Supporting Information

Tuning Molecular-level Polymer Conformations Enables Dynamic Control Over Both the Interfacial Behaviors of Ag nanocubes and Their Assembled Metacrystals

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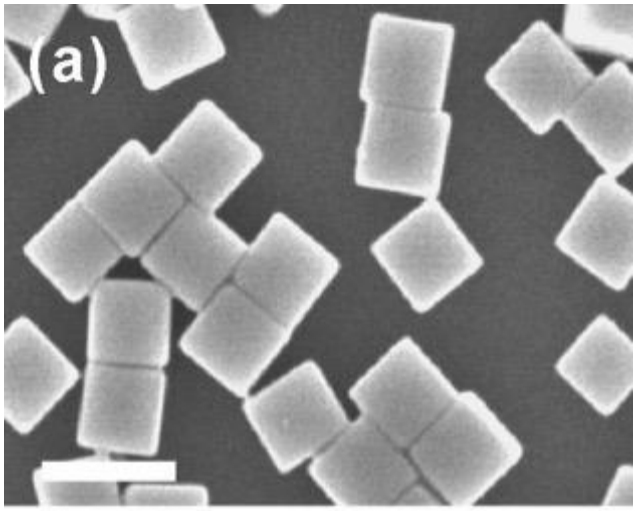

Figure S1. SEM characterization of Ag nanocubes after the synthesis and purification. Scale bar, 200 nm.

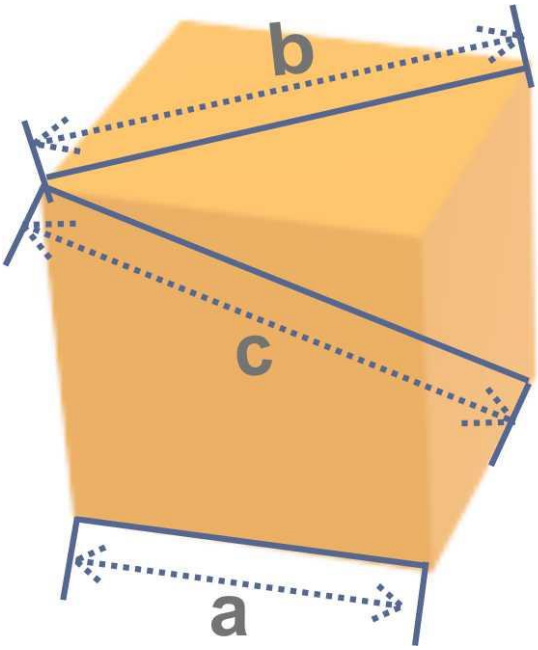

Figure S2. Scheme of the calculation of effective diameter of nanocubes.

a = *l*

b = *l**√2

c = *l**√3

l is the edge length of nanocubes

effective diameter = (a + b + c)/3

= (1 + √2 + √3) *106/3

= 147 nm

S3. Calculation of dispersion solvent polarity index

$P_M = P_A * V_A\% + P_B * V_A\%$

P_M: Polarity index of the mixture of binary solvents

P_A: Polarity index of solvent A

$V_A\%$: Volume ratio of solvent A

P_B: Polarity index of solvent B

$V_B\%$: Volume ratio of solvent B

For instance,

Calculation of IPA and water (volume are both 250 μL):

$P_M = P_A * V_A\% + P_B * \ln V_A\%$

$= 0.546*0.5+1*0.5$

$=0.77$

Table S1. Polarity index of binary solvent mixture with different compositions.

Solvent composition	Volume ratio	Polarity Index (PI)
H_2O	NA	1.00
Ethanol	NA	0.65
1-Hexanol	NA	0.56
IPA	NA	0.55
Chloroform	NA	0.27
THF	NA	0.21
Toluene	NA	0.10
Hexane	NA	0.01
IPA/H_2O	V_{IPA}% =33%	0.85
IPA/H_2O	V_{IPA}%=40%	0.82
IPA/H_2O	V_{IPA}%=50%	0.77
1-Hexanol/ethanol	$V_{1\text{-hexanol}}$%=50%	0.61
Chloroform/ethanol	$V_{chloroform}$%=33%	0.52
Chloroform/ethanol	$V_{chloroform}$%=40%	0.50
Chloroform/ethanol	$V_{chloroform}$%=46%	0.47
Chloroform/ethanol	$V_{chloroform}$%=50%	0.46
THF/ethanol	V_{THF}% =50%	0.43
Toluene/ethanol	$V_{toluene}$%=46%	0.40
Toluene/ethanol	$V_{toluene}$%=50%	0.38
Hexane/ethanol	V_{hexane}%=47%	0.35
Hexane/ethanol	V_{hexane}%=50%	0.33

Table S2. Comparison of hydrodynamic diameter of Ag nanocubes with functionalization of PEG, C16 and binary molecules.

Surface group	**67-C16%**	**PEG**	**C16**
Highest hydrodynamic diameter	208	215	178
Lowest hydrodynamic diameter	137	130	139
Swelling size	71	85	39

X-C16% is defined as the molar percentage of C16 in the feedstock of PEG and C16 mixture which is used for particle functionalization. It is calculated by the following equation,

x- C16 % = [C16]/([C16] +[PEG])).

67-C16% means 67% molar percentage of C16 in the feedstock of PEG and C16 mixture.

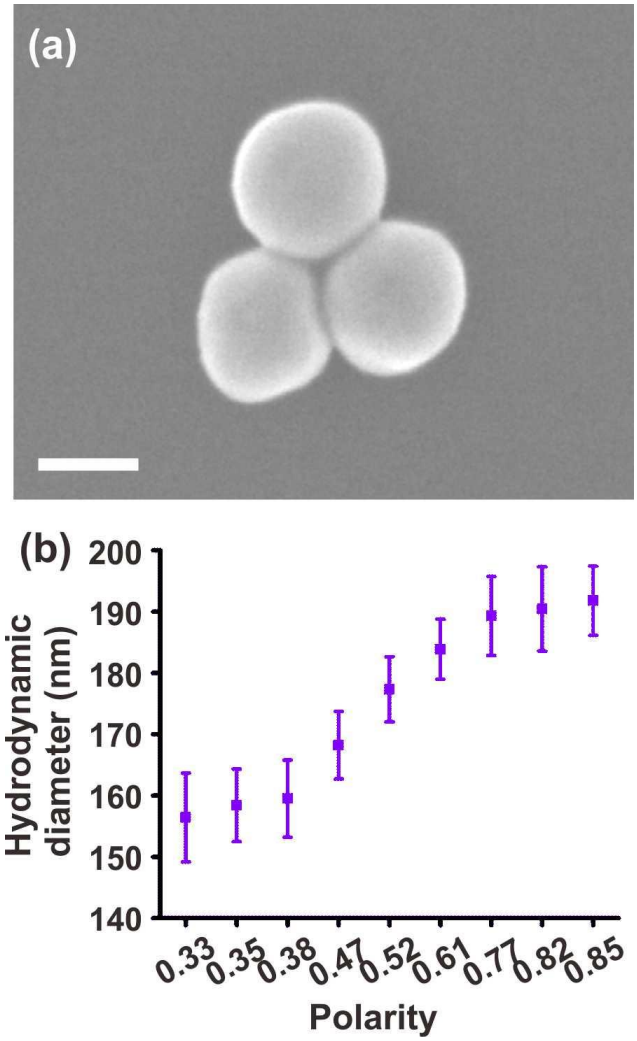

Figure S4. (a) SEM images of Au nanospheres, showing the size of (149±4) nm. (b) Hydrodynamic diameter of Au nanosphere functionalized with 67-C16%. Scale bar, 100 nm.

$$\%\ \text{of cube}_{oil} = (1 - H_{AFM} / H_{orientation}) * 100\%$$

Figure S5. Scheme of the calculation of cube percentage in contact with oil phase.

% of $cube_{oil}$ is the height ratio of cubes in contact with oil phase, H_{AFM} is the height of nanocubes above PDMS substrate, $H_{orientation}$ is the height of nanocubes with different orientation.

The calculation process is as follows.

l is defined as the edge length of cubes

For planar cubes,

$H_{orientation} = H_{planar} = l$

$\%\ \text{of cube}_{oil} = 1 - H_{AFM}/H_{planar}$

$= 1 - H_{AFM}/106$

For tilting cubes,

$H_{orientation} = H_{tilting} = l*\sqrt{2}$

$\%\ \text{of cube}_{oil} = 1 - H_{AFM}/H_{tilting}$

$= 1 - H_{AFM}/(106*\sqrt{2})$

For standing cubes,

$H_{orientation} = H_{standing} = l*\sqrt{3}$

$\%\ \text{of cube}_{oil} = 1 - H_{AFM}/H_{standing}$

$= 1 - H_{AFM}/(106*\sqrt{3})$

Table S3. AFM measurements of Ag nanocubes with 67-C16% functionalization dispersed in different solvents and oriented in different configurations.

Polarity index (PI)	AFM Height (in aqueous phase) / nm	Height in oil phase / nm	% Immersed in aqueous phase (%)	% Immersed in oil phase (%)
0.85	64 ± 10	42 ± 10	60 ± 4	40 ± 4
0.82	89 ± 11	65 ± 11	54 ± 4	46 ± 4
0.77	76 ± 8	74 ± 8	51 ± 5	49 ± 5
0.61	62 ± 3	121 ± 20	37 ± 2	63 ± 2
0.50	53 ± 8	113 ± 11	31 ± 7	69 ± 7
0.47	46 ± 12	119 ± 19	29 ± 2	71 ± 2
0.42	43 ± 5	131 ± 15	25 ± 6	75 ± 6
0.38	23 ± 10	108 ± 12	17 ± 4	83 ± 4
0.35	19 ± 7	129 ± 19	9 ± 4	91 ± 4
0.33	5 ± 3	101 ± 3	5 ± 2	95 ± 2

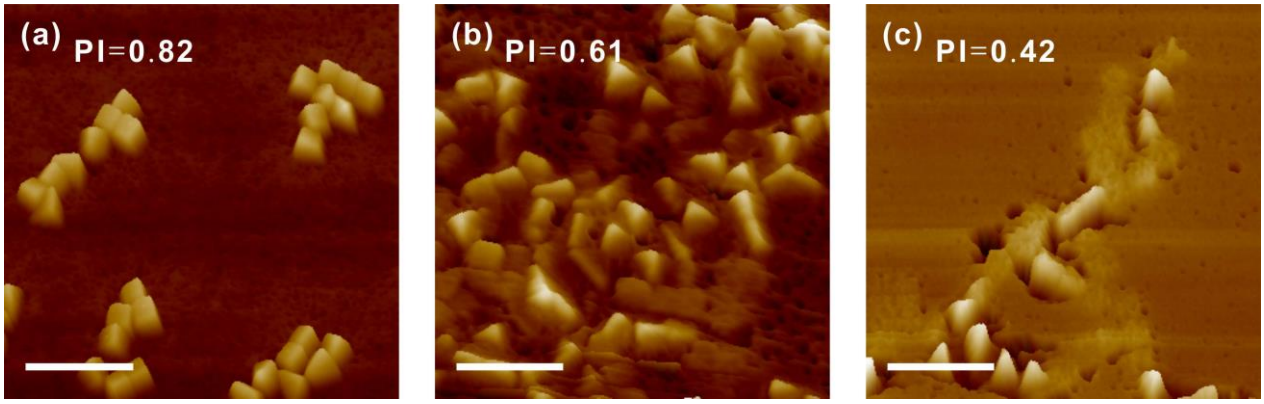

Figure S6. Large-area AFM topographical images of Ag nanocube in the solvent of (a) PI=0.82, (b) PI=0.61, (c) PI=0.42, which has various configuration at the oil-water interface. Scale bar, 1 μm.

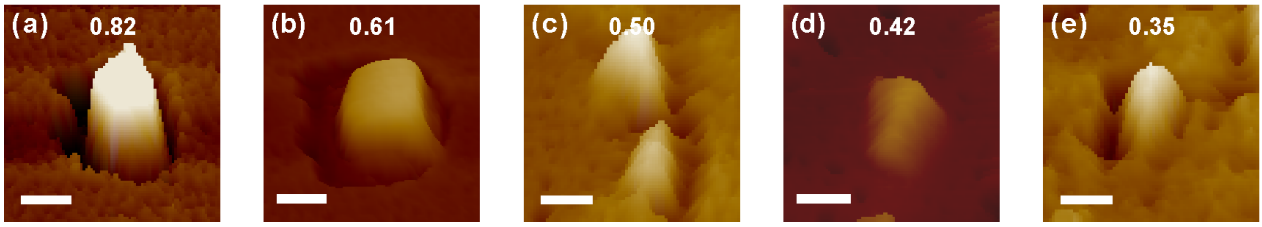

Figure S7. AFM measurements of Ag nanocubes in the solvent of PI: (a) 0.82, (b) 0.61, (c) 0.50, (d) 0.42, (e) 0.35. Scale bar, 100 nm.

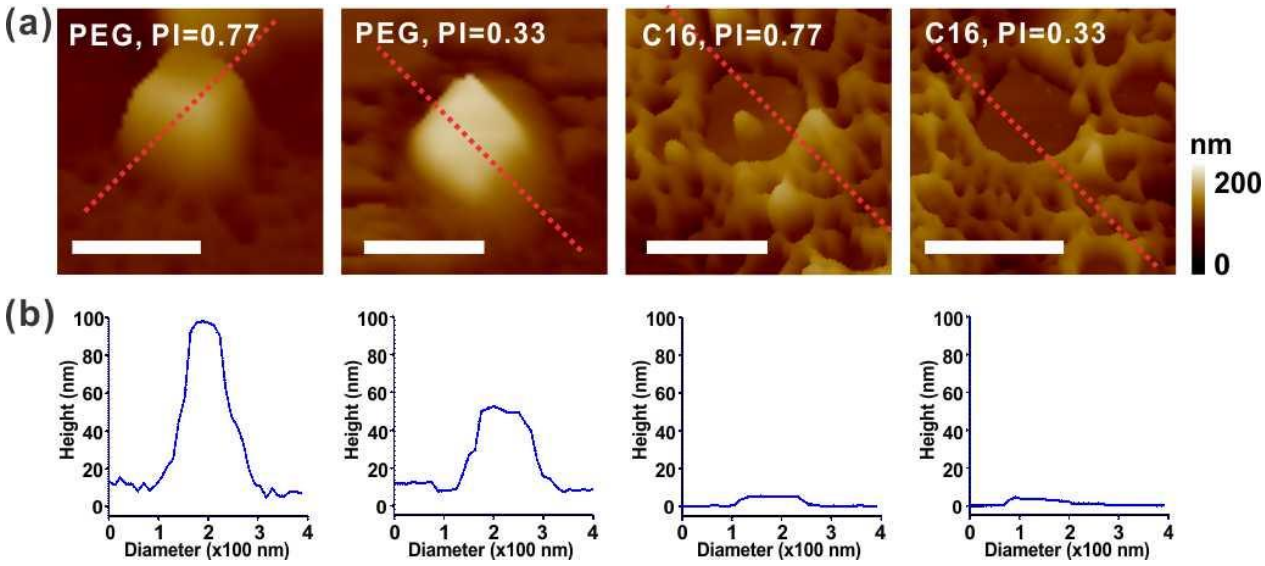

Figure S8. (a) AFM topographic images and (b) the corresponding height profile along the highlighted line. Scale bar, 150 nm.

Table S4. Collapsing percentage of PEG on Ag nanocubes with 67-C16% functionalization dispersed in different solvents.

Polarity index (PI)	Hydrodynamic diameter (nm)	Collapsing percentage (%)
1.00	230 ± 11	0
0.85	208 ± 6	24
0.82	206 ± 5	26
0.77	198 ± 4	34
0.61	173 ± 8	61
0.50	161 ± 11	74
0.47	157 ± 8	78
0.42	151 ± 9	85
0.38	142 ± 8	95
0.35	139 ± 10	98
0.33	137 ± 9	100

Calculation of collapsing percentage

The collapsed percentage at PI=1.00 and 0.33 is assumed to be 0% and 100% respectively.
The hydrodynamic diameter at PI=1.00 and 0.33 is assumed to be 230 nm and 137 nm respectively.
So collapsing percentage = (230 - hydrodynamic diameter) / (230 - 137) *100%

For instance,
Calculation of collapsing percentage at PI=0.77:
Collapsing percentage = (230-198) / (230-137) * 100%
= 34%

Table S5. Four polarity index points which leads to the ordered structures .

Solvent composition	Volume ratio	Polarity Index (PI)
IPA/H_2O	V_{IPA}%=50%	0.77
Chloroform/ethanol	$V_{chloroform}$%=46%	0.47
Toluene/ethanol	$V_{toluene}$%=50%	0.38
Hexane/ethanol	V_{hexane}%=50%	0.33

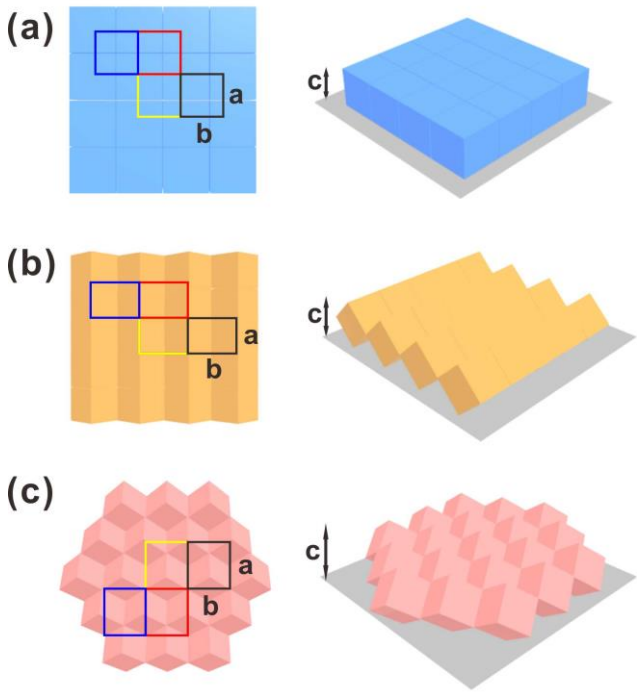

Figure S9. Scheme of packing efficiency of metacrystals of (a) planar Ag cubes, (b) tilting cubes, (c) standing cubes. (d) Changes in packing efficiency with variations in metacrystal structures.

The squares in (a) show the repeat unit of the planar Ag cubes, which is filled with one cube, with no remaining space filled with holes. The rectangles in (b) show the simplest repeat unit of tilting structure, which is filled with one cube, with the remaining space filled with two tetrahedral holes. The simplest repeat unit of the standing structure is shown by the rectangles in the figure above. The repeat unit is filled with one cube, with the remaining space filled with two tetrahedral holes.

The edge length of a single cube is l

In the square in (a)

Length of cube = l ($a = b = c = l$)

Volume of repeat unit = $l \times l \times l = l^3$

Volume of one cube $= l^3$

Packing efficiency of planar cubes = $\frac{l^3}{l^3}$

= 100%

In the rectangle in (b),

a = l, b = $\frac{\sqrt{2}}{2}l$, c = $\frac{\sqrt{2}}{2}l$

Volume of repeat unit = $a \times b \times c = \sqrt{2}l \times l \times \sqrt{2}l = 2l^3$

Volume of one cube $= l^3$

Packing efficiency of tilting cubes = $\frac{l^3}{2l^3}$

= <u>50%</u>

In the rectangle in (c),

a = $\sqrt{3}l$, b = $\sqrt{2}l$, c = $\sqrt{3}l$

Volume of repeat unit = $a \times b \times c = \sqrt{3}l \times \sqrt{2}l \times \sqrt{3}l = 3\sqrt{2}l^3$

Volume of one cube $= l^3$

Packing efficiency of standing cubes $= \frac{l^3}{3\sqrt{2}l^3}$

= <u>24%</u>

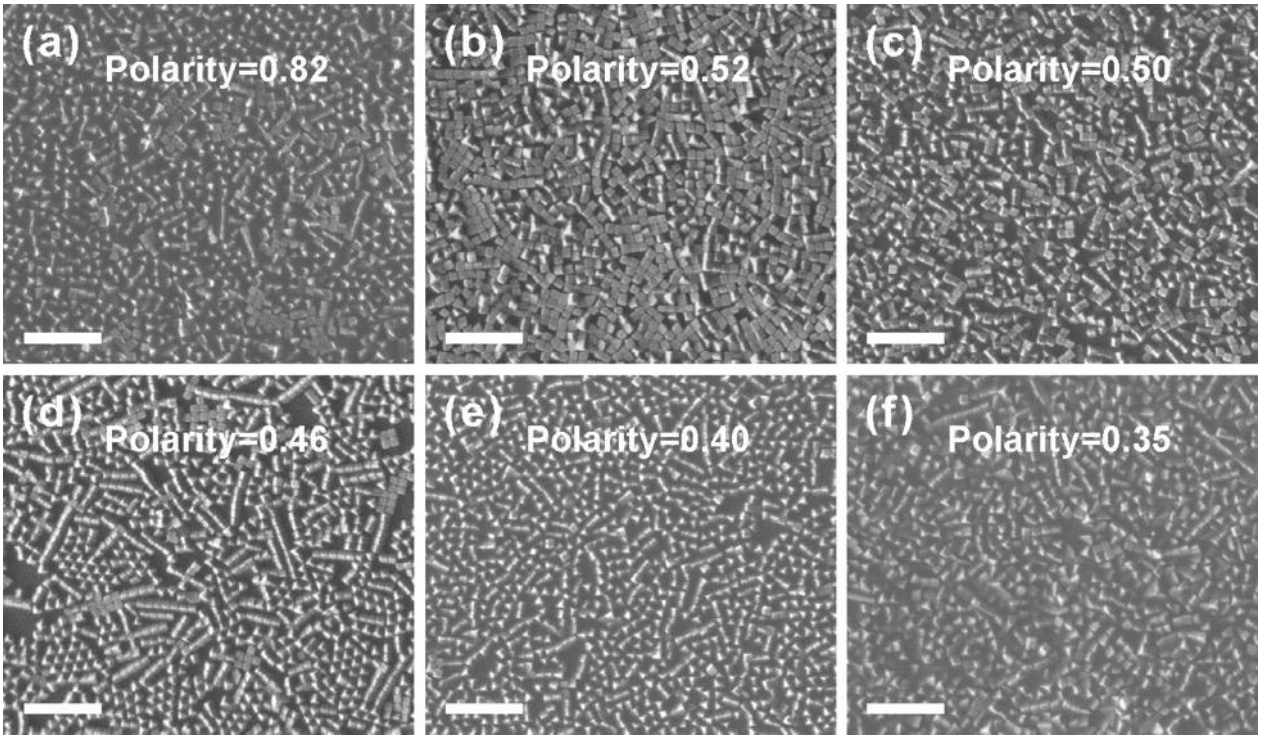

Figure S10. SEM images of assembled structure at other solvent polarity. Scale bar, 1 μm.

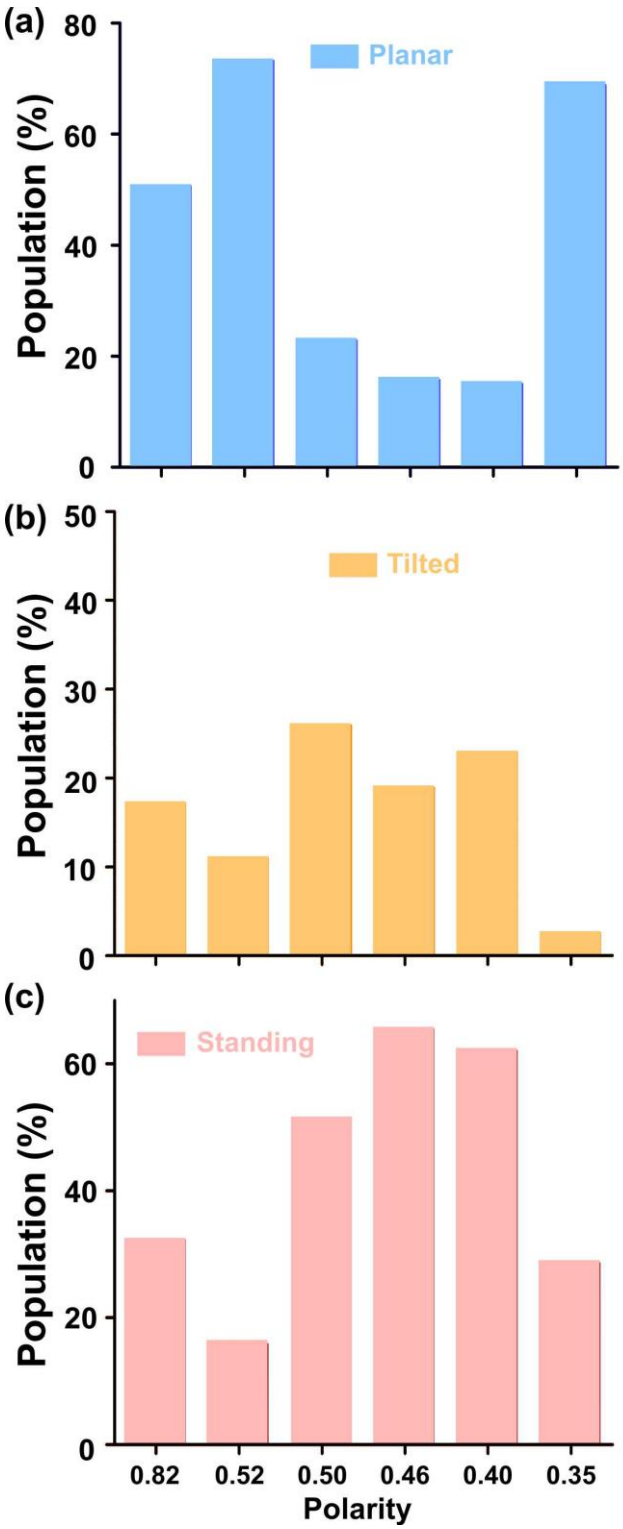

Figure S11. Population diagram of planar, tilted and standing nanocubes in the assembled structures which are shown in Figure S10.

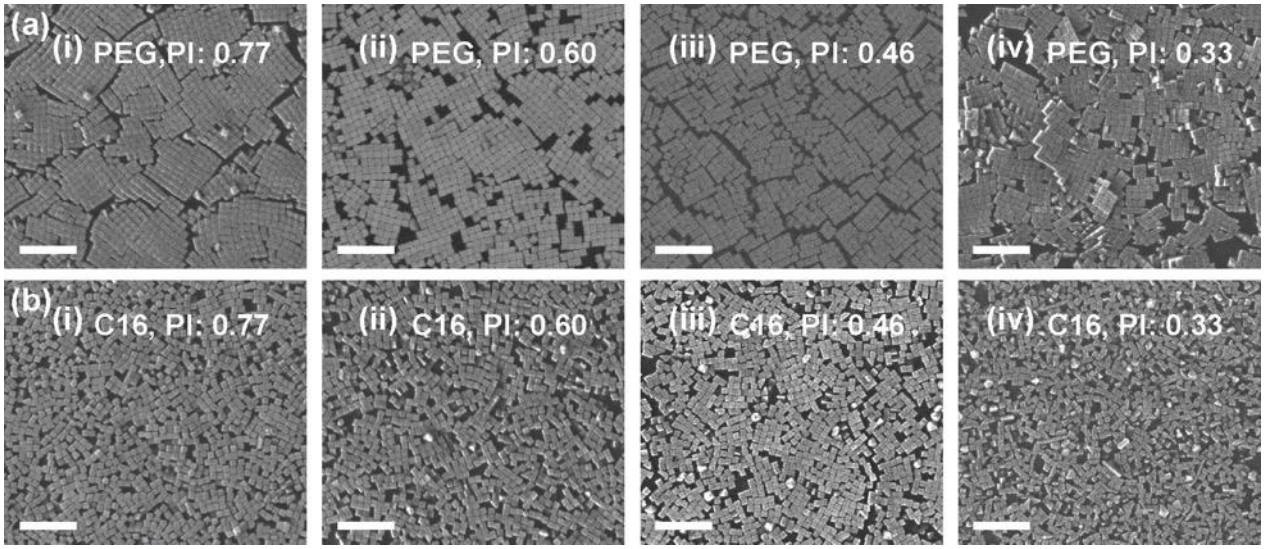

Figure S12. Assembly of (a) pure PEG- and (b) C16-functionalizaed nanocubes in different solvent can hardly achieve the tunability of superstructure, showing only one structure. Scale bar, 1 μm.

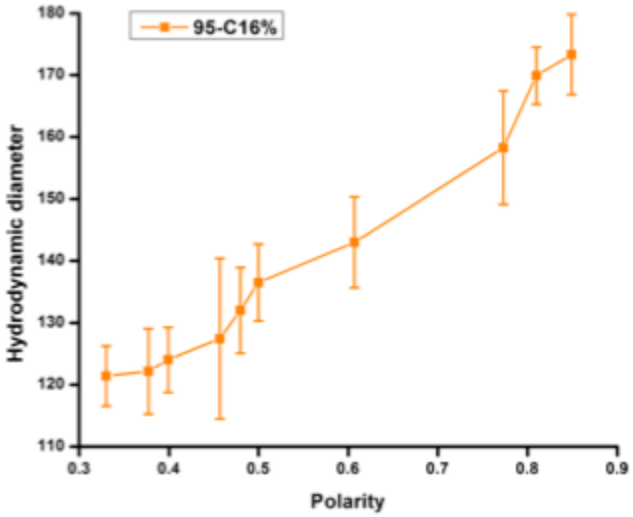

Figure S13. Hydrodynamic diameter of 95-C16%-functionalized nanocubes in different solvents.

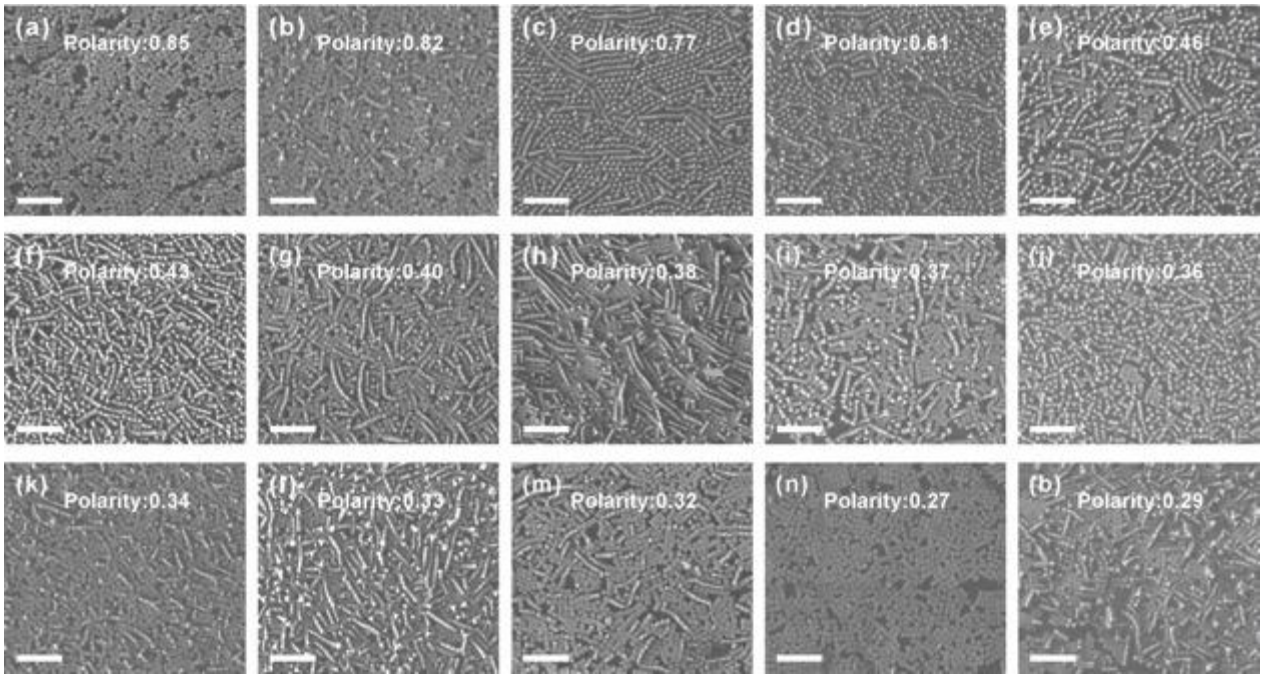

Figure S14. Gradual change of assembled structure of Ag nanocube with 95-C16% functionalization in different solvent. Scale bar, 1 μm.