Fig. S1. The influence of number density on the calculated potential energy (U), entropy (S) and free energy (F) of pairwise particles of AB type at θ = 15° and θ = 60° in the plane $\beta_{IJ} = 0$ at T=930 K. The system contains 2000 particles in a $12 \times 12 \times 12$ nm³ cubic box. Here, dark brown color represents the regions without samples. As number density increases, entropic effects become much more significant at θ = 60°and particles tend to stack orderly.
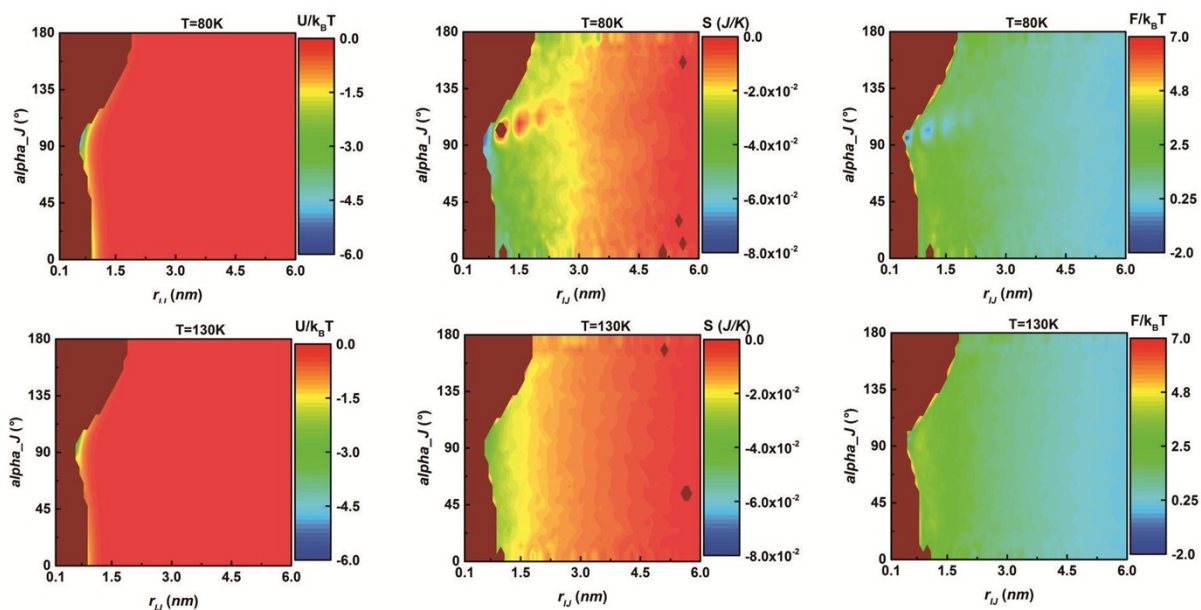

Fig. S2. The influence of temperature on the calculated potential energy (U), entropy (S) and free energy (F) of pairwise particles of AB type at θ = 15° in the plane $\beta_{IJ} = 0$. The system contains 1000 particles in a $12 \times 12 \times 12$ nm³ cubic box. Here, dark brown color represents the regions without samples. As temperature decreases, entropic effects become much more significant and particles tend to stack orderly.
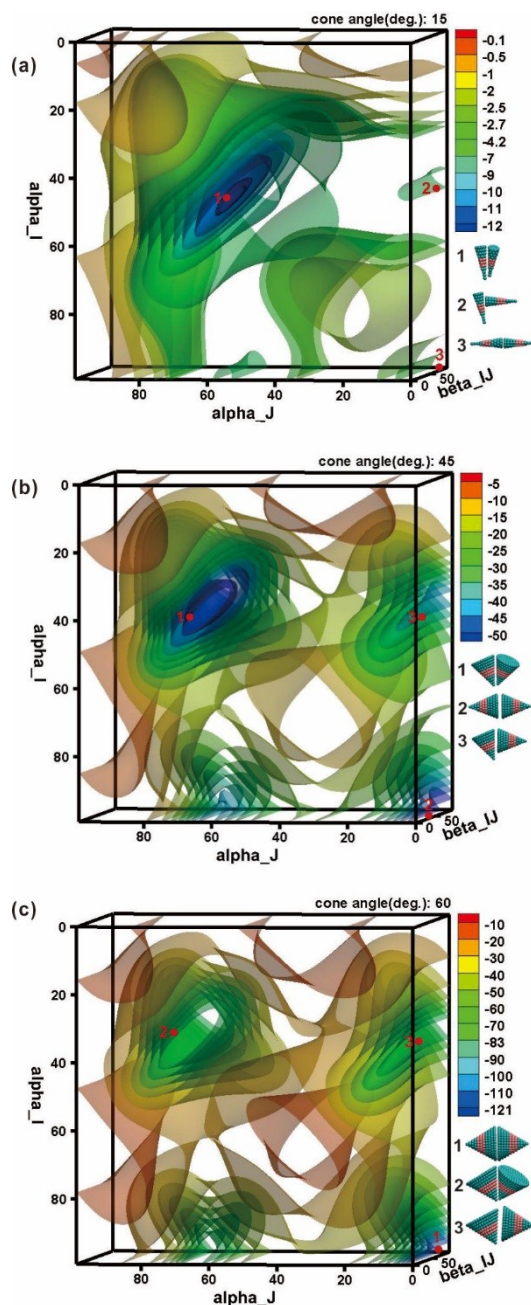
Fig. S3. The potential energy surfaces (PESs) of of BAB type particles at θ = 15°, 45° and 60°. These PESs are separated into three groups based on the similarity of their shapes. The first group contained PESs at θ = 15°, 20°, 25° and contained PESs at θ = 30°, 35° and 40° were divided into the second group and the third group included PESs at θ = 45° and 60°. The red points on these PESs are saddle points which are numbered in the order of the magnitude of potential energies, and the corresponding conformations are displayed at right corner.

Table S1. The defined characteristic parameters, f and transition energy barrier, ΔE_a of BAB type particle.

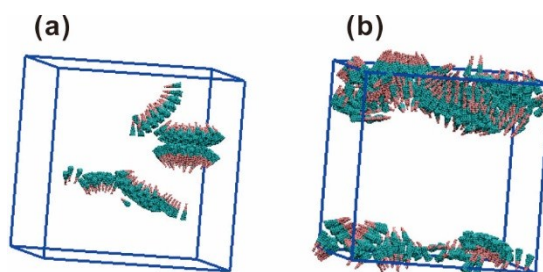|	The 1st group				The 2nd group			The 3rd group
deg.	15	20	25	30	35	40	45	60
$\lvert U_{\min}\rvert$	12.3	17.8	22.7	32.1	35.3	45.4	54.6	122
ΔE_a^{2-1}	0.76	2.28	4.65	8.80	22.0	33.4	47.6	75.8
ΔE_a^{3-1}	1.08	3.34	6.96	13.8	12.8	19.4	26.4	48.9
ΔE_a^{3-2}	0.61	2.06	4.32	8.90	11.8	17.0	22.2	58.9
f^{2-1}	0.06	0.13	0.21	0.27	0.62	0.74	0.87	0.63
f^{3-1}	0.09	0.19	0.31	0.43	0.36	0.43	0.48	0.40
f^{3-2}	0.05	0.12	0.19	0.28	0.33	0.37	0.41	0.49

Note: The unit of *ΔE* and U_{min} is *KJ/mol*, unless otherwise stated.

Fig. S4. Typical self-assembled structures for AB type particle at θ = 15. (a) 200 particles in a $12\times12\times12$ nm³ cubic box; (b) 400 particles in a $8.8\times8.8\times8.8$ nm³ cubic box.