Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Fabrication of Magnetic Colloidal Bicones and Their Switchable Self-Assembly

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This PDF file includes:

Fig. S1 to S15

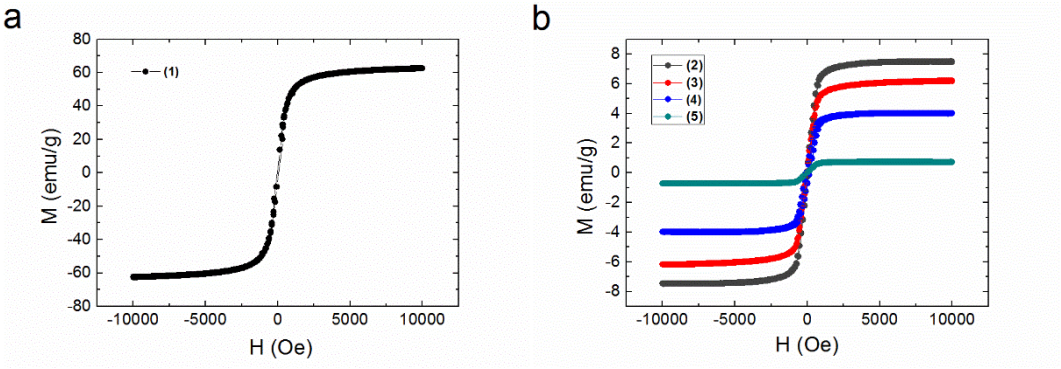

Fig. S1 Magnetic hysteresis loops of Fe_3O_4 NPs (a) and Fe_3O_4/SiO_2/PS particles (b). (1) Fe_3O_4 NPs; (2) Fe_3O_4/SiO_2/PS microspheres (663 ± 21 nm); (3) Fe_3O_4/SiO_2/PS microspheres (733 ± 24 nm); (4) Fe_3O_4/SiO_2/PS microspheres (831 ± 21 nm); (5) bicone-shaped SiO_2 particles (L/D = 4.5).

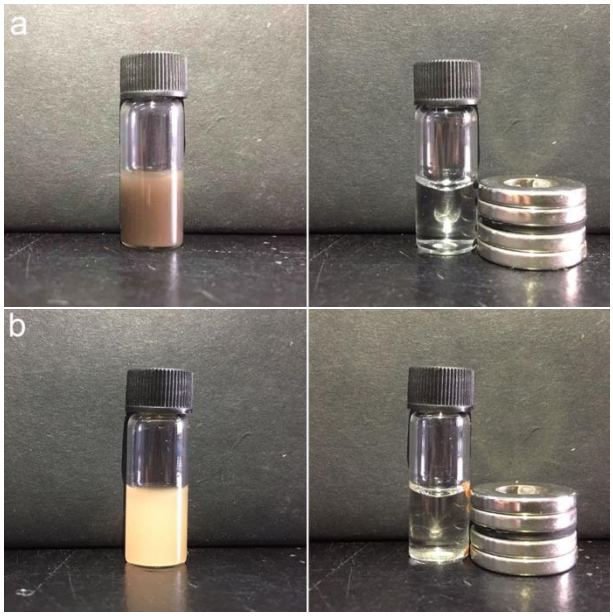

Fig. S2 Digital images showing the magnetic response of Fe_3O_4 nanoparticles (a) and SiO_2 colloidal bicones (L/D = 4.5) (b).

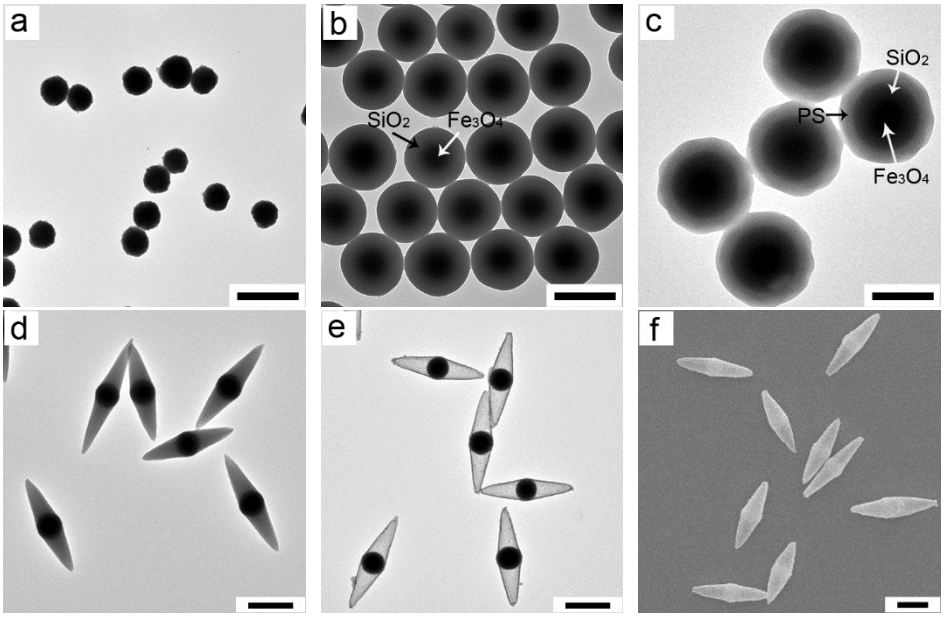

Fig. S3 TEM and SEM images of the particles at different stages during the synthesis of bicone-shaped particles. a) Fe_3O_4 NPs; b) Fe_3O_4/SiO_2 core/shell NPs; c) Fe_3O_4/SiO_2/PS spherical particles; d) bicone-shaped PS particles with L/D = 4.30, obtained by using a DR of 2.5. e-f) TEM (e) and SEM (f) image of SiO_2 bicone-shaped particles with L/D = 4.17, obtained by coating the particles shown in (d) with about 65 nm of SiO_2 layer and removing PS with THF. Scale bars: 1.0 μm.

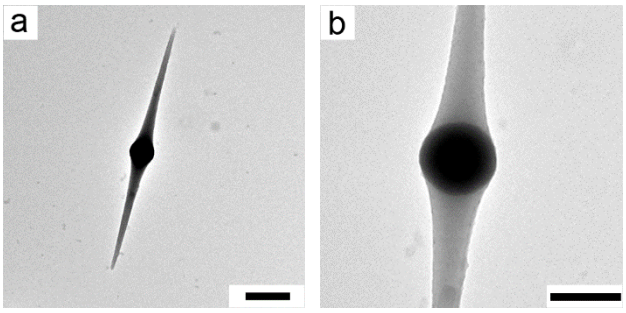

Fig. S4 TEM images of PS particles obtained with DR = 6.0. The initial core-shell Fe_3O_4/SiO_2/PS spherical particles used are the same as those shown in Fig. 1b in the main text. Clearly, too large DR values caused the particles to deviate from bicone shapes.

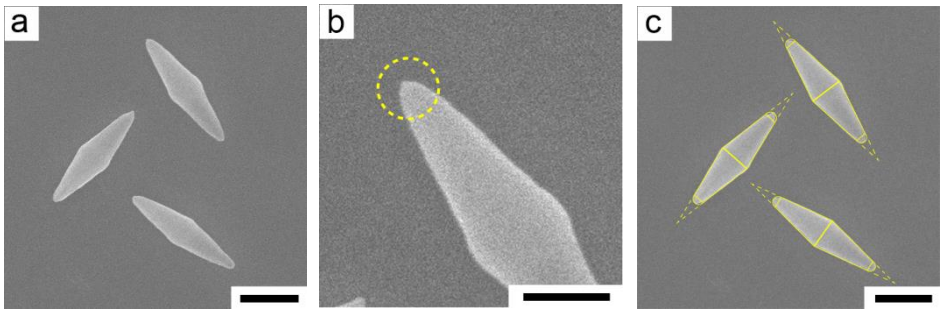

Fig. S5 a) SEM image of PS colloidal bicones, corresponding to the particles shown in Fig. 1b in the main text (DR = 2.5). b) SEM image with high magnification showing the tip shape deviates from a perfect cone shape, as indicated by the yellow circle. c) The bicones shown in (a) are well fitted with a truncated bicone model plus two hemispherical caps. Scale bars: 1.0 μm (a,c) and 500 nm (b).

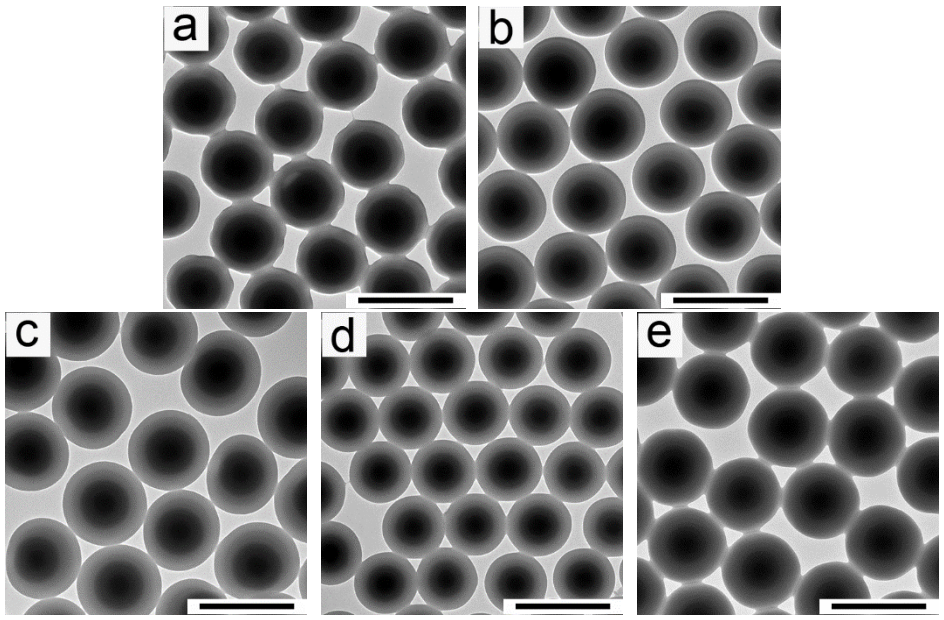

Fig. S6 TEM images of five kinds of Fe_3O_4/SiO_2/PS core/shell spherical particles. a) S1: 521 nm (4.4%)/733 nm (3.3%); b) S2: 413 nm (5.1%)/663 nm (3.2%); c) S3: 532 nm (3.9%)/872 nm (3.6%); d) S4: 427 nm (3.5%)/747 nm (2.8%); e) S5: 417 nm (3.6%)/831 nm (2.5%).The first number is the mean diameter of Fe_3O_4/SiO_2 particles, and the second is the mean diameter of the whole particles. The numbers in the bracket are the polydispersity, which is the mean diameters divided by its standard deviations. Scale bars: 1.0 μm

Table S1. The mean lengths, diameters and polydispersities of bicone-shaped particles

No.	*L* (nm)	Polydispersity* (%)	*D* (nm)	Polydispersity* (%)
S1-1**	2368.2	8.1	554.9	7.4
S1-2	2774.9	7.6	567.7	8.5
S1-3	3092.0	6.9	547.4	7.1
S2-1	3048.4	7.6	469.3	7.1
S2-2	3340.8	8.3	470.2	7.3
S2-3	3545.4	6.5	465.3	8.8
S3-1	3898.3	7.4	546.2	5.9
S3-2	4437.4	7.6	550.5	8.3
S3-3	4841.1	6.8	554.3	5.9
S4-1	3701.2	6.7	468.0	6.4
S4-2	4218.9	6.1	480.9	7.3
S4-3	4641.4	5.6	469.7	6.5
S5-1	4857.0	6.7	413.1	8.6
S5-2	5371.2	6.8	416.3	8.3
S5-3	6085.2	6.7	432.4	7.0

*Note: Polydispersity is defined by the mean divided by the standard deviation ** 1, 2, and 3, in turn, correspond to the increasing DR values shown in Figure 2.

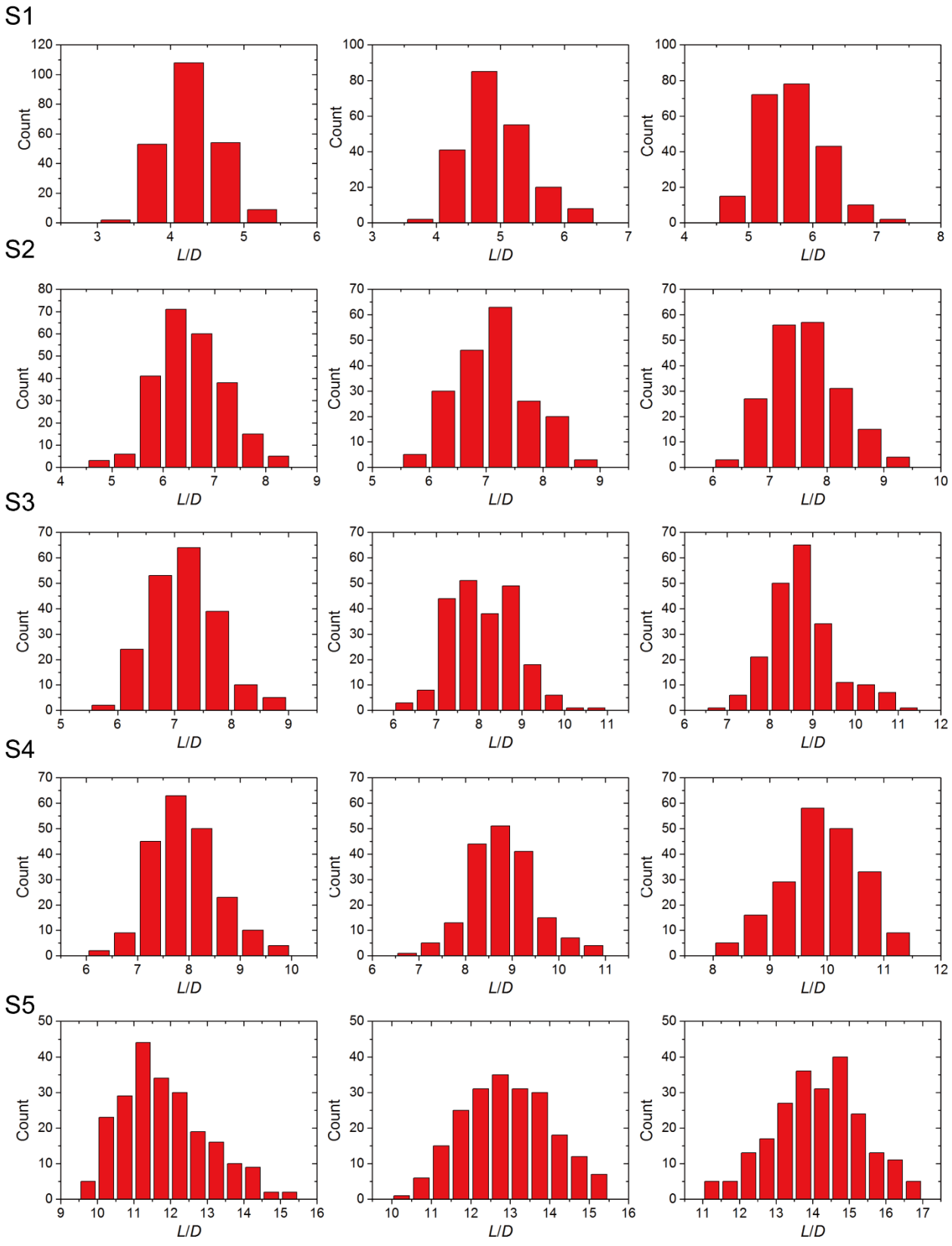

Fig. S7 Distribution of *L*/*D*s for all samples shown in Fig. 2a in the main text. The three images from left to right correspond to the increasing DR values for S1 to S5.

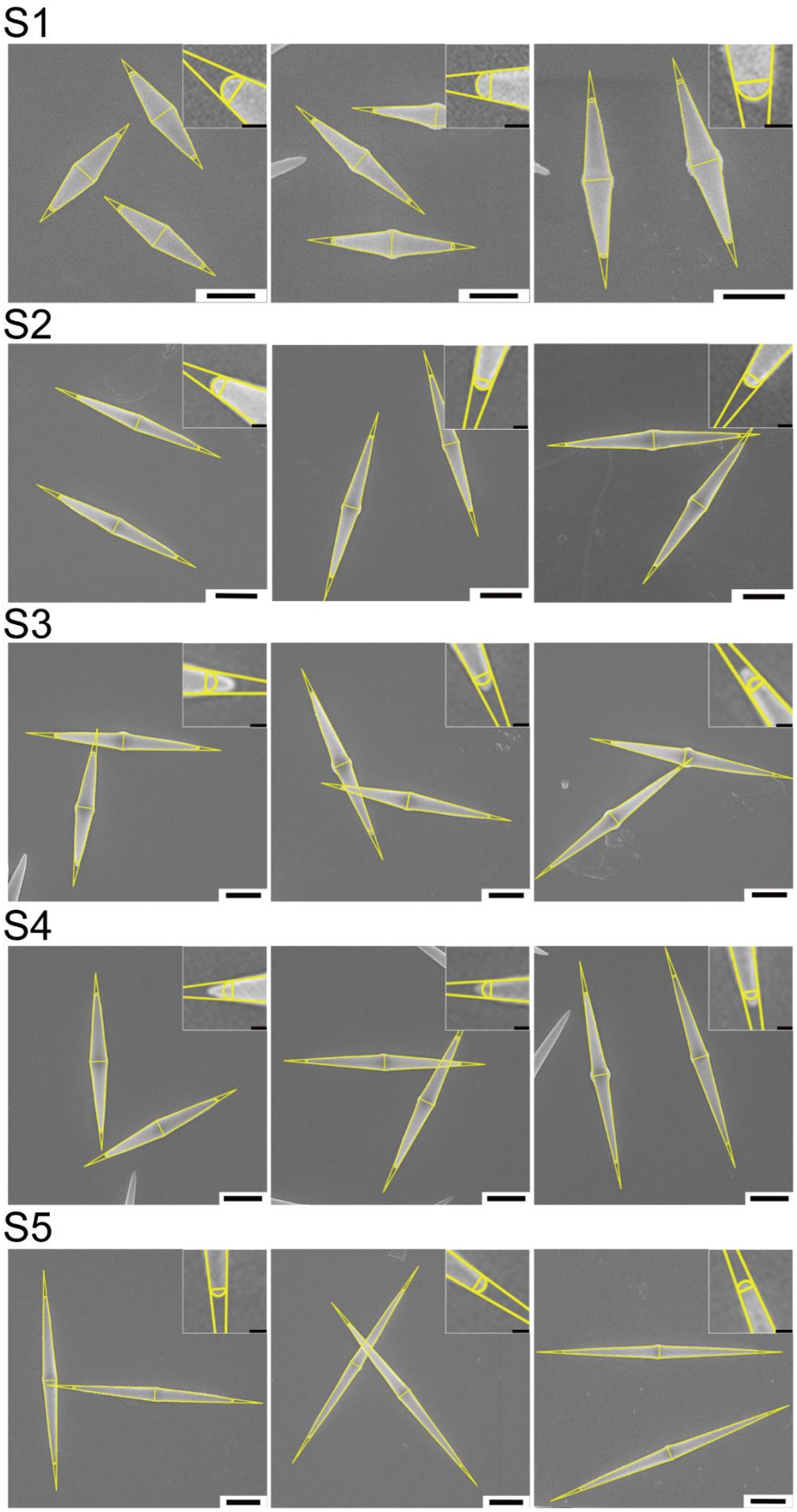

Fig. S8 Bicone-shaped particles fitted with truncated bicone plus two hemispherical caps for all samples shown in Fig. 2a in the main text. The three images from left to right correspond to the increasing DR values for S1 to S5. Scale bars: 1.0 μm (large) and 100 nm (insets).

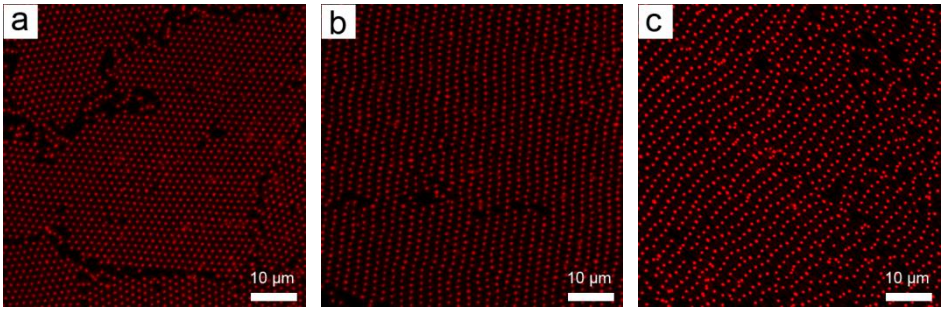

Fig. S9 Confocal microscopy images of the self-assembled structures of bicone-shaped colloidal particles with different L/D values. a) $L/D = 2.9$; (b) $L/D = 4.5$; c) $L/D = 6.0$. Only the core particles are shown here and the complete images are shown in Fig. 3d-f in the main text.

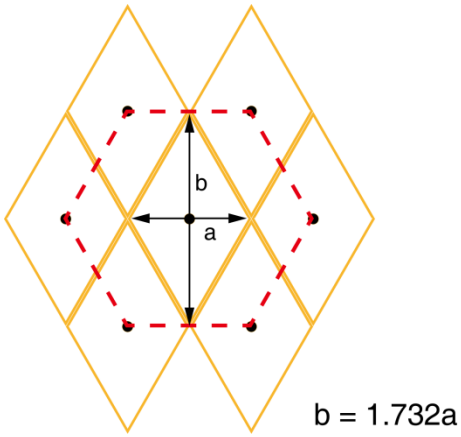

Fig. S10 Schematic illustrating how to self-assemble into an ordered lattice with hexagonal symmetry using perfect colloidal bicones, which requires the L/D to be the square root of 3, that is, 1.732.

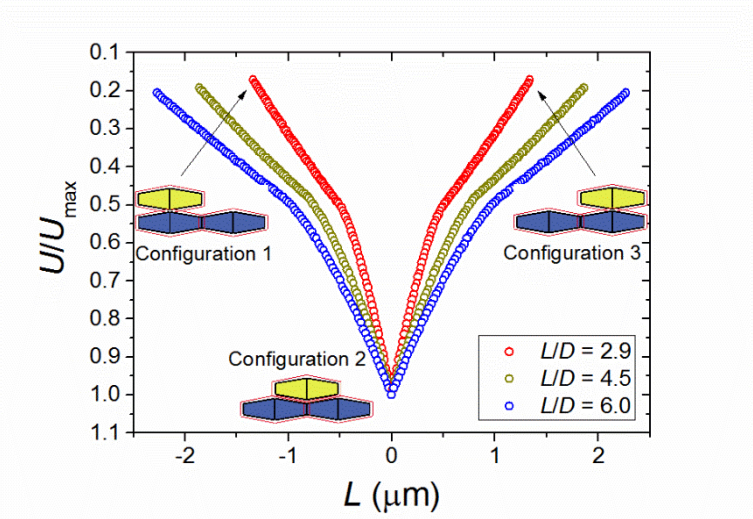

Fig. S11 A comparison of depletion potential when a particle moves from configuration 1 to configuration 2 to configuration 3 but keeps close contact with its neighbors. The *x*-axis is the length of the particles. The *L* value is 2.69 μm for particles with *L*/*D* = 2.9, 3.72 μm for particles with *L*/*D* = 4.5, 4.55 μm for particles with *L*/*D* = 6.0. U_{max} is the depletion potential for configuration 2, which is the equilibrium configuration in our systems. For particles of *L*/*D* = 2.9, the curve is the steepest, suggesting the particles have the smallest potential window along the direction of the long axis. When *L*/*D* increases, the curves are flatter, suggesting more significant motions. This is in line with our experimental observations. In this model, we neglect the possible tilt-up orientations of particles and assume all the particles orient in the plane.

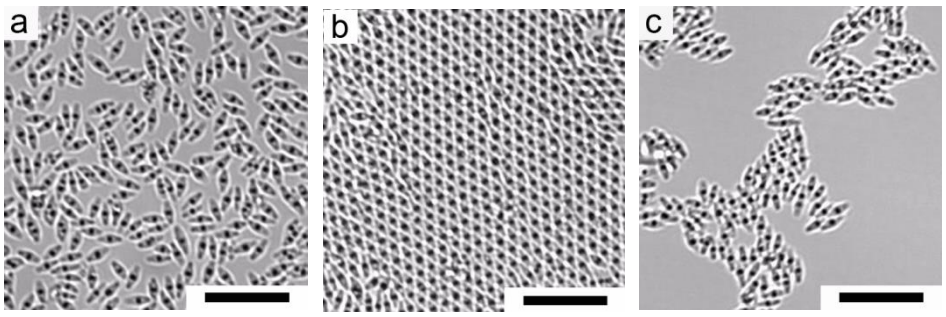

Fig. S12 Three typical states for particles with *L*/*D* of 2.9. a) The fluid state observed at a NaPSS concentration of 0.238 g L^{-1}; b) Crystal state observed at a depletant concentration of 0.275 g L^{-1}; c) Orientational aggregates observed at a depletant concentration of 0.375 g L^{-1}. Scale bars: 10 μm.

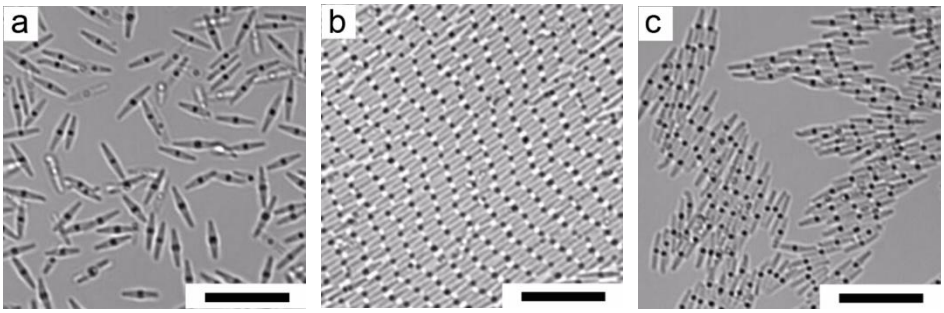

Fig. S13 Three typical states for particles with *L*/*D* of 6.0. a) The fluid state observed at a depletant concentration of 0.100 g/l; b) Crystal state observed at a depletant concentration of 0.125 g/l; c) orientational aggregates observed at a depletant concentration of 0.225 g/l. Scale bars: 10 μm.

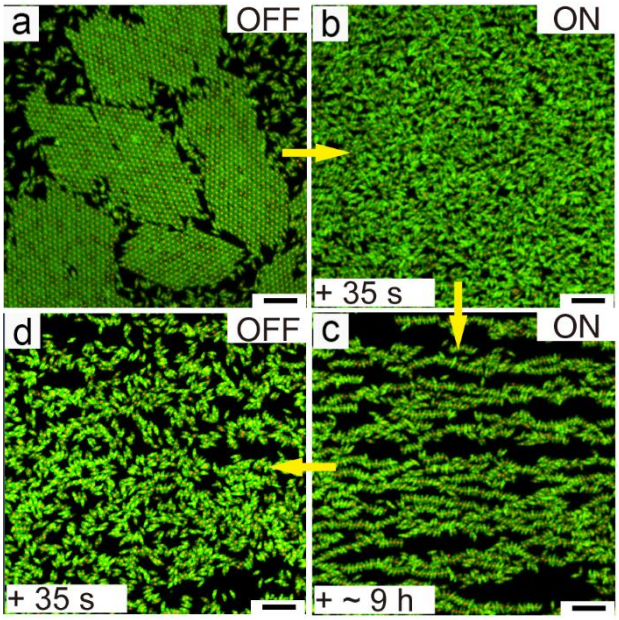

Fig. S14 Magnetically responsive self-assembly of bicone-shaped colloidal particles with *L*/*D* = 2.9. a) Crystal state formed for several days when the magnetic field is off. b) The transit state after the magnetic field is turned on for 35 s. c) Stable string fluid state when the magnetic field is on for about 9 h. d) The transit state after the magnetic field is turned off for 35 s. C_{NaPSS} = 0.255 g L^{-1}. Scale bars: 10 μm.

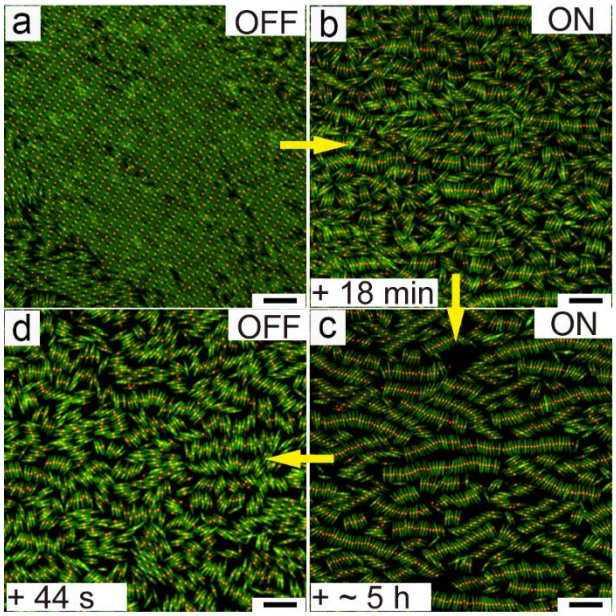

Fig. S15 Magnetically responsive self-assembly of bicone-shaped colloidal particles with L/D = 6.0. a) Crystal state formed for several days when the magnetic field is off. b) The transit state after the magnetic field is turned on for 18 min. c) Stable string fluid state when the magnetic field is on for about 5 h. d) The transit state after the magnetic field is turned off for 44 s. C_{NaPSS} = 0.15 g L^{-1}. Scale bars: 10 μm.