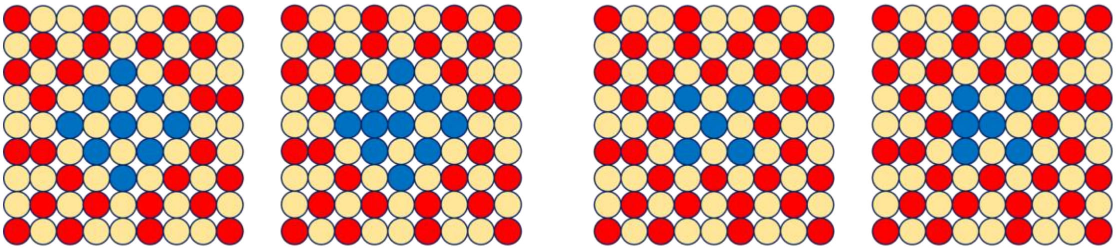


(a) Case 0 (b) Case 1



(c) Case 2 (d) Case 3

Fig. S1 Detailed positions of the polymer grafting sites for (a) the homogeneous grafting case (Case 0) and (b-c) the three heterogeneous grafting cases (Cases 1-3). In each grafting case, the polymer grafting sites on two faces of the cube correspond to the left diagram, while those on the other four faces correspond to the right diagram. In Case 0, the red dots indicate the polymer grafting sites. In Cases 1-3, the blue dots indicate the polymer grafting sites in the face-centered grafting regions, and the red dots indicate the polymer grafting sites in the non-face-centered grafting regions.

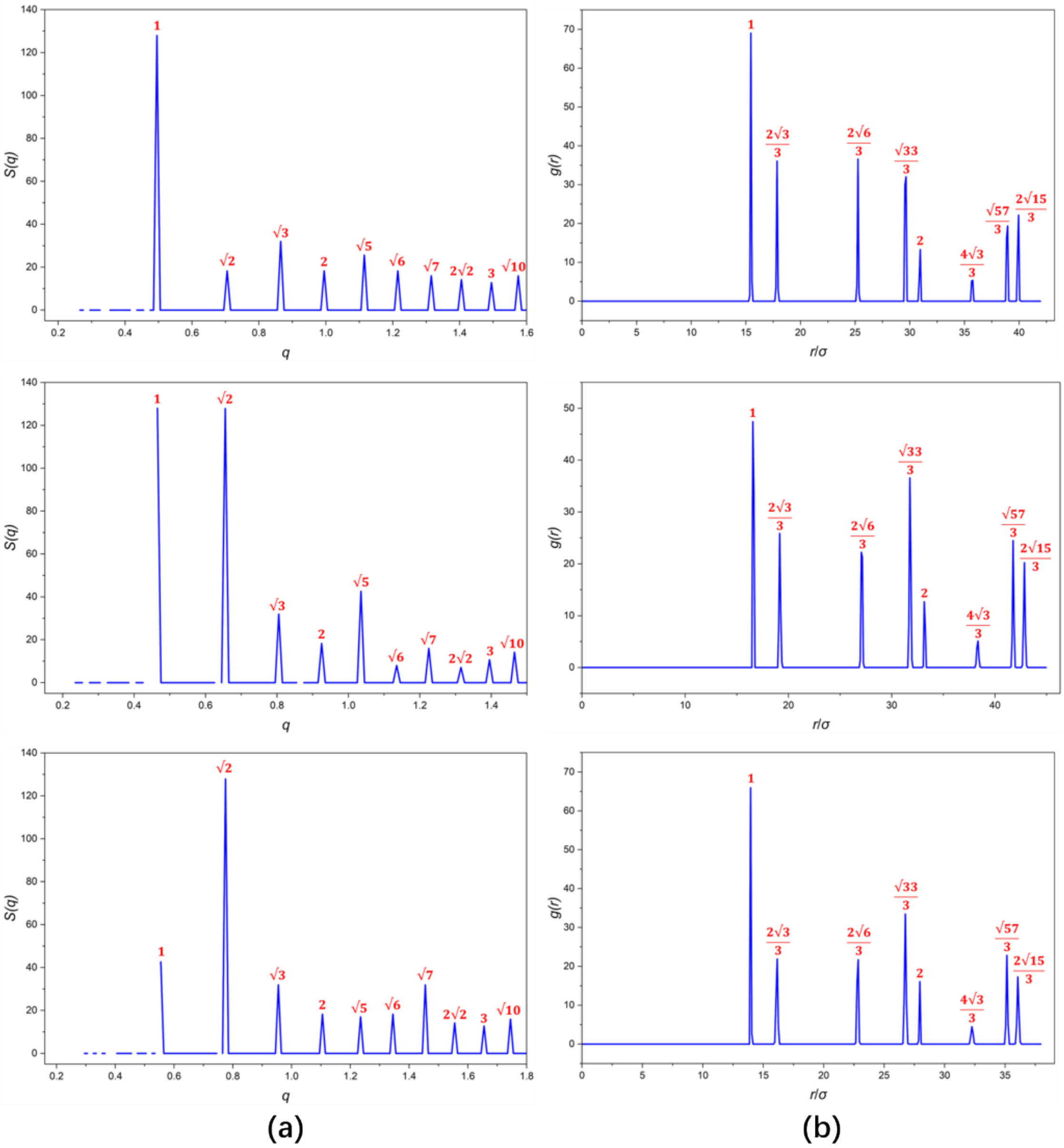


Fig. S2 Structural information of C-BCC (Case 1, $N_1 = 10$, $N_2 = 5$) (top), dC-BCC (Case 1, $N_1 = 10$, $N_2 = 8$) (medium), and E-BCC (Case 1, $N_1 = 6$, $N_2 = 5$) (bottom) superlattices. (a) Structure factor $S(\vec{q})$. The normalized peak positions q/q_0 are shown above the peaks, where q_0 is the q value of the first peak. (b) Radial distribution function $g(r)$. The normalized peak positions r/r_0 are shown above the peaks, where r_0 is the r value of the first peak.

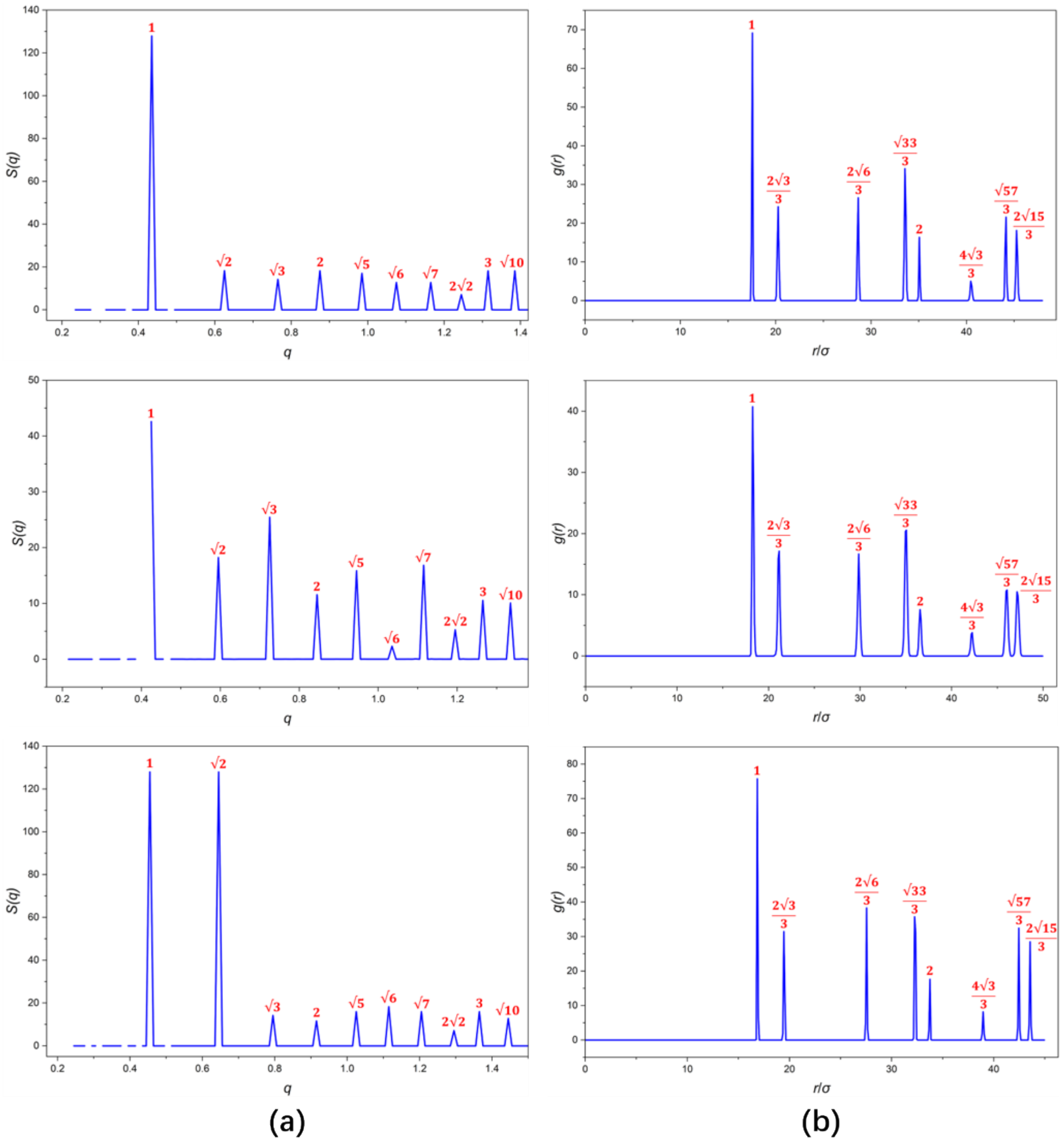


Fig. S3 Structural information of T-BCC (Case 3, $N_1 = 12$, $N_2 = 10$) (top), A-BCC (Case 3, $N_1 = 10$, $N_2 = 12$) (medium), and I-BCC (Case 2, $N_1 = 10$, $N_2 = 9$) (bottom) superlattices. (a) Structure factor $S(\vec{q})$. The normalized peak positions q/q_0 are shown above the peaks, where q_0 is the q value of the first peak. (b) Radial distribution function $g(r)$. The normalized peak positions r/r_0 are shown above the peaks, where r_0 is the r value of the first peak.

S1. Supplementary discussion for Section 3.2

S1.1. Supplementary discussion of the A-BCC phase in Case 1

When analyzing the A-BCC phase along the vertical direction (i.e., with the same N_1), the system in which the nanocrystals exhibit lower sphericity and stronger shape anisotropy shows higher orientational order degree, as indicated by the orange bars on the right side of the dark red bar in Fig. 3 as well as the orange data points in the right panel of Fig. 5a. This indicates that the directional entropy forces, originating from the shape anisotropy of the nanocrystals, still play a role in regulating nanocrystals' orientation alignment.

S1.2. Detailed discussion of the A-BCC phase region in Case 2

In the phase region of $N_1 < N_2$ (i.e., the A-BCC phase region), when analyzing the A-BCC phase along the vertical direction (i.e., with the same N_1), a similar tendency to that in Case 1 is observed in most cases: nanocrystals with lower sphericity, whose lower sphericity corresponds to stronger directional entropic forces, lead the system to exhibit a higher orientational order degree, as indicated by the blue bars on the right side of the dark red bar in Fig. 3 as well as the orange data points in the right panel of Fig. 5b. An exceptional case appears for the system with $N_1 = 6,\ N_2 = 12$. Although it has lower sphericity ($S = 0.978474$) and thus stronger directional entropic forces, when compared with the systems with $N_1 = 6,\ N_2 = 7$ and $N_1 = 6,\ N_2 = 8$ wherein the corresponding sphericity values are respectively 0.981312 and 0.980038, its orientational order degree is instead lower (i.e., 0.5921 for $N_1 = 6,\ N_2 = 12$, against 0.6472 for $N_1 = 6,\ N_2 = 7$ and 0.6739 for $N_1 = 6,\ N_2 = 8$). This is because when the chain length difference between the face-centered grafting regions and the non-face-centered grafting regions is large, and when a larger number of long polymer chains are grafted in the non-face-centered regions, achieving optimal packing of the grafted polymers becomes relatively difficult. This, in turn, hinders the nanocrystals from adjusting their orientations, leading to a decrease in the orientational order degree.