Electronic Supplementary Information (ESI)

Modulating Stacking Modes of Nanosized Metal-Organic Frameworks by Morphology Engineering for Isomer Separation

Ming Xu[a,b,+], Sha-Sha Meng[a,+], Peiyu Cai[b], Wen-Qi Tang[a], Yun-Dong Yin[a], Joshua A. Powell[b], Hong-Cai Zhou[b,c,*] and Zhi-Yuan Gu[a,*]

[a.] *Jiangsu Key Laboratory of Biofunctional Materials, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, China*

[b.] *Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, United States*

[c.] *Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77842, United States*

+ Ming Xu and Sha-Sha Meng contributed equally

** Corresponding authors: E-mail: guzhiyuan@njnu.edu.cn and E-mail: zhou@chem.tamu.edu*

Content

Section S1: Chemicals and Instrumentation

All chemicals employed were of analytical grade and used as supplied without further purification. The $ZrCl_4$, acetic acid, benzoic acid, zirconyl chloride octahydrate, xylene, ethyltoluene, chlorotoluene, dichlorobenzene, C_6H_{14}, C_8H_{18}, $C_9H_{20,}$ and $C_{10}H_{22}$ were purchased from Aladdin Industrial Inc (Shanghai, China). Ethanol (EtOH), methanol (MeOH), N,N-Dimethylformamide (DMF), and hydrochloride (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H_4TBAPy) was synthesized following the published procedures.[1] Powder X-ray diffraction (PXRD) patterns were obtained from Bruker-axs D8 davinci X-ray powder diffractometer with a CuKα radiation (1.54056 Å). Transmission electron microscopy (TEM) images were performed on JEOL JEM-2100F transmission electron microscopy ope, rated at an accelerating voltage of 200 kV. Scanning electron microscope (SEM) images were collected on a JSM-7600F (JEOL Ltd) scanning electron microscope. High-resolution TEM (HRTEM) studies were carried out using a JEOL 2010 TEM with an accelerating voltage of 200 kV. The high angle annular dark field images (HAADF) were recorded on an ARM-200CF TEM (JEOL, Tokyo, Japan) operated at 200 keV and equipped with double spherical aberration (Cs) correctors. The attainable resolution of the probe defined by the objective pre-field is 78 picometers. Thermogravimetric analysis (TGA) was collected on a Perkin-Elmer Pyris Diamond 1 TGA analyzer. The fluorescence spectroscopy was collected on a fluorescence spectrometer (Hitachi F-4600). Atomic force microscopy (AFM) measurements were performed with a Dimension ICON instrument (Bruker, US). Nitrogen sorption measurements were conducted on ASAP 2020 instrument. All of the separations were performed on an Agilent 7890B gas chromatographic system with a flame ionization detector (FID). Data acquisition and processing were controlled by ChemStation software. Nitrogen (99.999%, Air Liquide, France) was employed as the carrier gas. The inlet temperature of the GC was set to 250 ^oC, while the temperature of FID was set to 300 ^oC. A 3 μL analyte was introduced to a 20 mL gastight sealed

glass vial and homogenized at 120 ^{o}C before the injection for gas chromatographic separation.

Section S2. Synthesis of Different Materials

Synthesis of AA-X-Y

Typically, 10 mg $ZrCl_4$, different volumes of acetic acid (X = 60, 120, 140, 160, 180, 200, 220, 240, 260, 600 μL), and different volumes of H_2O (Y = 0, 10, 40, 50, 60, 80 μL) were added in 2 mL DMF into a 20 mL vial. The mixture was kept under ultrasonication for 5 min. Then, 10 mg H_4TBAPy was further added to the above-mentioned solution and kept under ultrasonication for 10 minutes at room temperature. The resulting dispersions were put into an oven at 120 ^oC for 24 h. The AA-X-50 was separated via centrifugation and further washed with DMF and EtOH three times, respectively.

Synthesis of BA-X-50

Typically, 10 mg $ZrCl_4$, different volumes of benzoic acid (X = 120, 240 mg), and 50 μL H_2O were added in 2 mL DMF into a 20 mL vial. The mixture was kept under ultrasonication for 5 min. Then, 10 mg H_4TBAPy was further added to the above-mentioned solution and kept under ultrasonication for 10 minutes at room temperature. The resulting dispersions were put into an oven at 120 ^oC for 24 h. The BA-X-50 was separated via centrifugation and further washed with DMF and EtOH three times, respectively.

Synthesis of HCl-X-50

Typically, 10 mg $ZrCl_4$, different volumes of HCl (X= 120, 240 μL), and 50 μL H_2O were added in 2 mL DMF into a 20 mL vial. The mixture was kept under ultrasonication for 5 min. Then, 10 mg H_4TBAPy was further added to the above-mentioned solution and kept under ultrasonication for 10 minutes at room temperature. The resulting dispersions were put into an oven at 120 ^oC for 24 h. The HCl-X-50 was separated via centrifugation and further washed with DMF and EtOH three times, respectively.

Table S1. Detailed Compositions of the Mixture for Synthesizing NU-901 with Different Morphologies

Sample Name[a]	$ZrCl_4$ (mg)	Modulators		DMF (mL)	H_4TBApy (mg)
		Acetic Acid (μL)	H_2O (μL)		
AA-60-50	10	60	50	2	10
AA-120-50	10	120	50	2	10
AA-140-50	10	140	50	2	10
AA-180-50	10	180	50	2	10
AA-200-50	10	200	50	2	10
AA-220-50	10	220	50	2	10
AA-240-50	10	240	50	2	10
AA-260-50	10	260	50	2	10
AA-600-50	10	600	50	2	10
AA-120-0	10	120	0	2	10
AA-120-10	10	120	10	2	10
AA-120-40	10	120	40	2	10
AA-120-60	10	120	60	2	10
AA-120-80	10	120	80	2	10
		Benzoic Acid (mg)	H_2O (μL)		
BA-120-50	10	120	50	2	10
BA-240-50	10	240	50	2	10
		Hydrochloride (μL)	H_2O (μL)		
HCl-120-50	10	120	50	2	10
HCl-240-50	10	240	50	2	10

[a]The synthetic material was named with the acid modulators-modulator amount-water volume. For example, AA-120-50 represents a material synthesized by using 120 μL acetic acid (AA) as modulators with 50 μL H_2O.

Synthesis of Bulk NU-901

NU-901 was synthesized according to the literature procedure with few changes.[2] Zirconyl chloride octahydrate (35 mg, 0.011 mmol) and benzoic acid (1.35 g, 11.5 mmol) were added into a 20 mL vial and dissolved in 15 mL of DMF via ultrasonication. Then, the solution was put into an oven at 80 °C for 2 h. After cooling to room temperature, 20 mg (0.03 mmol) H_4TBAPy was added to the vial. The solution was then ultrasonicated and subsequently heated at 120 °C for 24 h. The NU-901 was separated via centrifugation and further washed with DMF and EtOH three times, respectively.

Section S3. Characterization of the Synthesized Materials

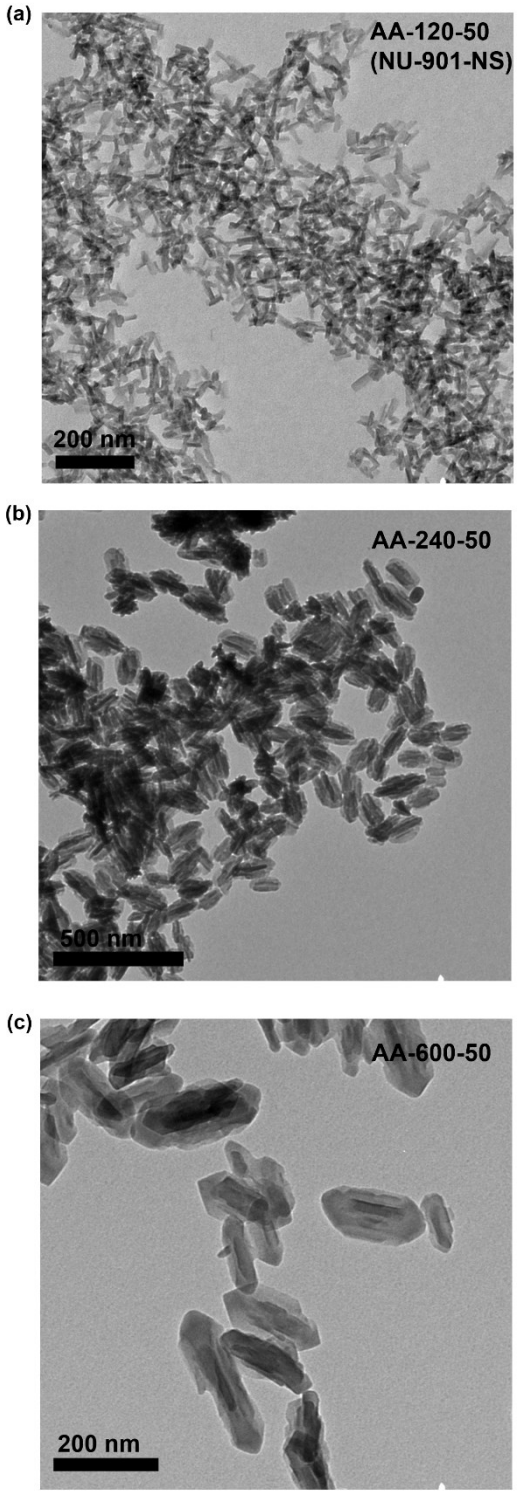

Figure S1. TEM images of (a) AA-120-50 (NU-901-NS), (b) AA-240-50 and (c) AA-600-50.

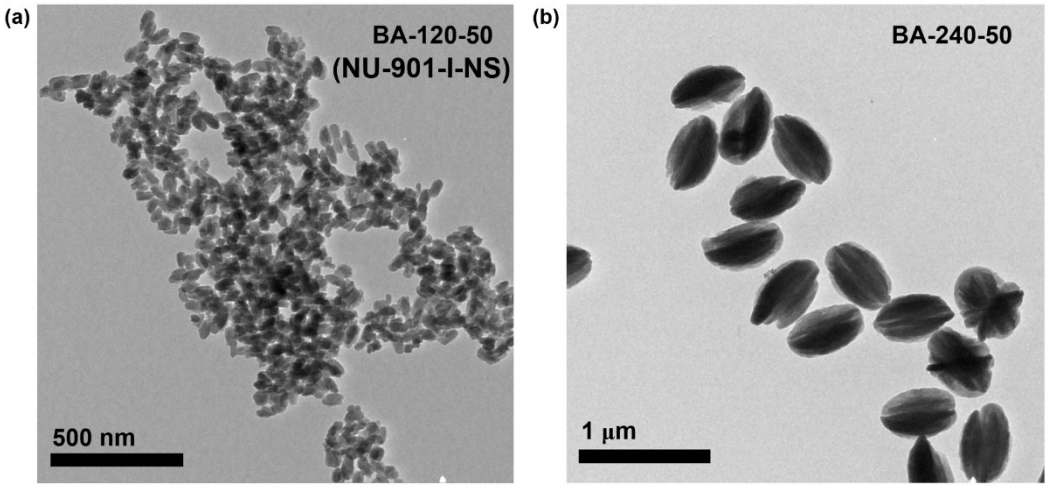

Figure S2. TEM images of (a) BA-120-50 (NU-901-I-NS) and (b) BA-240-50.

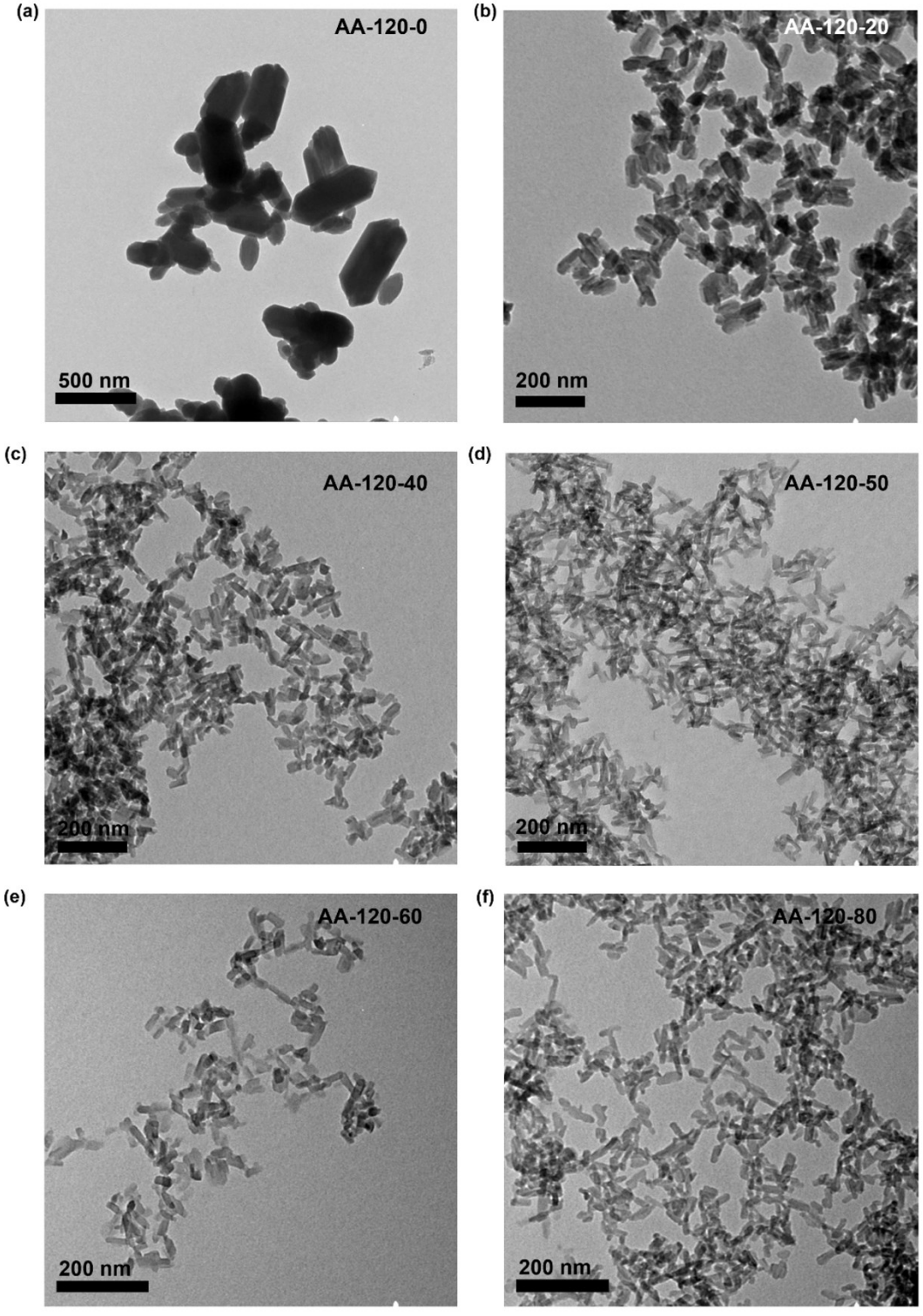

Figure S3. TEM images of (a) AA-120-0, (b) AA-120-20, (c) AA-120-40, (d) AA-120-50 (NU-901-NS), (e) AA-120-60 and (f) AA-120-80.

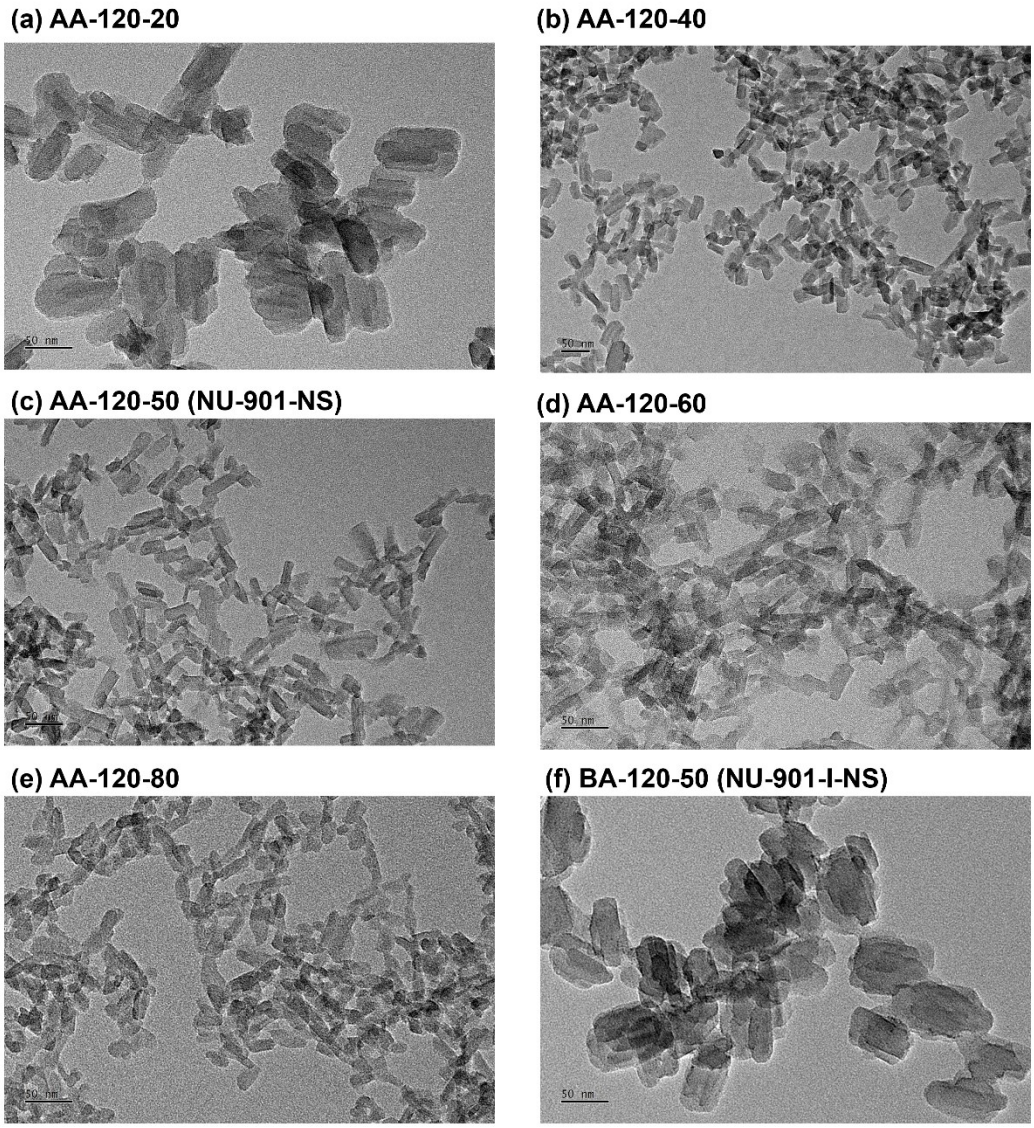

Figure S4. HRTEM images of (a) AA-120-20, (b) AA-120-40, (c) AA-120-50 (NU-901-NS), (d) AA-120-60, (e) AA-120-80 and (f) BA-120-50 (NU-901-I-NS).

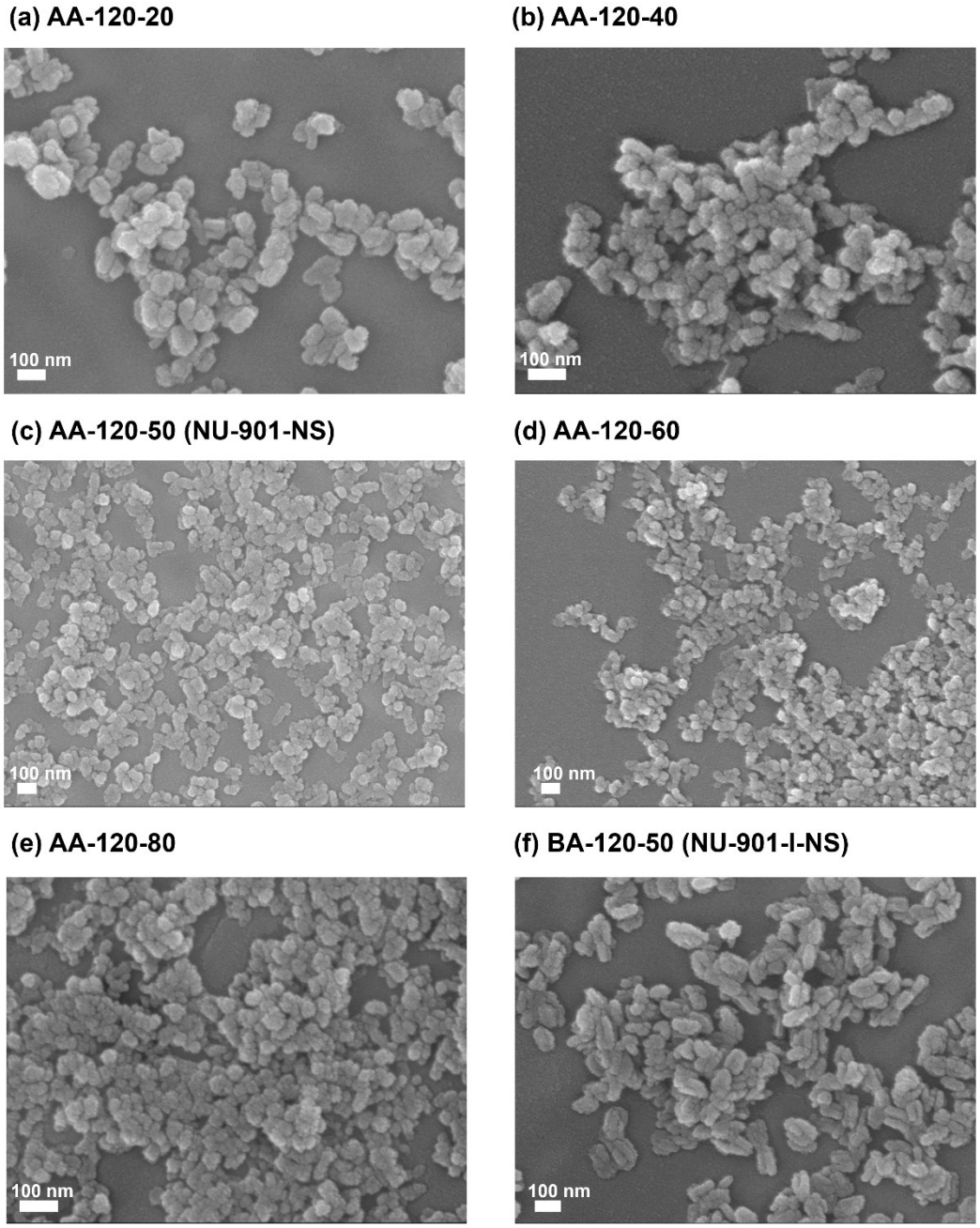

Figure S5. SEM images of (a) AA-120-20, (b) AA-120-40, (c) AA-120-50 (NU-901-NS), (d) AA-120-60, (e) AA-120-80 and (f) BA-120-50 (NU-901-I-NS).

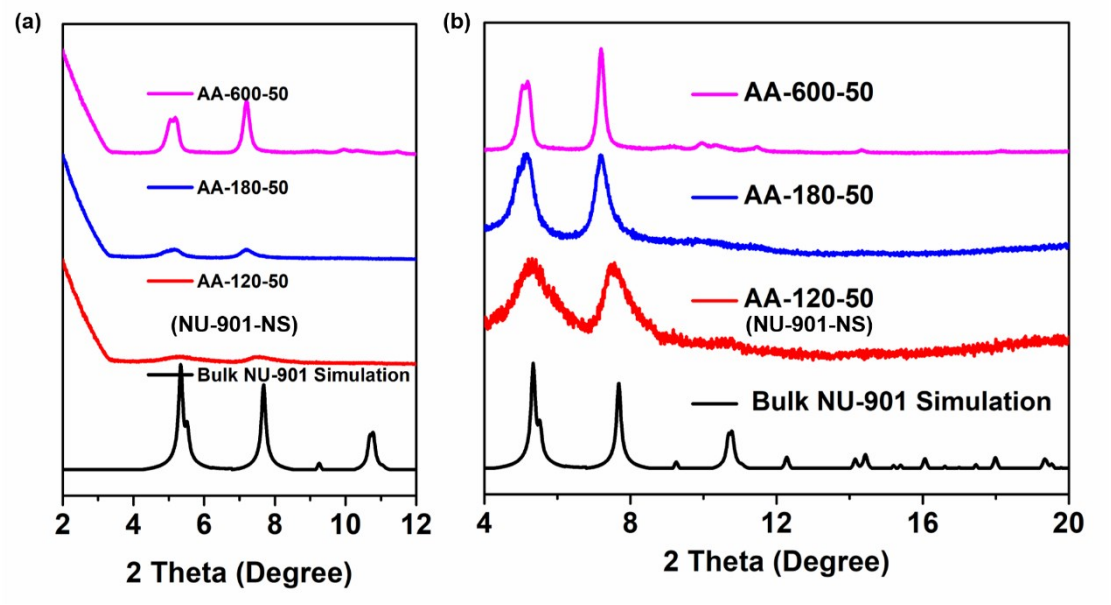

Figure S6. (a) and (b) PXRD patterns of NU-901 modulated by different volumes of AA.

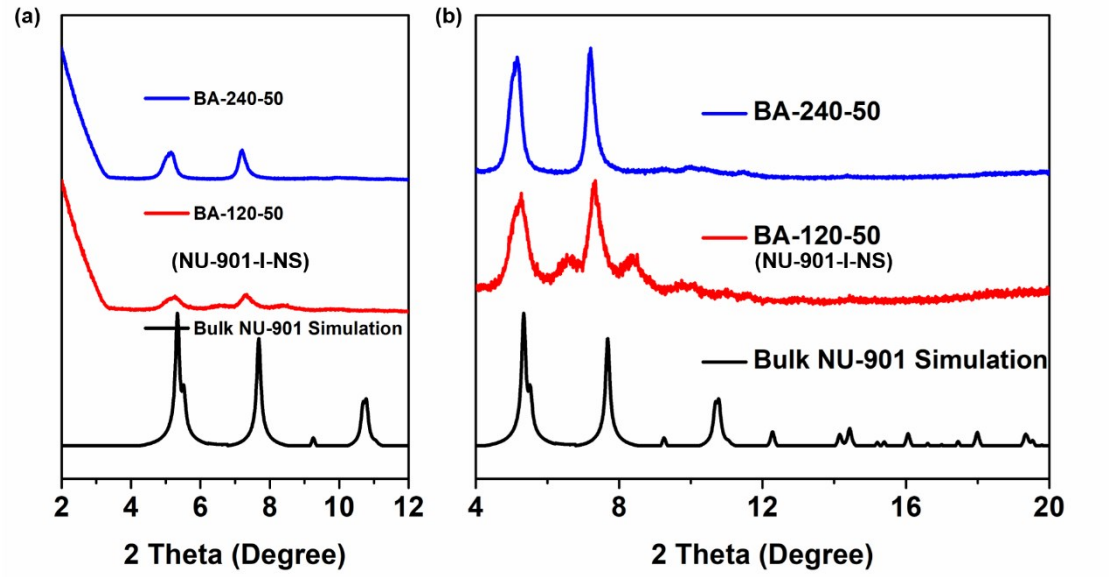

Figure S7. (a) and (b) PXRD patterns of NU-901 modulated by different amounts of BA.

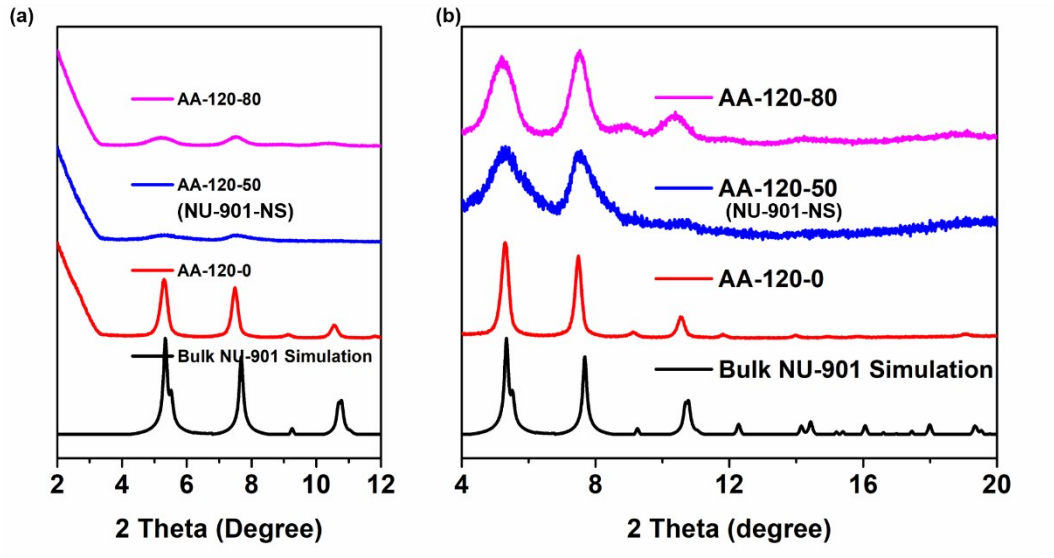

Figure S8. (a) and (b) PXRD patterns of NU-901 modulated by different volumes of water.

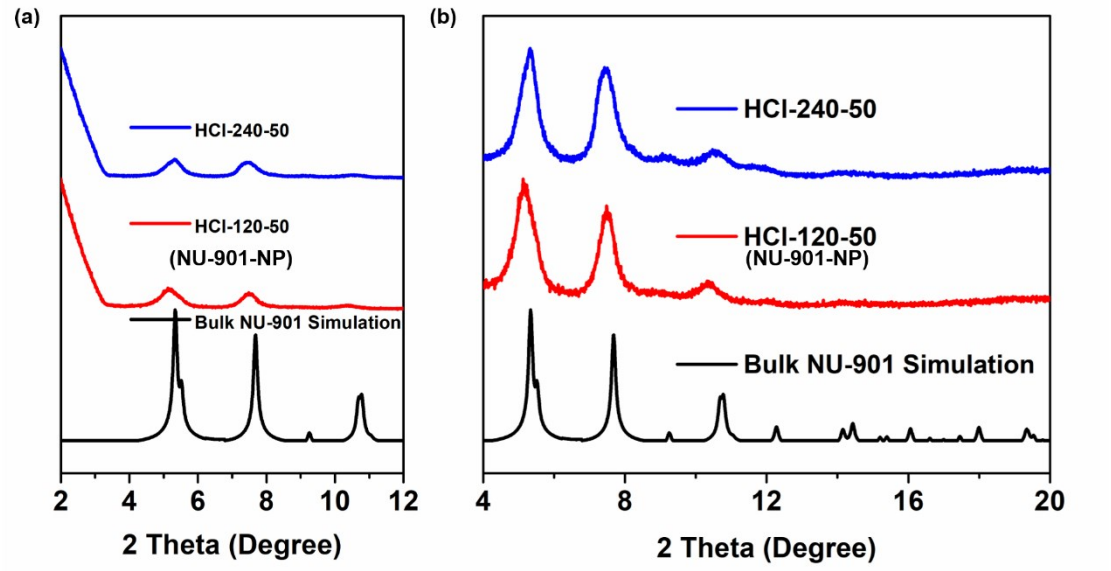

Figure S9. (a) and (b) PXRD patterns of NU-901 modulated by different volumes of HCl.

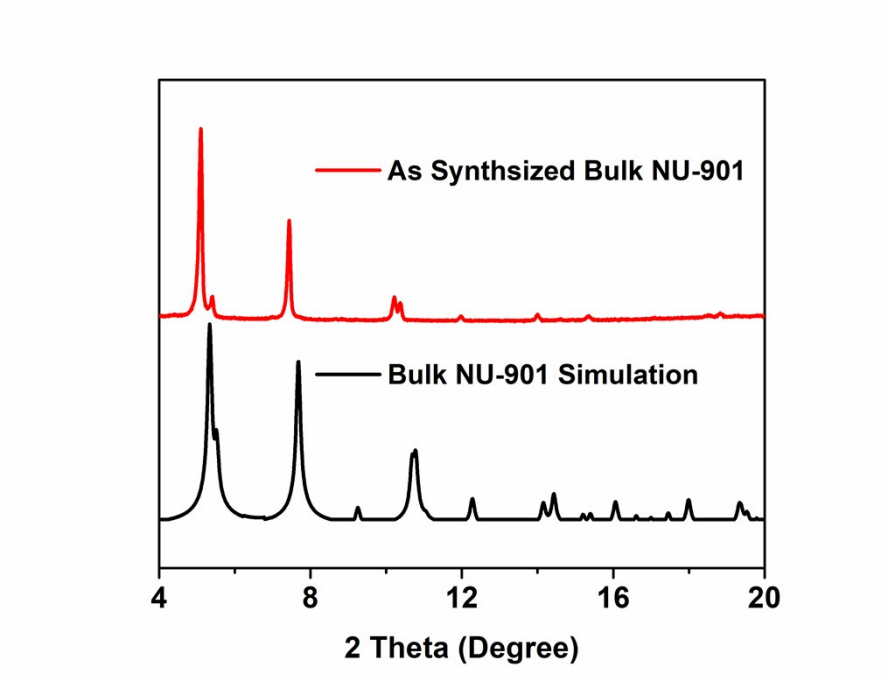

Figure S10. PXRD patterns of bulk NU-901.

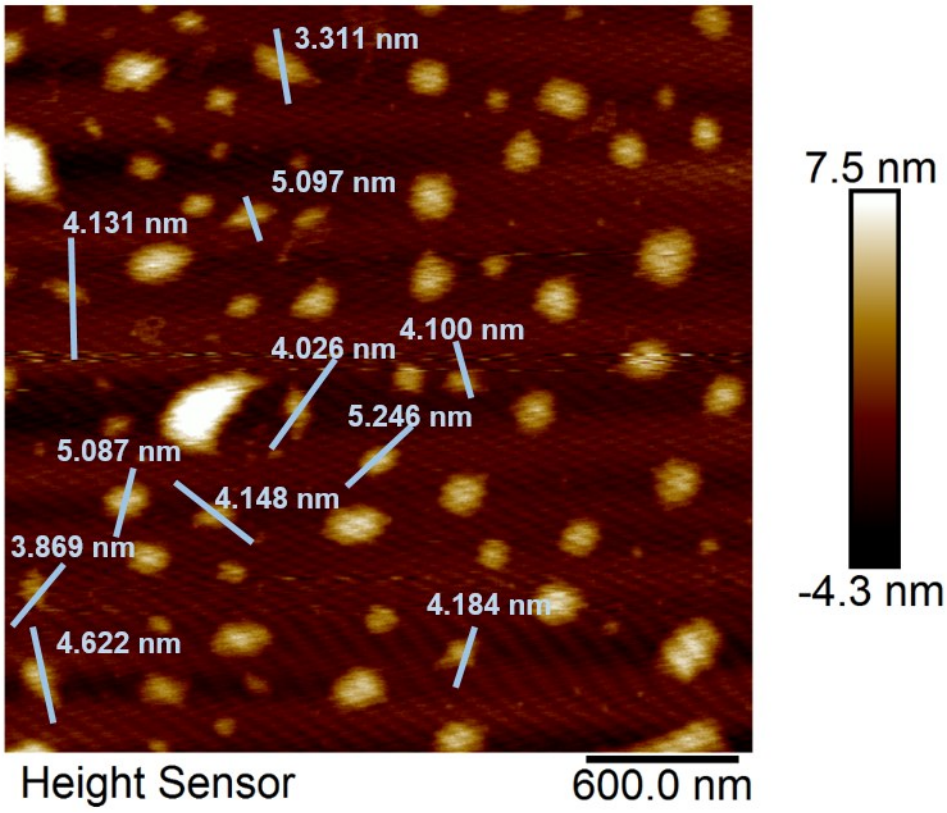

Figure S11. AFM images of NU-901-NS. Because of the ultrasonication procedure, the materials are a bit broken.

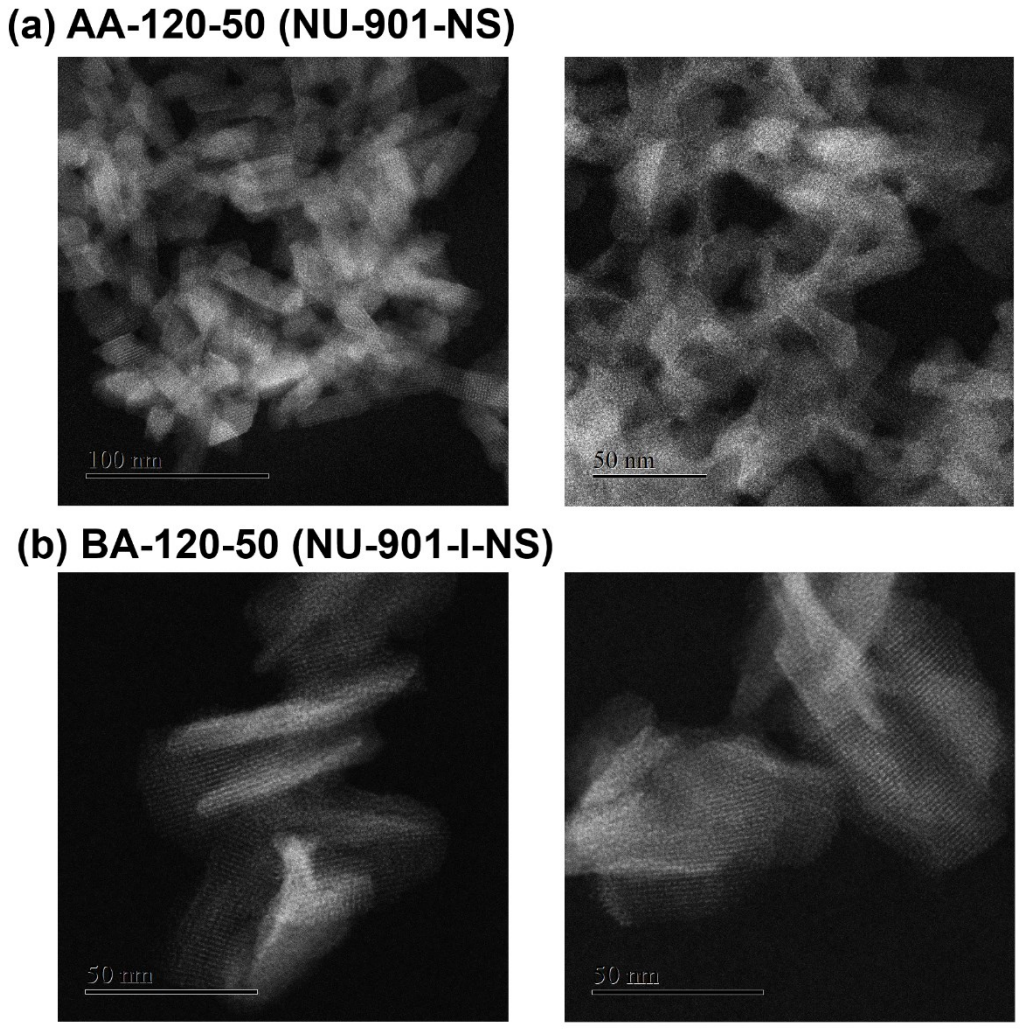

Figure S12. HAADF images of (a) NU-901-NS and (b) NU-901-I-NS.

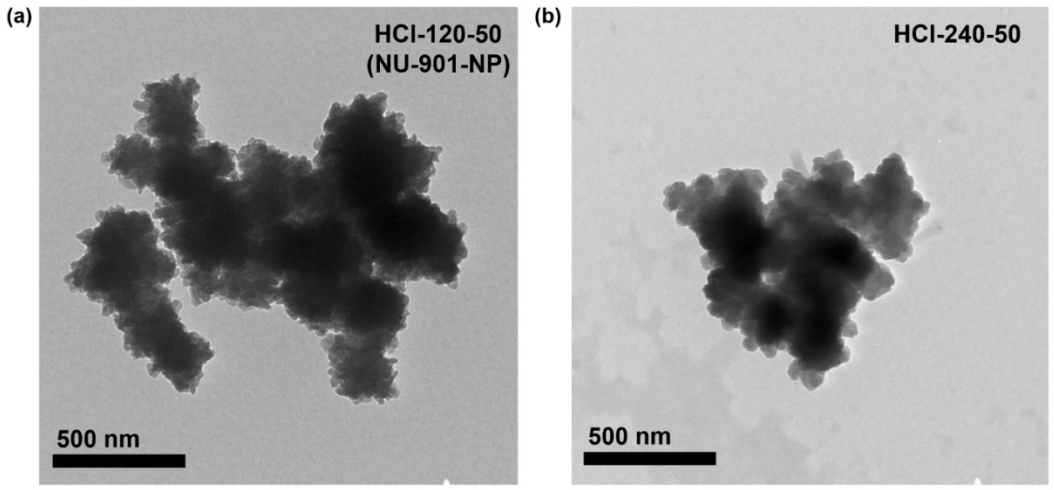

Figure S13. TEM images of (a) HCl-120-50 (NU-901-NP) and (b) HCl-240-50.

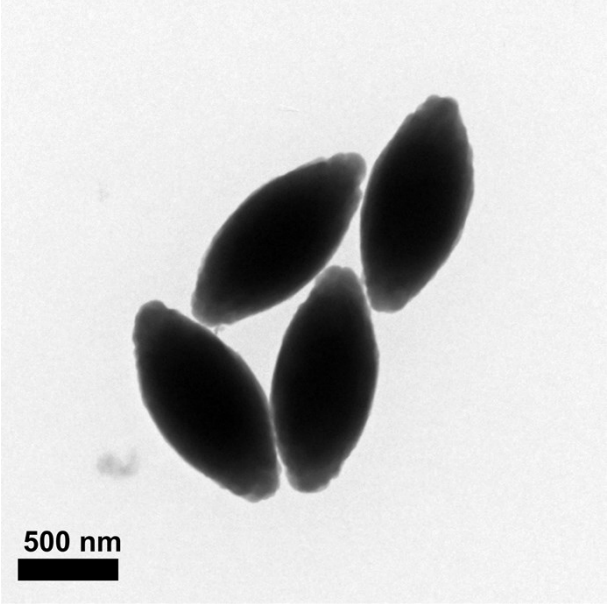

Figure S14. TEM images of bulk NU-901.

Section S4. Fluorescence Spectra of NU-901-NP

Fluorescence spectroscopy was performed on a fluorescence spectrometer (Hitachi F-4600). After the materials were synthesized and washed, before drying, the materials were dispersed into 10 mL acetone. Then, 1 mL of the dispersion was transferred into each of two 10 mL vials, respectively. One of the vials was capped tightly (vial A) and the other vial was allowed to dry under room temperature (vial B). After all the acetone in vial B was volatilized, 1 mL of fresh acetone was added into vial B. Then, the emission spectra of the materials in the two vials were measured, respectively.

Section S5. Coating Methods.

Capillary pretreatment:

A fused silica capillary (15 m long × 0.25 mm i.d., Yongnian Optic Fiber Plant, Hebei, China) was pre-treated according to the following recipe before dynamic coating with the materials: the capillary was washed sequentially with 1 mol/L NaOH for 2 h, ultrapure water for 30 min, 0.1 mol/L HCl for 2 h, ultrapure water again until the outflow reached pH=7.0, and finally MeOH for 30 min. After the above process, the capillary was modified with 3-aminopropyltriethoxysilane (APTES) to provide the amino groups to enhance the interactions with nanosheets on the inner wall of the capillary column. The pretreated capillary was filled with a MeOHic solution of APTES (50%, v/v), and incubated in a 40 ^{o}C water bath overnight with both ends of the capillary sealed. The APTES-modified capillary was rinsed with MeOH to flush out the residuals and dried with a stream of nitrogen at 120 ^{o}C.

Coating the materials:

NU-901 with different morphologies were coated onto the pretreated capillary column by a simple dynamic coating method as follows: 1 mL (2 mg/mL) ethanol suspension of each material was first filled into the capillary column and then pushed through the column at a velocity of 30 cm/min to leave a wet coating layer on the inner wall of the capillary column. After coating, the capillary column was settled for conditioning under nitrogen for 2 h to remove the solvent. Further conditioning of the capillary column was carried out using a temperature program: maintain 30 ^{o}C for 30 min, then ramp to 250 ^{o}C at a rate of 2 ^{o}C/min and keep 250 ^{o}C for 180 min. The temperature program was repeated 3 times.

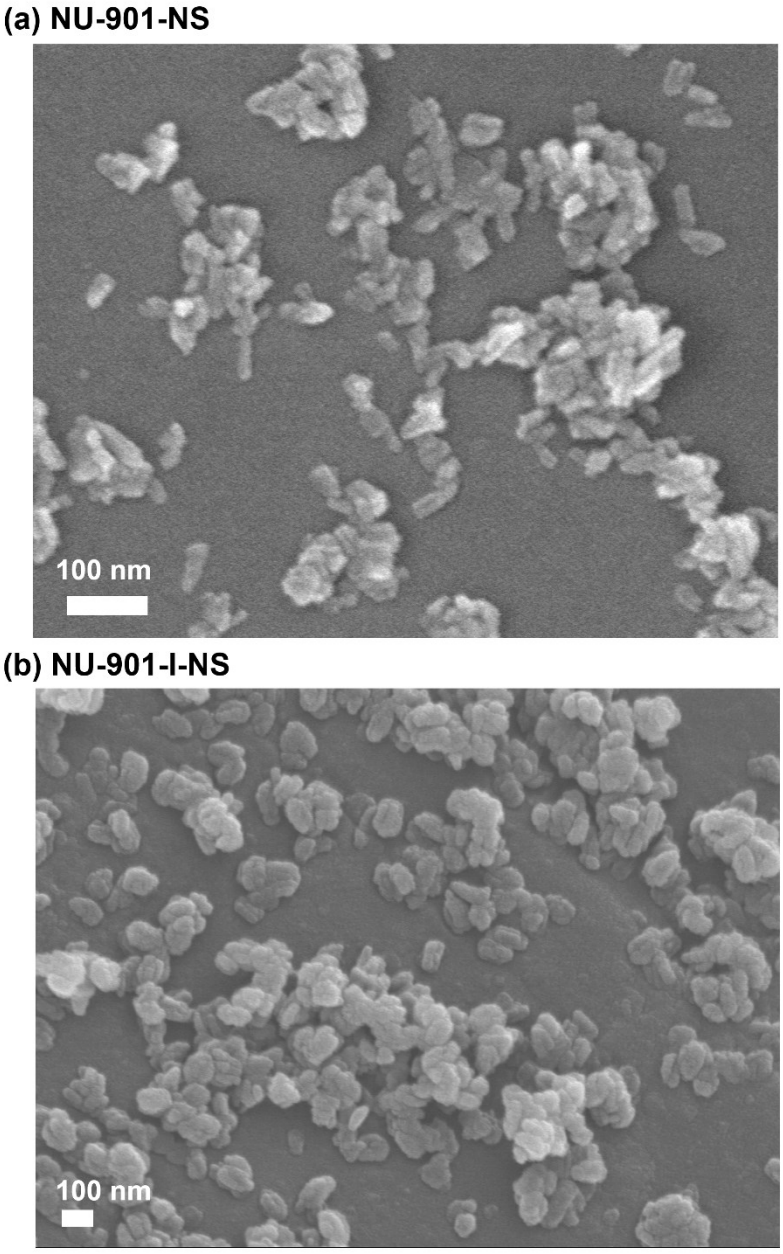

Figure S15. The SEM images of stacked (a) NU-901-NS and (b) NU-901-I-NS coated on the inner wall of capillary columns. The capillary columns coated with materials were cut open. Then, the SEM images were taken from the top-down view of them.

Section S6. TGA Spectrum of the Synthesized Materials

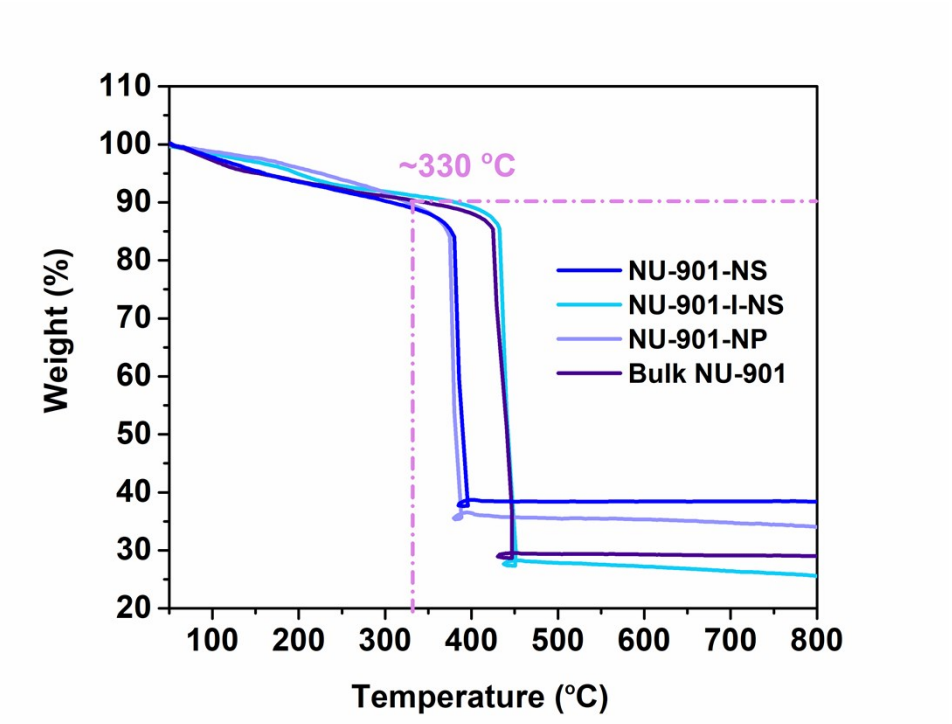

Figure S16. The TGA spectrum of NU-901-NS, NU-901-I-NS, NU-901-NP and bulk NU-901.

Section S7. Coating Quantity.

The coating quantity of each material on the capillary column was calculated. First, the standard cave of NU-901 with different morphologies was measured by detecting the UV absorbance of each material (410 nm) dispersed in MeOH with different concentrations (0, 50, 100, 200 μg/mL). The standard cave was shown in Figure S17. Then, 1 mL of each material (2 mg/mL) was utilized to coat the capillary column. During the coating procedure, the effluent liquid was continually collected and used for UV detection. After calculating the amount of the material in the effluent liquid, the coating quantity of each material on the capillary column could be obtained, respectively.

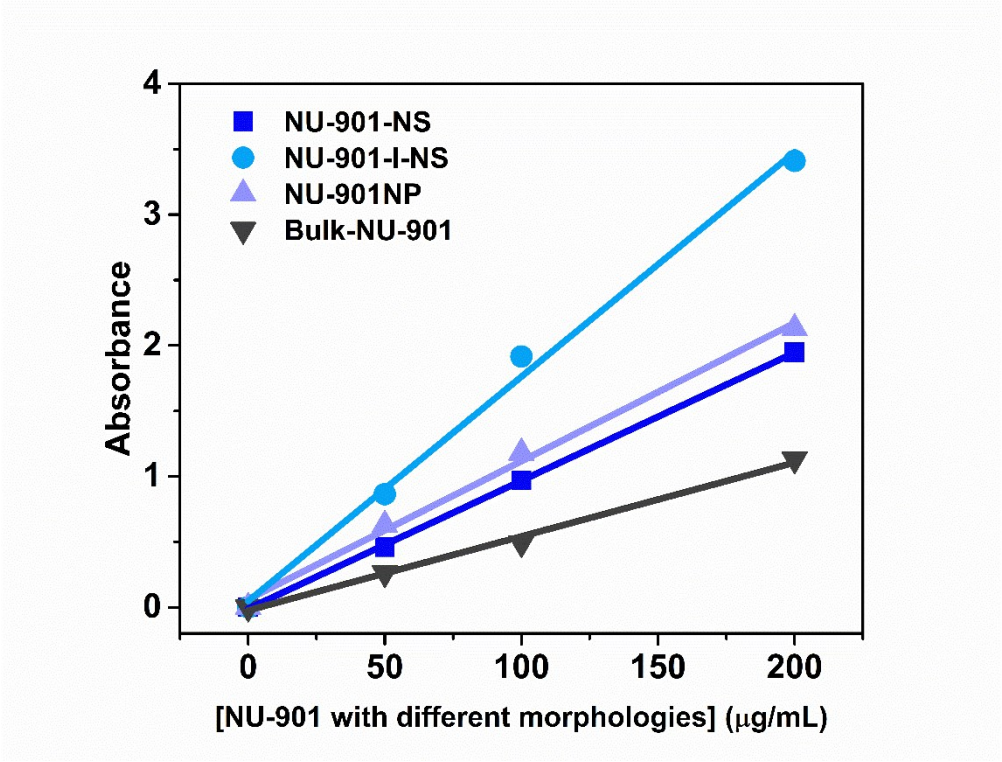

Figure S17. The standard cave of NU-901 with different morphologies with UV detection.

Section S8. Gas Chromatogram for the Separation of Different Analytes.

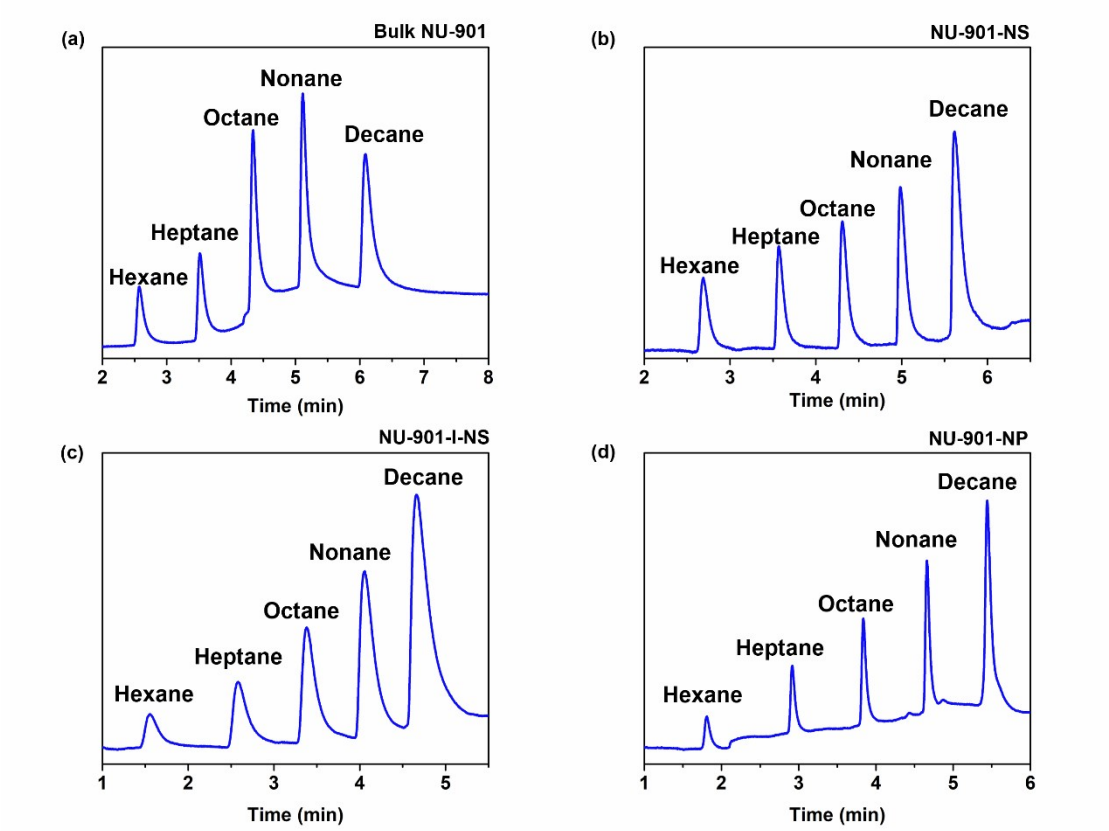

Figure 18. Gas chromatogram on the (a) bulk NU-901, (b) NU-901-NS, (c) NU-901-I-NS and (d) NU-901-NP coated columns for the separation of linear alkanes from C_6H_{14} to $C_{10}H_{22}$.

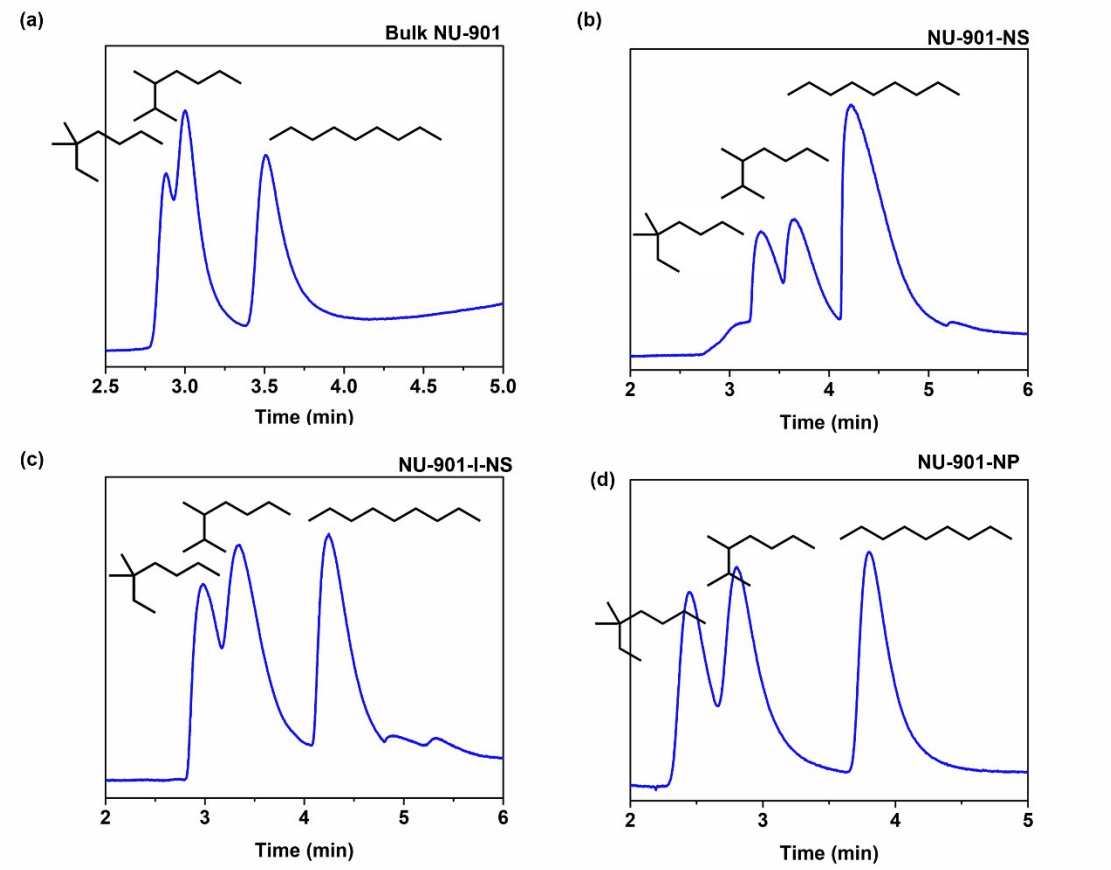

Figure 19. Gas chromatogram on the(a) bulk NU-901, (b) NU-901-NS, (c) NU-901-I-NS and (d) NU-901-NP coated columns for the separation of C_9H_{20} isomers.

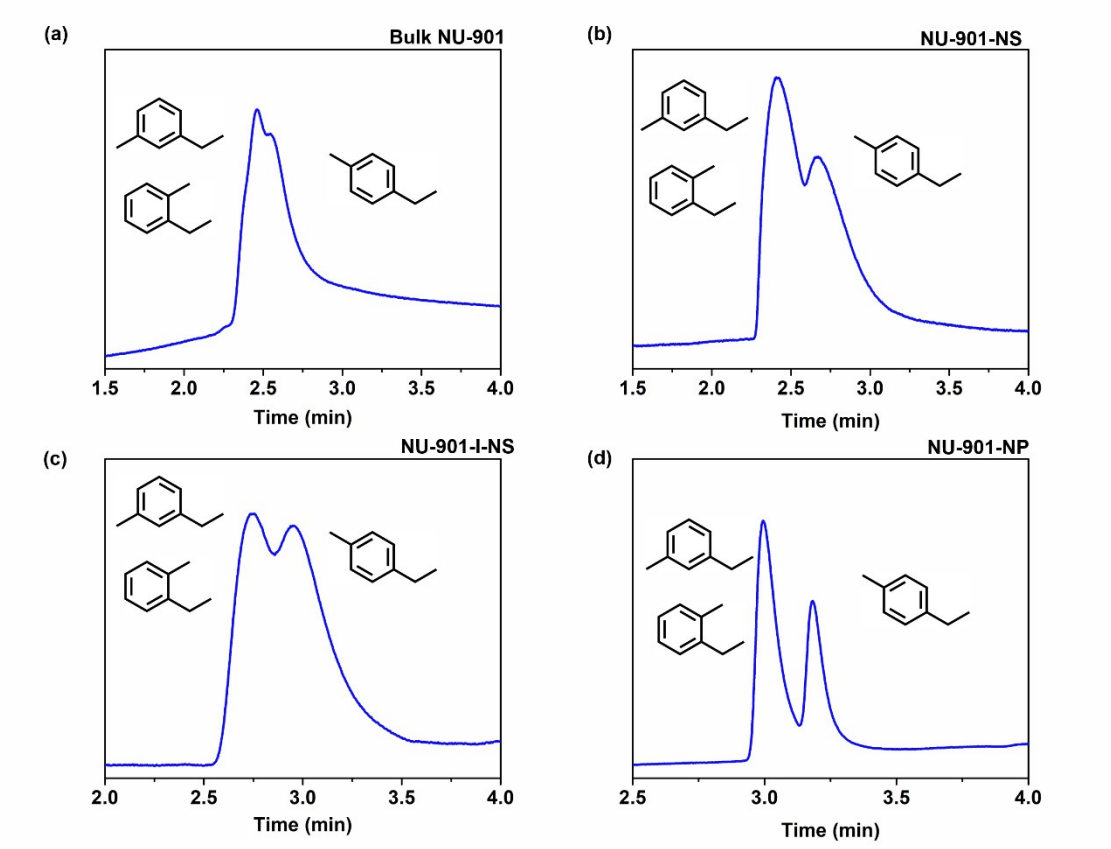

Figure 20. Gas chromatogram on the (a) bulk NU-901, (b) NU-901-NS, (c) NU-901-I-NS and (d) NU-901-NP coated columns for the separation of ethyltoluene isomers.

Table S2. Separation resolution (Rs) for different isomers on the NU-901-coated capillary columns for different NU-901 morphologies.

	Bulk NU-901	NU-901-NS	NU-901-I-NS	NU-901-NP
Rs (2,4-dimethylhexane/3-methyl heptane)	0.39	0.53	0.68	0.87
Rs (2,4-dimethylhexane/n-octane)	0.86	1.96	1.92	2.30
Rs (3-methyl heptane/n-octane)	0.45	1.10	1.15	1.13
Rs (3,3-dimethylheptane/2,3-dimethylheptane)	0.26	0.48	0.50	0.91
Rs (3,3-dimethylheptane/n-nonane)	0.99	2.43	2.46	2.87
Rs (2,3-dimethylheptane /n-nonane)	0.82	1.64	1.77	1.80
Rs (o-chlorotoluene/m-chlorotoluene)	0.00	0.53	0.00	0.53
Rs (o-chlorotoluene/p-chlorotoluene)	0.56	0.85	0.56	1.00
Rs (m-chlorotoluene/p-chlorotoluene)	0.42	0.45	0.27	0.63
Rs (2-ethyltoluene /4-ethyltoluene)	0.20	0.60	0.49	0.91
Rs (3- ethyltoluene /4-ethyltoluene)	0.20	0.60	0.49	0.91

Reference

1. T. C. Wang, N. A. Vermeulen, I. S. Kim, A. B. F. Martinson, J. F. Stoddart, J. T. Hupp and O. K. Farha, *Nat. Protoc.*, 2016, **11**, 149-162.
2. P. Deria, J. Yu, T. Smith and R. P. Balaraman, *J. Am. Chem. Soc.*, 2017, **139**, 5973-5983.