Supporting Information

Selective Recognition Induced Nanostructures in a Cucurbit[7]uril-based Host-Guest System: Micelles, Nanorods, and Nanosheets

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1. Experimental and calculation details

1.1 Materials. Chemicals were analytical or higher purity grade and used without further purification. CB[7] and hexadecyl-dimethyl-benzyl-ammonium chloride (HDBAC) were purchased from Aldrich Chemical Co., Inc. Trixton X-100, N,N-dimethyl-N-(2-phenoxyethyl)-1-dodecanaminium chloride (Domiphen), dodecyl-trimethyl-ammonium bromide (DTAB), tetradecyl-trimethyl-ammonium bromide (TTAB) and cetyl-trimethyl-ammonium bromide (CTAB) were from TCI (Shanghai) Development Co., Ltd. Sodium dodecyl-sulphate (SDS) and sodium dodecyl-benzene-sulfonate (SDBS) were from Beijing Chemistry Co., Ltd. Dioctadecyl-dimethyl-ammonium bromide (DODAB) was from Acros Organics, Belgium. Double deionized water with a resistivity of 18.2 MΩ·cm was used throughout except the NMR measurements, where D_2O (99.9% of deuterium, from Cambridge Isotopes) was used. The chemical structures of Triton X-100, Domiphen and HDBAC are shown in Fig. S1.

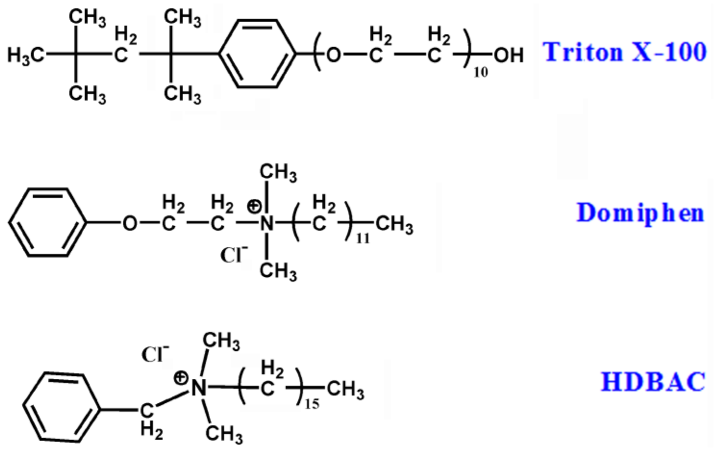

Fig. S1 The molecular structures of Triton X-100, Domiphen and HDBAC.

1.2 Isothermal Titration Calorimetry (ITC). Titration experiments were carried out at 30°C on a VP-ITC calorimeter (MicroCal Inc., Northampton, MA). In the CMC determination experiments, surfactant was in the injection syringe, and pure water was in the sample cell. In the binding assays, the host solution (CB[7], 2-3 mM) was in the injection syringe and the guest solution (HDBAC, 0.11mM) was in the sample cell. We also titrated ~5 mM HDBAC into ~0.5 mM CB[7] solution. The titration schedule consists of 29 or 57 consecutive injections of 2-10 μL with about 360 s interval between injections. Before every fitting, dilution heat is subtracted from the observed heat of combination.

1.3 ^{1}H NMR Spectroscopy. One-dimensional NMR spectra were collected in D_2O at 25 °C on a JOEL JNM-ECA300 (300 MHz) Fourier transform spectrometer. The concentration of HDBAC was 0.5 mM, and the HDBAC/CB[7] molar ratio ranged from 10:1 to 1:2.

1.4 Dynamic Light Scattering (DLS) DLS measurements were conducted on Malvern ZETASIZER Nano series Nano-ZS90 at 25°C.Stock HDBAC was 50 mM. The concentration of HDBAC was 2.0 mM when it was mixed with CB[7], and the HDBAC/CB[7] molar ratio ranged from 6:1 to 1:2.

1.5 Transmission Electron Microscopy (TEM). TEM experiments were conducted on a JEMO 2010 electron microscope at an acceleration voltage of 110 kV. The samples were prepared by drop-coating the aqueous solution on the carbon-coated copper grid.

1.6 Atomic Force Microscope (AFM). AFM measurements were performed on a SPM-9500J3 tapping-mode atom force microscope (Shimadzu, Japan). The samples for AFM were prepared by drop-coating the mixed HDBAC and CB[7] solution on the fresh silica surface newly cleaved by concentrated H_2SO_4.

1.7 Small-Angel X-ray Scattering (SAXS). SAXS experiments were performed at the beamline 1W2A of the Beijing Synchrotron Radiation Facility (BSRF) (λ=1.54 Å).A standard silver behenate sample was used for the calibration of diffraction spacings. X-ray scattering intensity patterns were recorded during 120 s exposure of the samples to the synchrotron beam.Samples for the SAXS experiments were prepared by mixing 100 mM HDBAC and the proper amount of CB[7] powder to have a 1:1 molar ratio. After 3 minutes of sonication, gel-like dispersions of the HDBAC-CB[7] mixtures formed. The X-ray scattering intensity data were analyzed using the program Fit2D.

1.8 Quantum Chemical Calculations. The energy minimized geometries of HDBAC, CB[7] and CB[7]@HDBAC were obtained by DFT B3LYP method at the 6-31G(d,p) basis set with the Gaussian03 program.[1] All the optimized geometries were recognized as local minima with no imaginary frequency.

2. ITC results

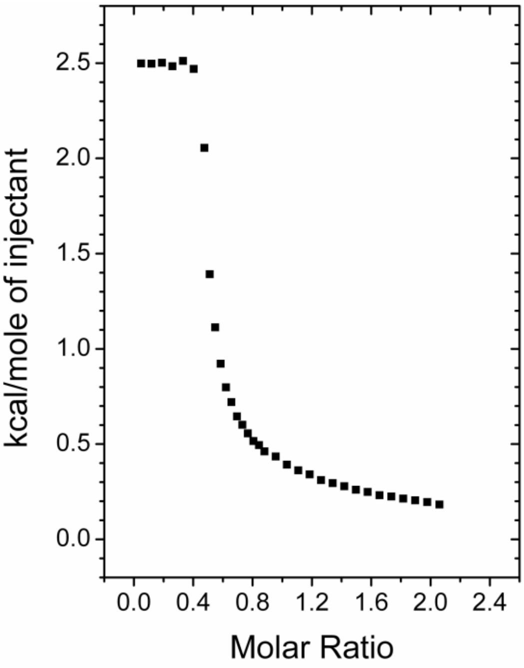

Fig. S2 The enthalpy changes in ITC assay of the titration of 5mM HDABC into water at 30°C.

The CMC and the demicellization enthalpy of HDBAC were determined to be 0.45 mM and 2.5 kcal/mol, respectively.

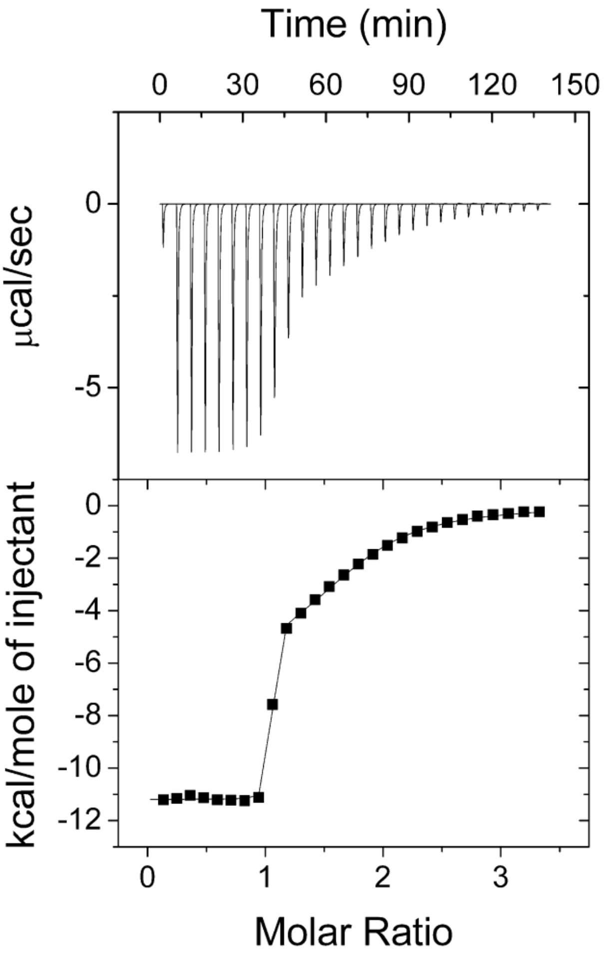

Fig. S3 ITC assay of the titration of 2.5 mM CB[7] into the solution of 0.11 mM HDABC at 30°C.

Fig. S3 shows the titration results of 2.5 mM CB[7] into the solution of 0.11 mM HDABC, which is a typical two-set of sites in ITC fitting models.

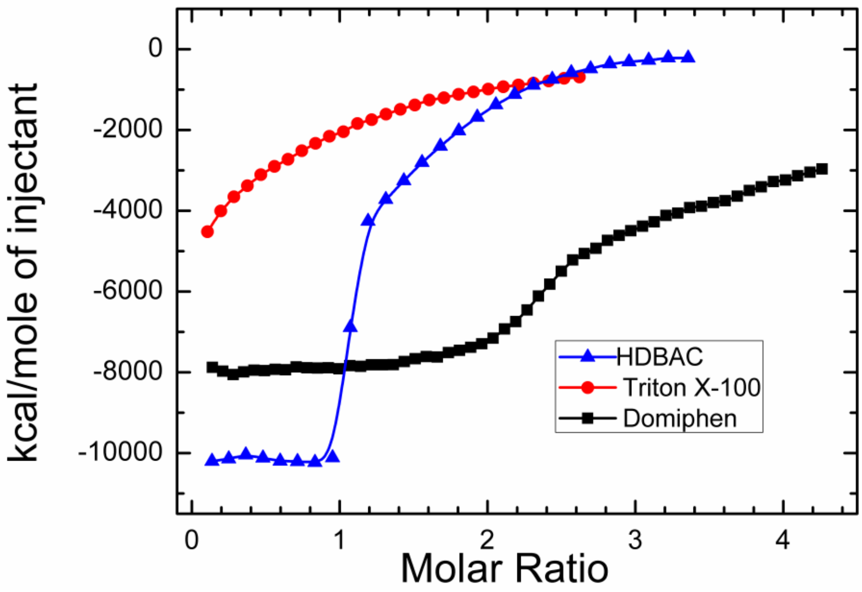

Fig. S4 ITC results of the titration of CB[7] into the solution of HDABC (blue), Triton X-100 (red) and Domiphen (black) at 30°C.

There are two interaction modes in CB[7]–HDBAC and CB[7]–Domiphen systems. HDBAC and Domiphen have similar chemical structures as shown in Fig. S1. The first set of binding sites on Domiphen molecule can bind 2 CB[7] molecules, but that of HDBAC molecule just bind one CB[7] molecule

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3. NMR results

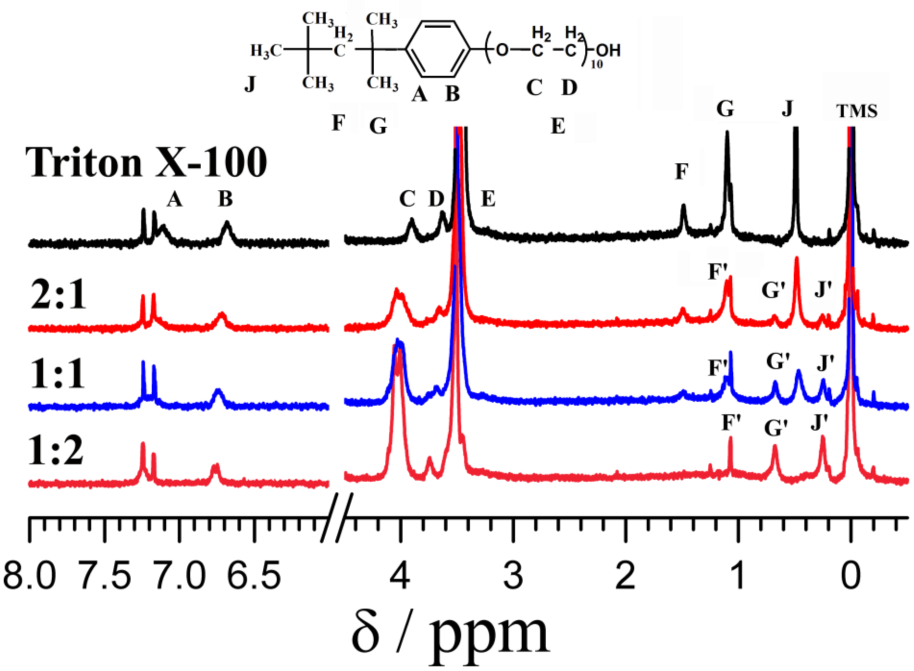


Fig. S5 ^{1}H NMRresults of Triton X-100 (black), and mixture of CB[7] and Triton X-100.The Triton X-100/CB[7] molar ratio was ranged from 2:1 to 1:2. TMS was used as the reference material.

The hydrogen atoms of the surfactant are ranked by their chemical shifts and labeled with letters A to K as shown on the top of Fig. S5. The chemical shifts of H_A to H_J are 7.22, 6.68, 3.90, 3.63, 3.44, 1.50, 1.10 and 0.49 ppm, respectively. When the Triton X-100/CB[7] molar ratio is 2:1, there are two sets of chemical shifts for H_F, H_G and H_J which indicate the slow exchange binding process of CB[7] and the iso-octyl of Triton X-100. But no upfield shift of the chemical shift of the aromatic hydrogens H_A and H_B is seen even when the Triton X-100/CB[7] molar ratio is 1:2. So, CB[7] mainly binds to the iso-octyl group of Triton X-100.

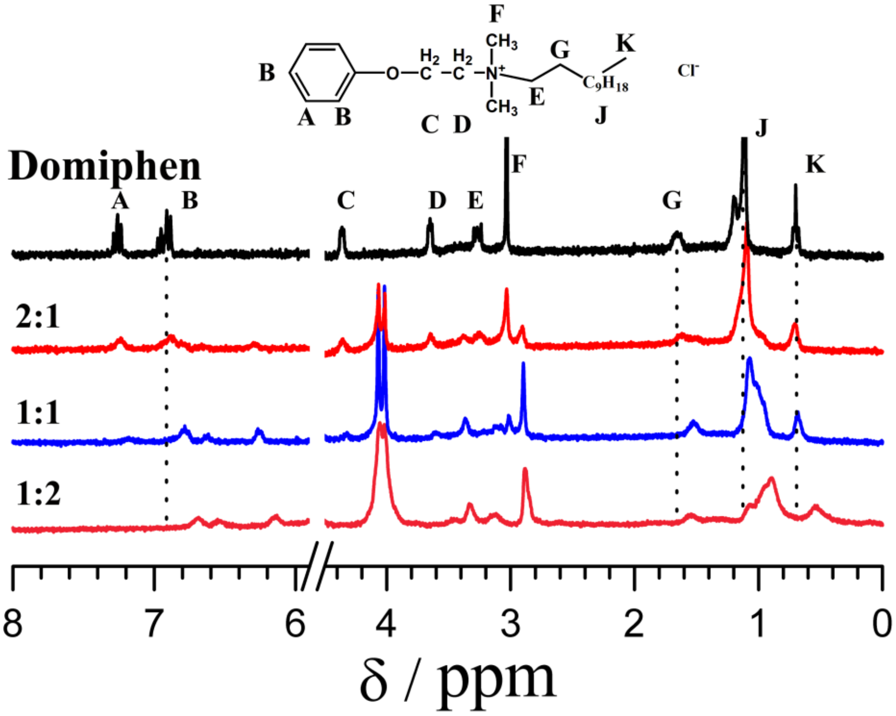
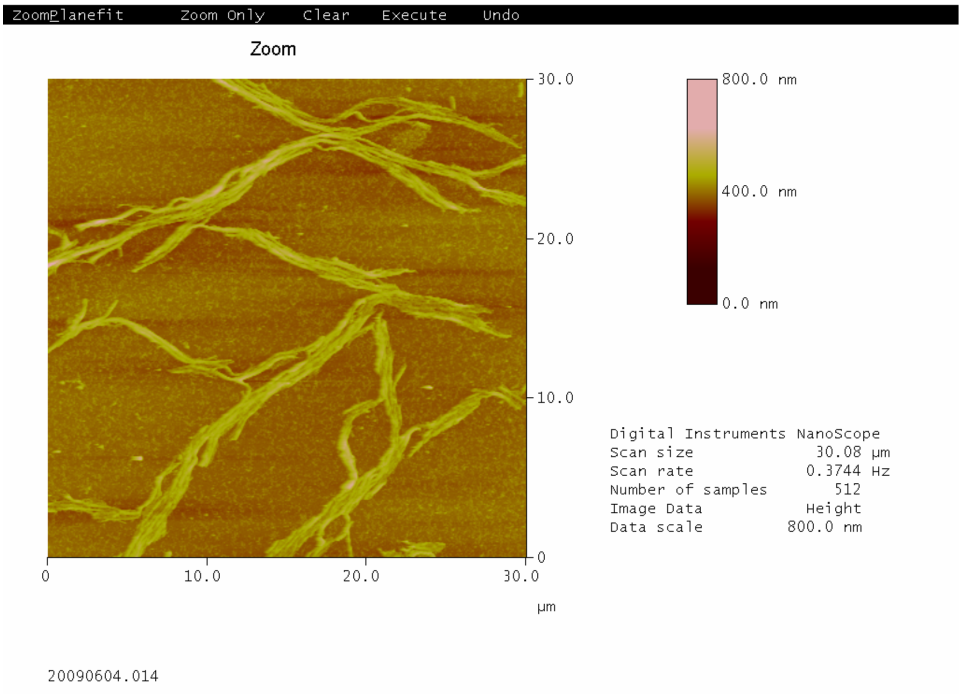


Fig. S6 ^{1}H NMR results of Domiphen (black), and mixture of CB[7] and Domiphen. The Domiphen/CB[7] molar ratio ranges from 2:1 to 1:2.

The hydrogen atoms of the surfactant are ranked by their chemical shifts and labeled with letters A to K as shown on the top of Fig. S6.The chemical shifts of H_A to H_K are 7.26, 6.91, 4.35, 3.65, 3.27, 3.03, 1.68, 1.20~1.10 and 0.70 ppm, respectively. When the Domiphen/CB[7] molar ratio is 2:1, there are two sets of chemical shifts for H_A and H_B which indicate the slow exchange binding process of CB[7] and the phenyl group of Domiphen, but we do not see the upfield shift of the chemical shift of the hydrogens of dodecyl ($H_G$to H_K). So, we conclude that CB[7] can simultaneously bind to both the phenyl and the dodecyl groups of Domiphen even when Domiphen is in excess. There is no selective recognition of a particular part of the guest molecule in this system. That is why the first set of binding sites of on

Domiphen molecule can bind 2 CB[7] molecules as detected by ITC.

4. AFM images



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Digital Instruments NanoScope
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Scan rate             0.3744 Hz
Number of samples        512
Image Data            Height
Data scale          800.0 nm
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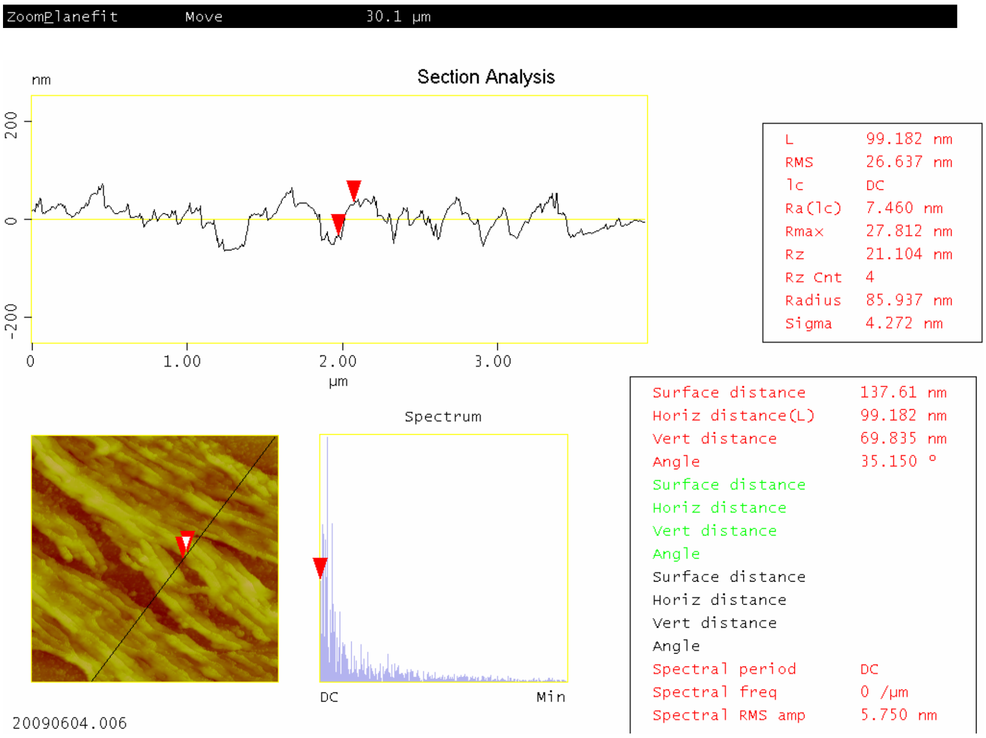

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L          99.182 nm
RMS        26.637 nm
lc         DC
Ra(lc)     7.460 nm
Rmax       27.812 nm
Rz         21.104 nm
Rz Cnt     4
Radius     85.937 nm
Sigma      4.272 nm
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Surface distance       137.61 nm
Horiz distance(L)      99.182 nm
Vert distance          69.835 nm
Angle                  35.150 °
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period        DC
Spectral freq          0 /µm
Spectral RMS amp       5.750 nm
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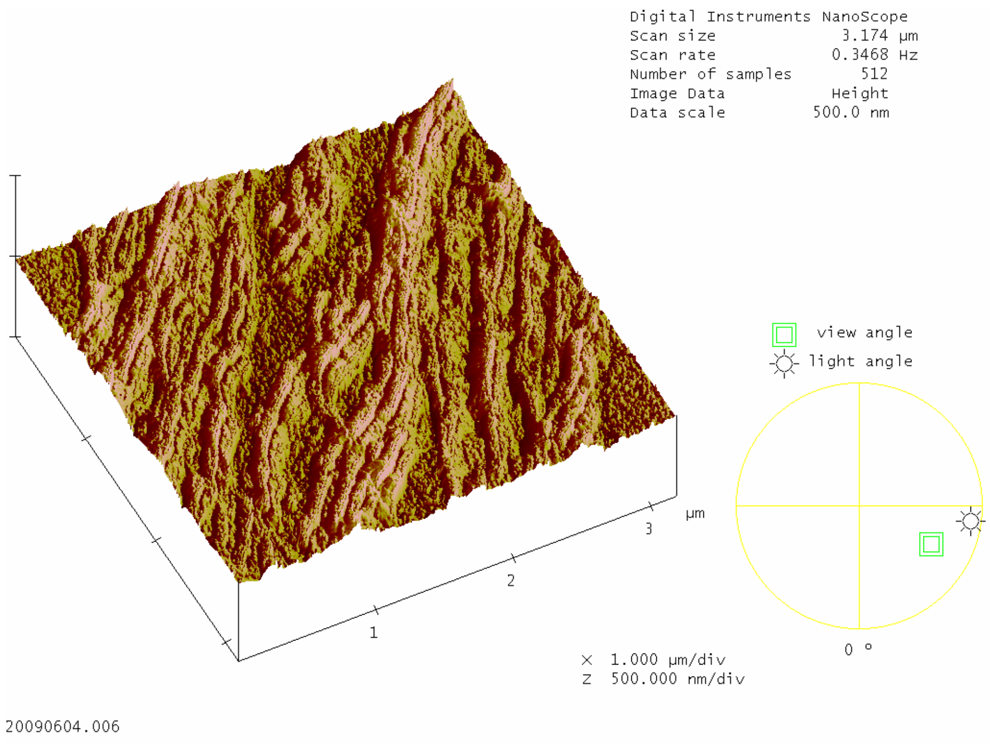

Fig.S7 AFM images of the nanorods at the HDBAC/CB[7]molar ratio of 1.3:1.

5. References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheesman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 03, Revision B. 03; Gaussian Inc: Pittsburgh, PA, 2003.