

## Supporting information

### Colloidal Tectonics for Tandem Synergistic Pickering Interfacial Catalysis: Oxidative Cleavage of Cyclohexene Oxide into Adipic Acid

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## **Materials and general information.**

Aerosil®200 was generous gift from Evonik Industries AG (Germany). Trimethoxy(propyl)silane (97%), trimethoxy(octyl)silane (97%) and (3-mercaptopropyl)trimethoxysilane (95%) were purchased from ABCR (Germany). Trimethoxy(octadecyl)silane (90%) was purchased from Aldrich (USA). Amberlite IRA-400 (Cl<sup>-</sup>) ion exchange resin and dodecyl trimethylammonium bromide (99%) were purchased from Alfa Aesar (USA). Tungstophosphoric acid (> 99%) were purchased from Acros (USA). Cyclohexene oxide (98%) was purchased from TCI (Japan) and hydrogen peroxide (50%) from VWR International (France). All other reagents were purchased from Aldrich (USA) with the highest purity. DMSO-d<sub>6</sub> (99.8%) and CDCl<sub>3</sub> (99.8%) were purchased from Euriso-top (France). All other chemical were purchased from Sigma-Aldrich and used without further purification. The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded using an Advance 300 Bruker spectrometer at 300.13, 75.49 and 121.49 MHz respectively. Chemical shifts were given in ppm (δ) and measured relative to residual solvent for <sup>1</sup>H and <sup>13</sup>C, and to an external reference (H<sub>3</sub>PO<sub>4</sub>) for <sup>31</sup>P{<sup>1</sup>H} NMR. Fourier transform infrared spectroscopy (FTIR) was carried out with a IRTracer-100 FTIR (equipped with an attenuated total reflector (MiRacle 10, Shimadzu, Japan). For centrifugation, a Sigma 2-16PK apparatus was used. Elemental analysis was carried out by inductively coupled plasma (ICP-AES) on a LECO CHNS-932 analyzer. For all experiments, the Millipore water (18.2 MΩ/cm; Simplicity 185) was used. All the catalytic tests were conducted in a thermostated water bath. The temperature was stabilized with a thermoregulated Lauda RC6 bath and was estimated to be better than ±0.05 °C. All the experiments were preformed at least three times to ensure repeatability.

**Synthesis of tri(dodecyltrimethylammonium) phosphotungstate nanoparticles ([C<sub>12</sub>]<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>]).**

Dodecyltrimethylammonium bromide [C<sub>12</sub>][Br] (19.5 mmol) was dissolved in water (100 mL). An aqueous solution of [C<sub>12</sub>][Br] was eluted on an hydroxide ion exchange resin to obtain an aqueous solution of [C<sub>12</sub>][OH]. The aqueous solution of H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] (around 6.5 mmol, 10<sup>-4</sup> M) was added dropwise (3 mL/min) to the aqueous [C<sub>12</sub>][OH] solution (3 × 10<sup>-4</sup> M) until pH 7 at 25 °C under dry Ar and vigorous magnetic stirring (1,500 rpm). The colorless precipitate of tri(dodecyltrimethylammonium) phosphotungstate formed within a few minutes was washed with water and lyophilized (Yield: 99%).

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, 20 °C, TMS): δ (ppm) = 0.82-0.89 (m, 3H; CH<sub>3</sub>), 1.18-1.31 (m, 18H; CH<sub>2</sub>), 1.66 (m, 2H; N-CH<sub>2</sub>-CH<sub>2</sub>), 3.03 (s, 6H; NCH<sub>3</sub>), 3.24 (m, 4H; NCH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>, 20 °C): δ (ppm) = 14.4, 22.5, 22.6, 26.2, 28.9, 29.2, 29.3, 29.4, 29.5, 31.8, 52.6, 65.8. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, DMSO-d<sub>6</sub>, 20 °C): δ (ppm) = -15.6. Anal. Calc. for (C<sub>45</sub>H<sub>102</sub>N<sub>3</sub>; PW<sub>12</sub>O<sub>40</sub>); 2.5(H<sub>2</sub>O): C, 14.98%; H, 2.99%; N, 1.16%; P, 0.86%; W, 61.15%. Found: C, 15.39%; H, 2.99%; N, 1.35%; P, 0.80%; W, 60.79%.

### **Synthesis of alkyl/propylsulfonic acid-grafted silica nanoparticles ( $[C_n/SO_3H]@SiO_2$ ).**

Alkyltrimethoxysilane (with alkyl = propyl, octyl or octadecyl) (10 mmol) and (3-mercaptopropyl)trimethoxysilane (10 mmol) were hydrolyzed in a 100 mL water/ethanol (1/1 v/v) solution (pH = 9.6) at room temperature overnight. The mixture was added dropwise to a suspension of Aerosil®200 (1 g / 50 mL water / 50 mL ethanol, pH = 9.6). The reaction mixture was stirred for 24 h under reflux. The suspension was cooled down and the product was filtered and washed with ethanol (3 x 30 mL) and acetone (30 mL). The white powder was recovered and dried overnight at 80 °C. The dried powder was grinded and the thiol groups were oxidized using 50% H<sub>2</sub>O<sub>2</sub> (60 mL). Acetonitrile was added dropwise until a homogeneous suspension was obtained (3 to 4 mL). The reaction mixture was stirred at 40 °C for 24 h. The powder was filtered, washed and dried (Yield: 98%).

Anal. Found for ( $[C_3/SO_3H]@SiO_2$ ): C, 16.32%; H, 3.87%; N, 0.84%; S, 5.20%.

Anal. Found for ( $[C_8/SO_3H]@SiO_2$ ): C, 24.83%; H, 4.75%; N, 0.82%; S, 2.69%.

Anal. Found for ( $[C_{18}/SO_3H]@SiO_2$ ): C, 47.63%; H, 8.54%; N, 0.80%; S, 1.75%.

### **Characterization of nanoparticles.**

Elemental analysis was performed using Elementar Vario EL cube (Elementar Analysensysteme GmbH, Germany). Thermogravimetric analysis (TGA) was carried out on a Q50 (TA Instrument, US) by heating the samples from room temperature to 900 °C at a rate of 10 °C/min under air atmosphere (100 mL(STP)/min). The morphology of the modified silica nanoparticles was inspected by high-resolution transmission electron microscopy (HR-TEM) using a JEOL JSM-6360LV microscope operating at 200 kV. The zeta potential of the samples was measured on a Zetasizer (Nano ZS ZEN 3600, Malvern, UK) equipped with a 4.0 mW He-Ne laser light source with a wavelength  $\lambda = 632.8$  nm. The measurements were performed by dispersing the nanoparticles in ethanol at 25 °C. The contact angle of the nanoparticles was measured using the powder compressing method. The NP pellets were prepared with a pellet compressor ( $\approx 2$  g of NPs were compressed at 20 tons for 1 min). Then, the contact angle was measured by DSA 100 (Krüss GmbH, Germany) by depositing a 5  $\mu$ L water drop onto the surface of the pellet. To measure the acidity of NPs, aliquots of 50 mg of the NPs were stirred with NaCl (5.85 g / 20 mL ethanol / 30 mL water) to wet the amphiphilic nanoparticles at room temperature for 24 h. Then, the given solid was filtered off and the resulting solution was titrated with a 0.025 M NaOH solution using a pH-meter (Meterlab PHM250 Ion Analyzer, Radiometer Analytical).

**Emulsions preparation.**

To obtain Pickering emulsions, water (1.5 mL) and oil (1.5 mL) were weighed before adding  $[C_n/SO_3H]@SiO_2$  and  $[C_{12}]_3[PW_{12}O_{40}]$  (50 mg each, 3.6 wt.%). The emulsification was performed using Ultraturrax T10 basic at 20 °C and 11,500 rpm during 60 s (IKA Works, Inc., Germany) in a 5 mL sealed container. To destabilize the emulsion, the emulsion was centrifuged at 4,000 rpm for 20 min.

### **Emulsion characterization.**

The type of emulsion was inferred by observing the evolution of a drop of each emulsion when a volume of either oil or water was added (dilution test). Microphotographs were taken using a light microscope Standard 25 ICS (Carl Zeiss AG, Germany) coupled with a camera Axiocam ERc-5s (Carl Zeiss AG, Germany). The emulsions were diluted with the continuous phase before observation and several photographs from different locations of the emulsion drop were taken to represent the general view of the whole emulsion droplets. The images were analyzed with ImageJ software (National Institutes of Health, USA) to measure the droplet diameter. The distribution function (log-normal) of droplet diameters was obtained by treatment of at least 250 individual measurements of droplet diameters in the microphotographs using OriginPro 8® (USA)

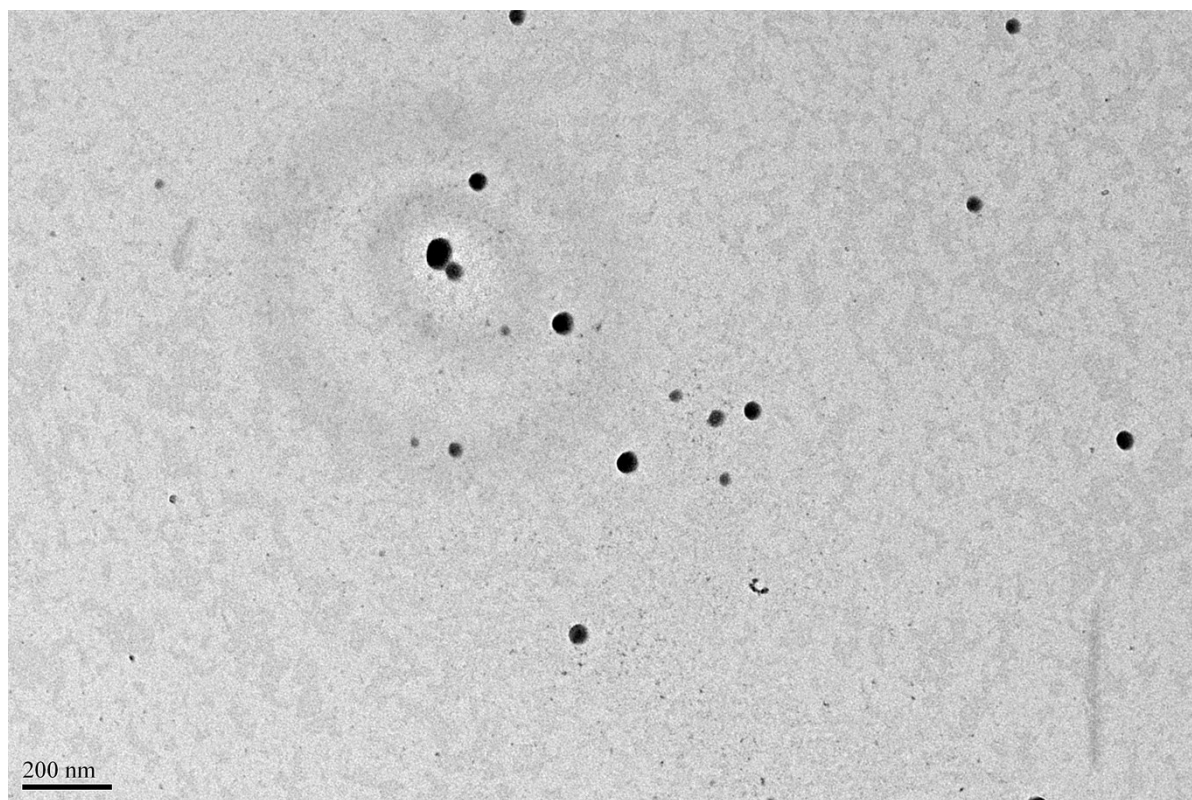
$$y = \frac{A}{\sqrt{2\pi\omega d}} \exp \frac{-\left(\ln \frac{d}{d_m}\right)^2}{2\omega^2}$$

where  $y$  is the probability for having particles of diameter ( $d$ ),  $\omega$  is an asymmetric factor (i.e. measure of width), the peak will be approximately symmetric when  $\omega$  is small,  $d_m$  is the median droplet diameter ( $d_m$  corresponds to the peak center when the log-normal is approximately symmetric), and  $A$  is the amplitude and corresponds to the area under the curve. The  $d_m$ ,  $\omega$ , and  $A$  parameters represent the size distribution of droplets in the corresponding emulsion. The stability was examined by the change in emulsion volume fraction as a function of storage time at 20 °C.

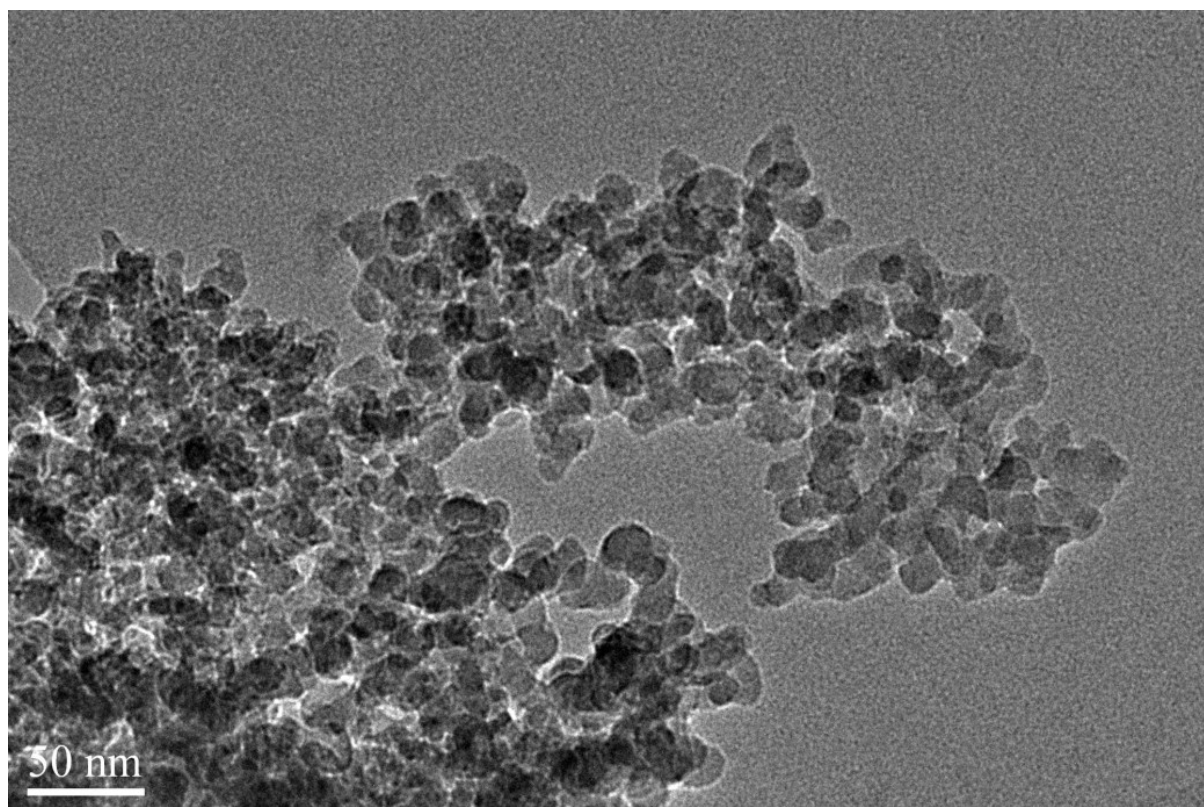
### Typical catalytic experiments.

Toluene (1.5 mL) containing cyclohexene epoxide (0.5 mol/L) and water (1.5 mL) containing 3.5 equiv. H<sub>2</sub>O<sub>2</sub> (5.25 mmol, 50%) was added into a 5 mL container before adding [C<sub>n</sub>/SO<sub>3</sub>H]@SiO<sub>2</sub> (50 mg) and [C<sub>12</sub>]<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] nanoparticles (50 mg). The system was pre emulsified with Ultra-Turrax<sup>®</sup> (IKA T 25) at 11,500 rpm for 2 min. The reactor was sealed, stirred at 500 rpm and heated at 80 °C. The reaction medium was sampled during the reaction for <sup>1</sup>H NMR analyses of the organic and water phases after decantation. CDCl<sub>3</sub> was used as deuterated solvent whereas *n*-dodecane was used as internal standard for the analysis of the organic phase. The aqueous phase was diluted in deuterated DMSO using *n*-dodecanol as internal standard. The results presented are the average of at least 3 runs under each set of conditions. After the reaction, the emulsion was broken by centrifugation at 4,000 rpm for 20 min. The system was then washed with ethanol (3 × 5 mL) and then analyzed by NMR after solvent evaporation. For the recycling of the catalytic system, mixed catalytic NPs were dried and a new batch of fresh cyclohexene oxide (1.5 mmol) in toluene (1.5 mL), as well as H<sub>2</sub>O<sub>2</sub> (5.25 mmol) in water (1.5 mL), were added to the NPs.

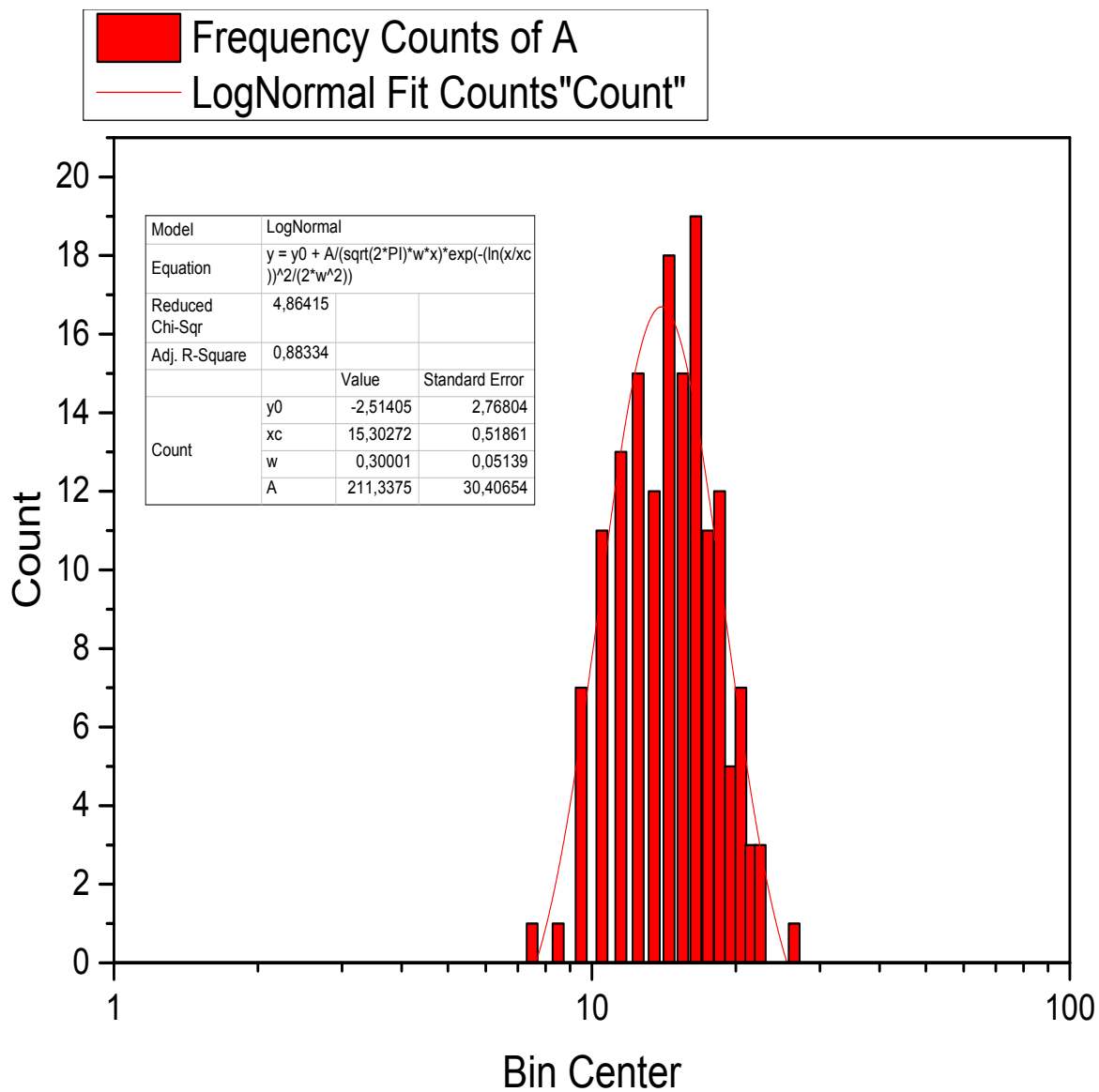




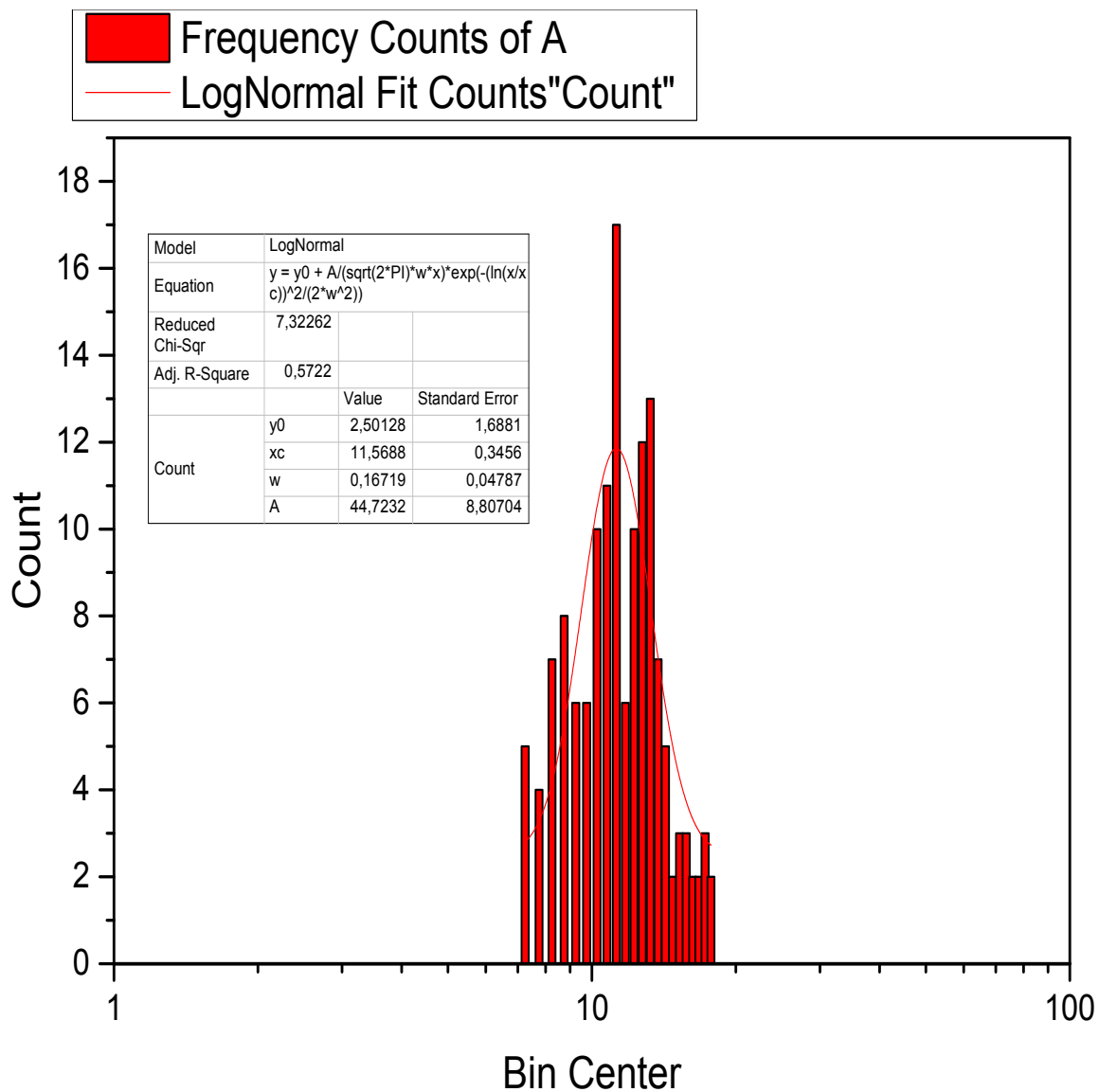
**Figure S1.** TEM micrographs of  $[C_{12}]_3[PW_{12}O_{40}]$  NPs.



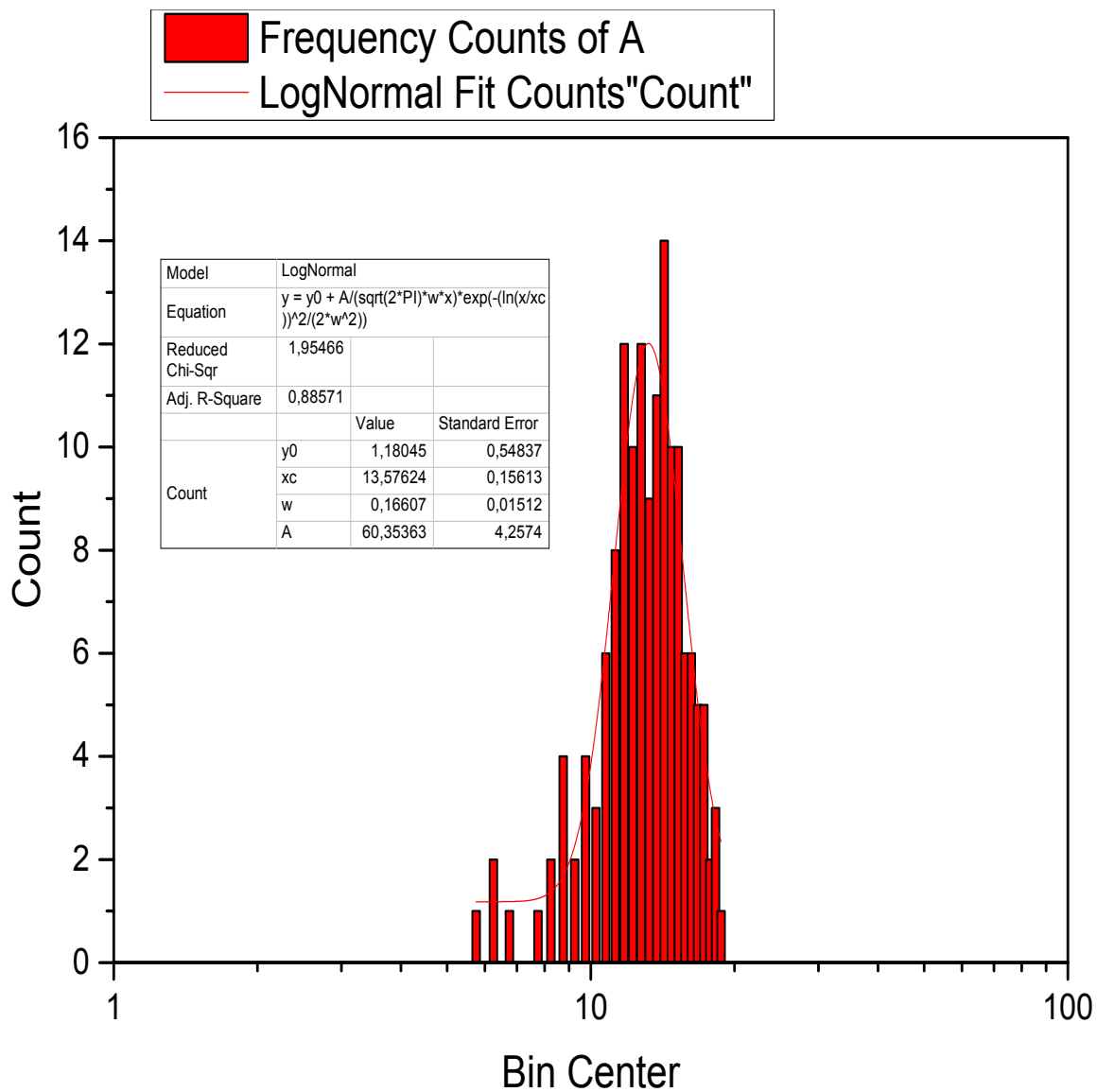
**Figure S2.** TEM micrographs of  $[C_{18}/SO_3H]@SiO_2$  NPs.



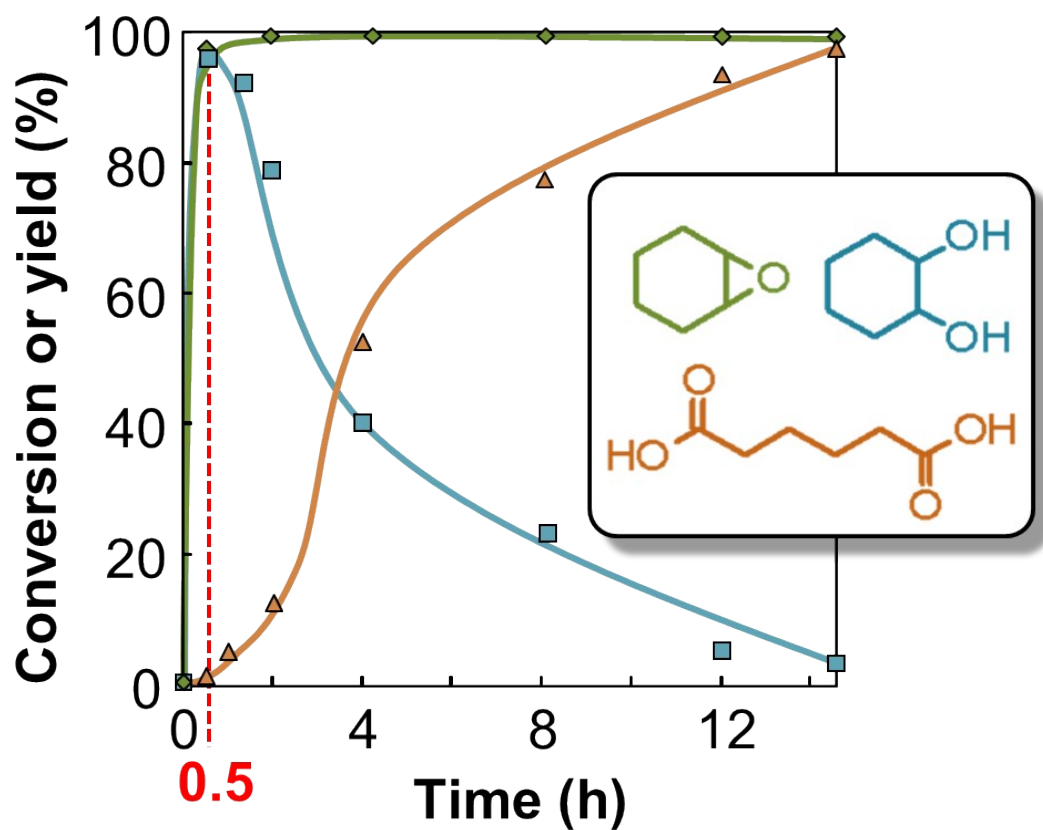
**Figure S3.** Size distribution profile of [C<sub>3</sub>/SO<sub>3</sub>H]@SiO<sub>2</sub> NPs based on TEM micrographs.



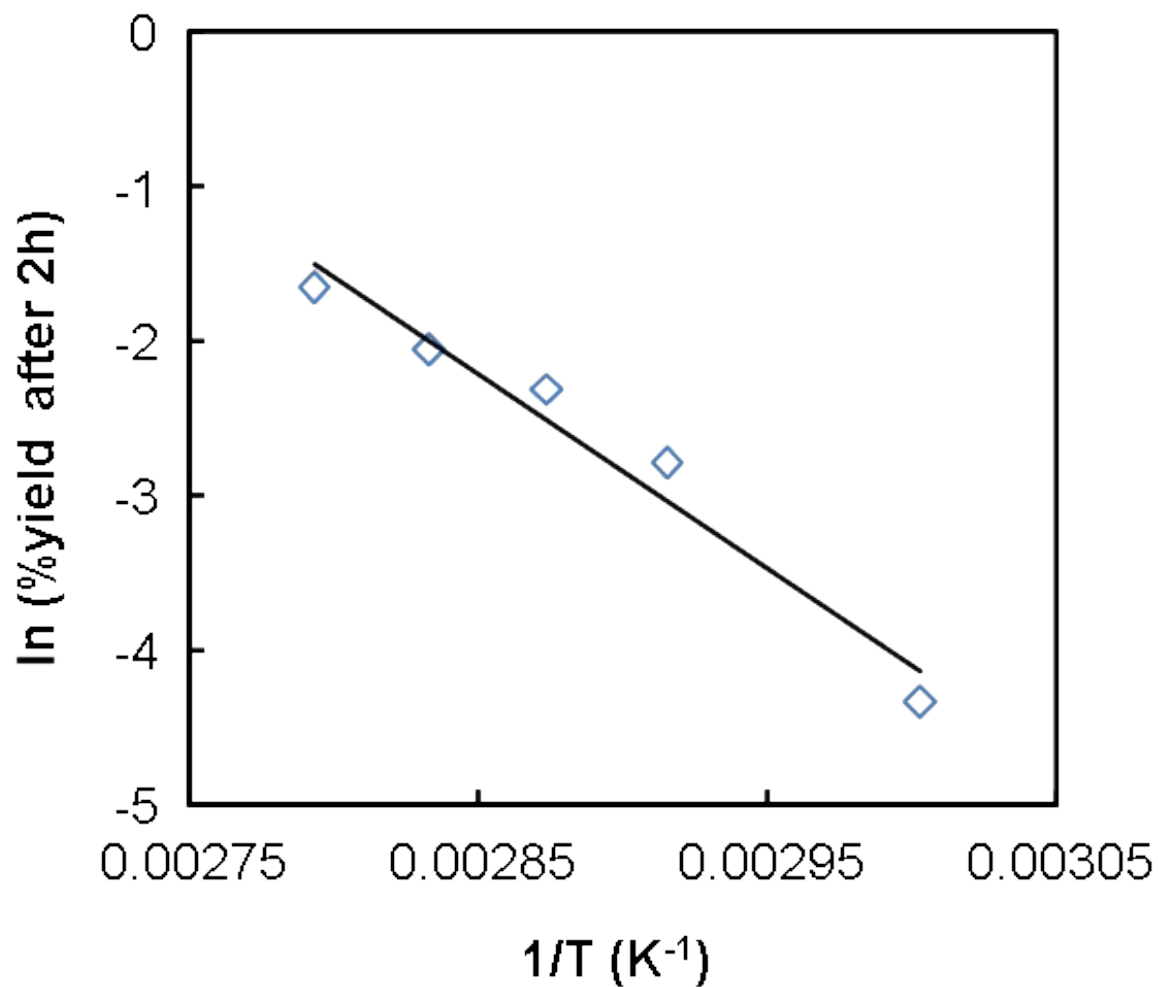
**Figure S4.** Size distribution profile of [C<sub>8</sub>/SO<sub>3</sub>H]@SiO<sub>2</sub> NPs based on TEM micrographs.



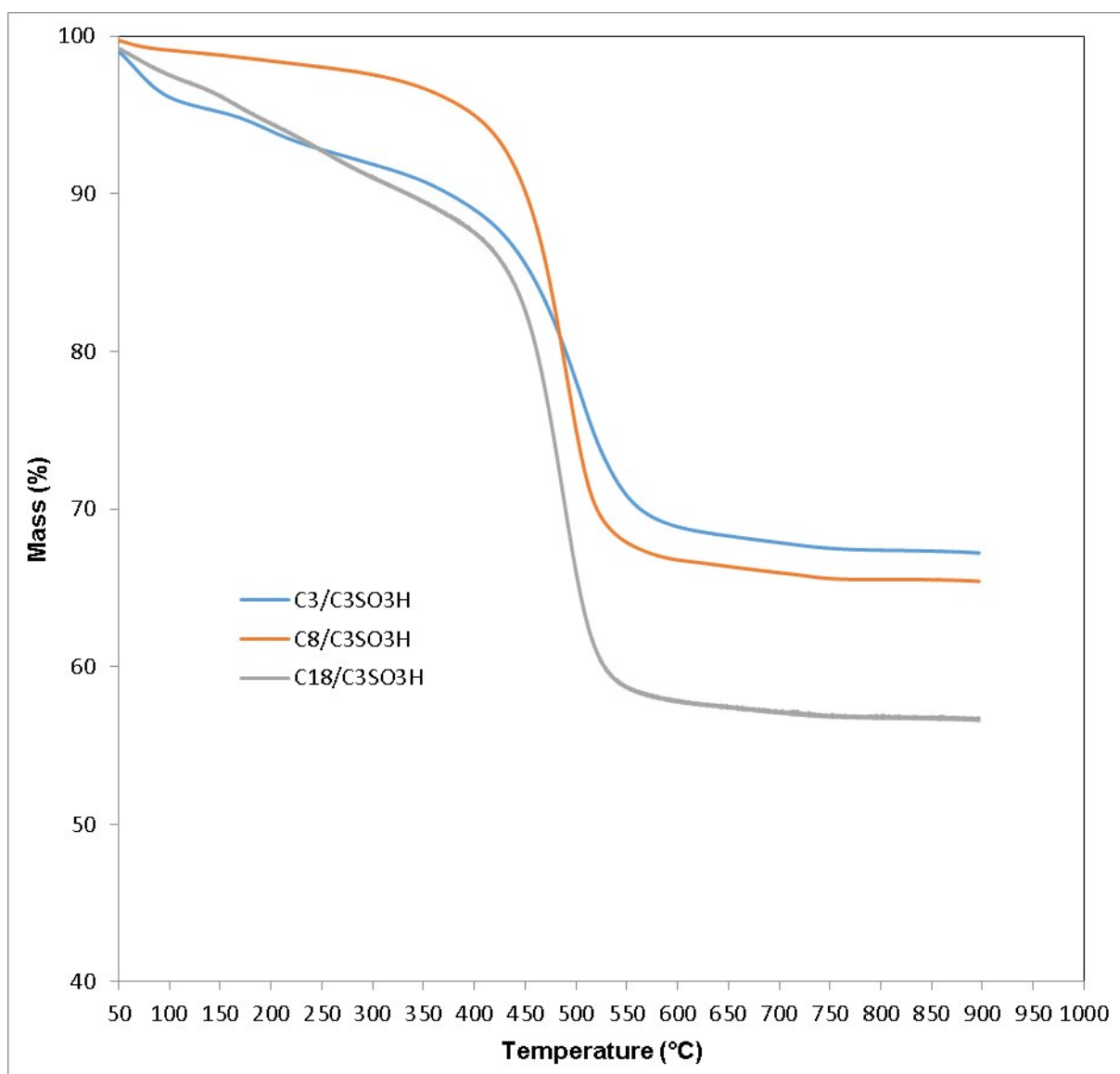
**Figure S5.** Size distribution profile of [C<sub>18</sub>/SO<sub>3</sub>H]@SiO<sub>2</sub> NPs based on TEM micrographs.



**Figure S6.** Reaction profiles for the conversion of cyclohexene oxide to adipic acid in a water/toluene Pickering emulsion stabilized by  $[C_{18}/SO_3H]@SiO_2/[C_{12}]_3[PW_{12}O_{40}]$  mixtures (3.6 wt.%,  $H_2O = 1.5$  mL, toluene = 1.5 mL, cyclohexene oxide = 1.5 mmol,  $H_2O_2 = 5.25$  mmol, 80 °C, 500 rpm).



**Figure S7.** Arrhenius plot for oxidative cleavage of cyclohexene oxide in water/toluene Pickering emulsion stabilized by  $[C_{18}/SO_3H]@SiO_2/[C_{12}]_3[PW_{12}O_{40}]$  mixtures (3.6 wt.%,  $H_2O$  = 1.5 mL, toluene = 1.5 mL, cyclohexene oxide = 1.5 mmol,  $H_2O_2$  = 5.25 mmol, 500 rpm). The straight line is calculated from Arrhenius equation.



**Figure S8.** Thermogravimetric analysis of  $[C_n/SO_3H]@SiO_2$  NPs.