Supplementary Information

Effect of Carboxylic Acid on Micelles of an Neutral Amphiphilic Dendro-Calix[4]arene

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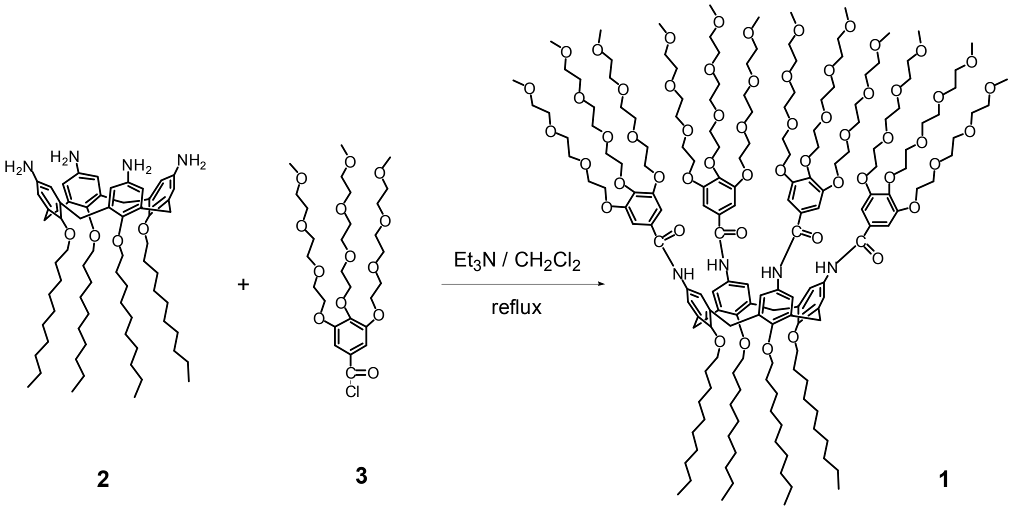
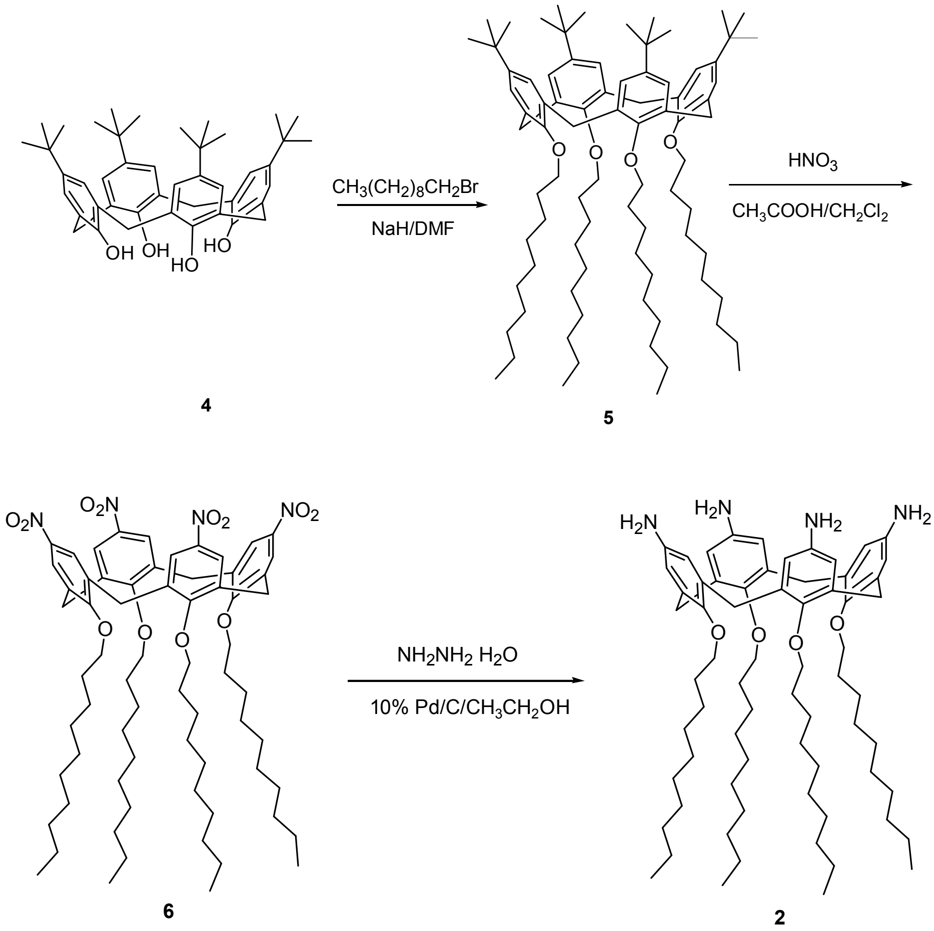
Synthesis of amphiphilic calixarene 1



2 3 1

Synthesis of 2 (*Langmuir*, **2008**, *24*, 8522 – 8526)



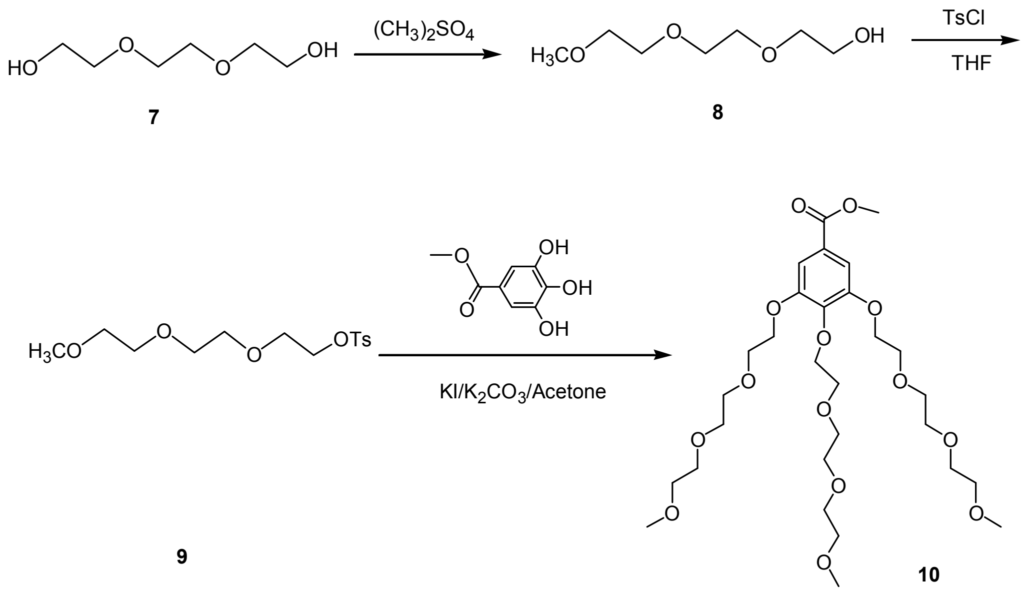
4 5 6 2

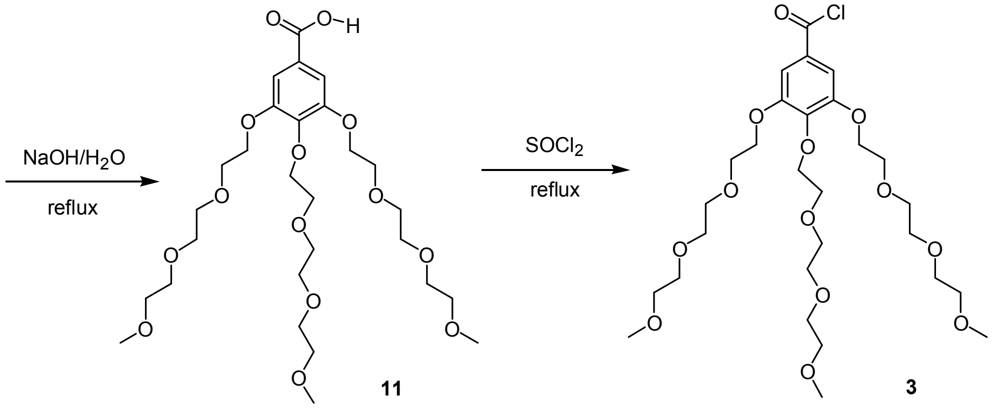
Compound **5**: To a 250mL flask was added **4** (3.0 g, 4.6 mmol), sodium hydride (80% in mineral oil, 2.05 g, 68 mmol), dried DMF (140 mL). After the mixture was stirring for 0.5 h, 1-bromodecane (8.9 g, 40.5 mmol) was added. Upon finished addition, the mixture was stirred at 85 ^{o}C for about 4h. Then methanol and water were carefully added to decompose the remained sodium hydride after the reaction mixture was cooled with an ice bath. The crude product was collected by filtering and was washed three times with water and methanol respectively. The solid was dissolved in chloroform and the solution was evaporated to dryness to remove the remained 1-bromodecane. The resultant solid was recrystallized from methanol to give white powder (3.0 g, 54%).

Compound **6**: To a flask was added **5** (3.0 g, 2.5 mmol), dichloromethane (190 mL), acetic acid (25 mL). After the mixture was cooled to 0 ^{o}C, concentrated nitric acid was slowly dropped into the solution. The solution was continued to stir for 0.5 h at 0 ^{o}C. Then it was heated to room temperature and stirred until the color of the solution turned into yellow. Water (100 mL) was added, and the separated organic phase was washed two times by water (2×130 mL). Upon dried over anhydrous sodium sulfate and filtered, the filtrate was evaporated to dryness. The resultant solid was washed two times by methanol and then by water to give yellow powder (2.5 g, 86%).

Compound **2**: To a flask was added **6** (2.0 g, 1.7 mmol), ethanol (50 mL), 10% Pd/C (0.2 g, 0.19 mmol), hydrazine hydrate (2.5 mL, 51 mmol). The mixture was refluxed for about 4h. After cooled to room temperature, the mixture was filtered through a layer of celite. The filtrate was evaporated to dryness by a rotary evaporator and the residue was recrystallized from ethanol to give white power (1.7 g, 86%).

Synthesis of 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoyl chloride (3,4,5-TMEEE benzoyl chloride) 3. (*J. Am Chem. Soc.*, **2001**, *123*, 6536 – 6542; *Chem. Mater.* **2005**, *17*, 2267 – 2275).





Compound **8**: To a one-neck flask was added triethylene glycol (80 mL, 0.59 mol), sodium hydroxide (8.0 g, 0.2 mol). The mixture was stirred under heating until it turned into viscous liquid. Then dimethyl sulfate (20 mL, 0.20 mol) was slowly added by dropping. The solution was heated at 120 °C for about 4 h under stirring. The color of the solution became deeper during heating. Upon cooled to room temperature, water (50 mL) was added. The aqueous phase was extracted three times with dichloromethane. After the combined organic phase was dried over anhydrous $MgSO_4$ and filtered, the low boiling point solvent was removed by a rotary evaporator. The concentrated liquid was distillated in vacuum to give methyl triethylene glycol monoether **8** (19.5 g, 59%).

Compound **9**: To a 100 mL flask was added **8** (6.3 g, 38 mmol), sodium hydroxide (2.2 g, 55 mmol), THF (50 mL), and water (12.5 mL). *p*-Toluenesulfonyl chloride (TsCl, 6.0 g, 32 mmol) in THF (30 mL) was slowly dropped into the mixture at 0 °C, and continued to stir at 0 °C for about 4 h. Then the solvent was evaporated by a rotary evaporator, and the residue was extracted by dichloromethane. The combined organic phase was washed two times with water and brine respectively. Dried over anhydrous sodium sulfate and filtered, the filtrate was evaporated to give a viscous liquid (7.0 g, 69%).

Compound **10**: To a flask was added **9** (21.0 g, 66 mmol), methyl gallate (3.0 g, 16 mmol), potassium iodide (2.1 g, 13 mmol), potassium carbonate (22.6 g, 164 mmol), and acetone (175 mL). The mixture was refluxed for about 7 days. Then the acetone was evaporated and the residue was dissolved in water. The aqueous phase was extracted three times with chloroform. The combined organic phase was dried, filtered and evaporated by rotary evaporator. The residue was subjected to flash column chromatography (silica gel, $CHCl_3/CH_3OH$ 60:1) to give an oil (5.2 g, 52%).

Compound **11**: To a flask was added **10** (1.0 g, 1.6 mmol), sodium hydroxide (0.48 g, 12 mmol), and water (15 mL). The mixture was refluxed for about 4h. After cooled to room temperature, the mixture was adjusted to acidity with diluted hydrochloric acid. The aqueous phase was extracted three times with chloroform. The combined organic phase was dried, filtered and evaporated to give an oil (0.9 g, 92%).

Compound **3**: Compound **11** (1.2 g, 2.0 mmol) was dissolved in thionyl dichloride (5.0 mL, 69 mmol). After the solution was refluxed for about 3h, the thionyl dichloride was removed by a rotary evaporator under reduced pressure. The remained thionyl dichloride in the product was completely taken away by addition and evaporation of dry dichloromethane at least three times to give an oil (1.1 g, 89%).

Supporting Figures

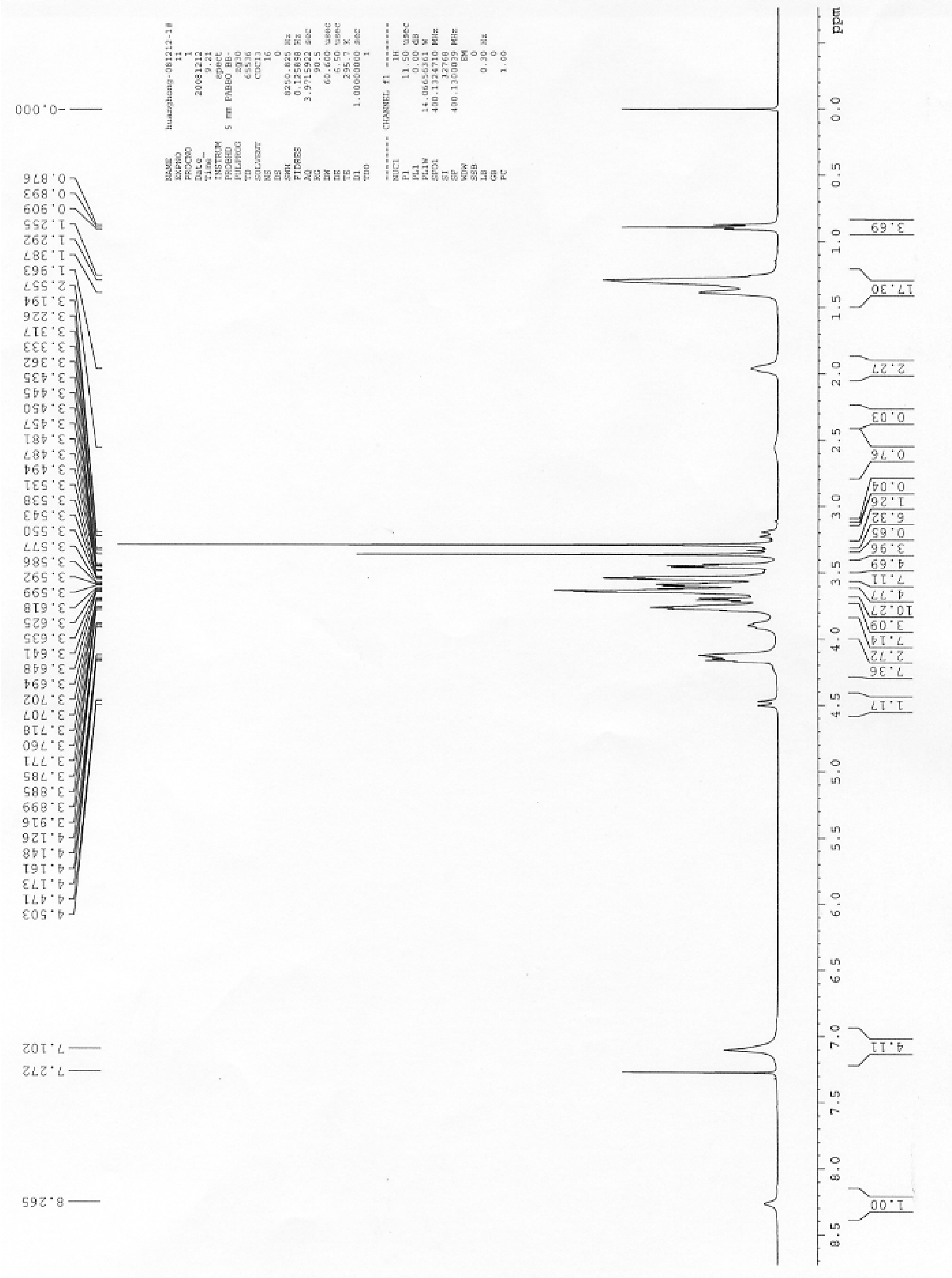


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

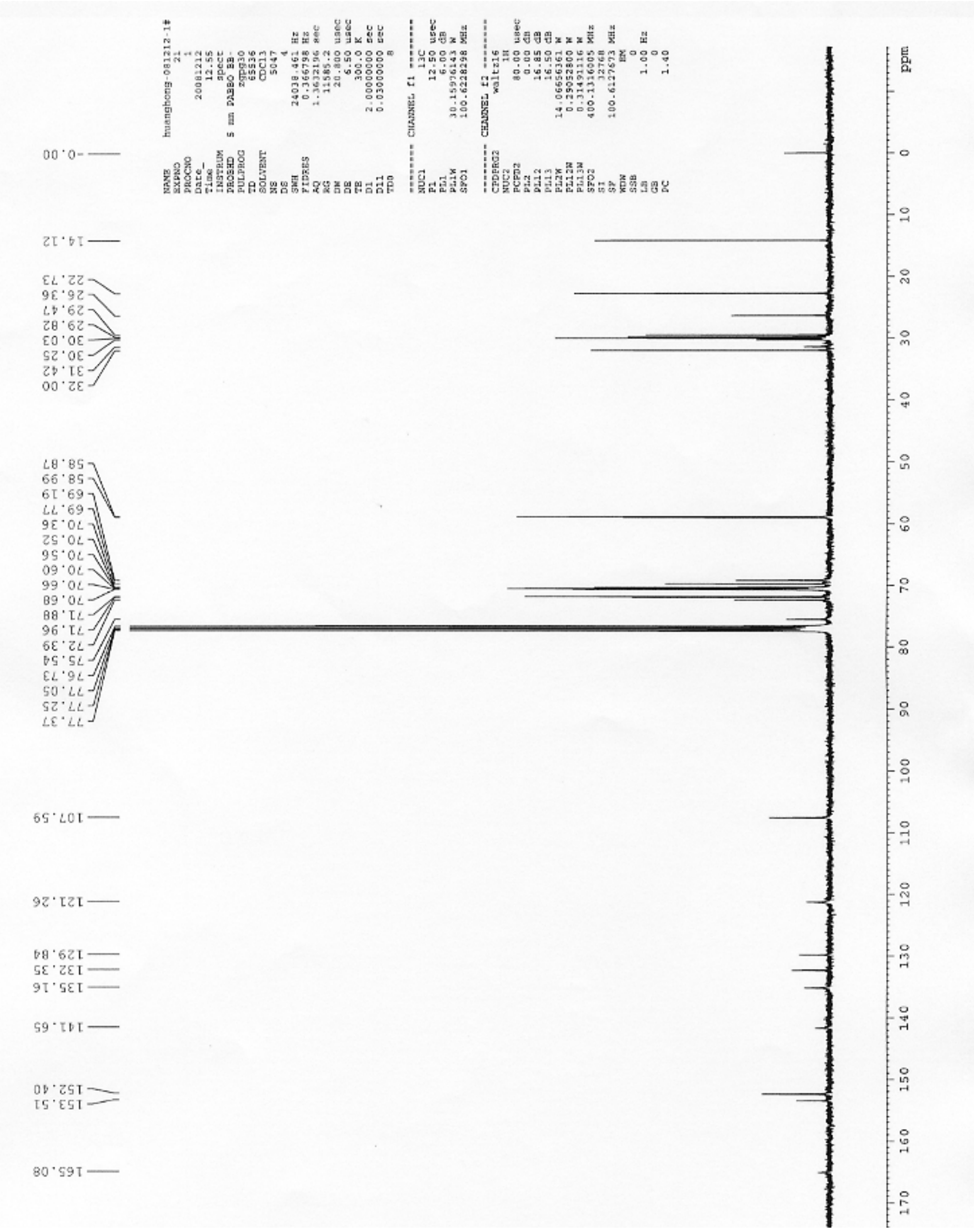


Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

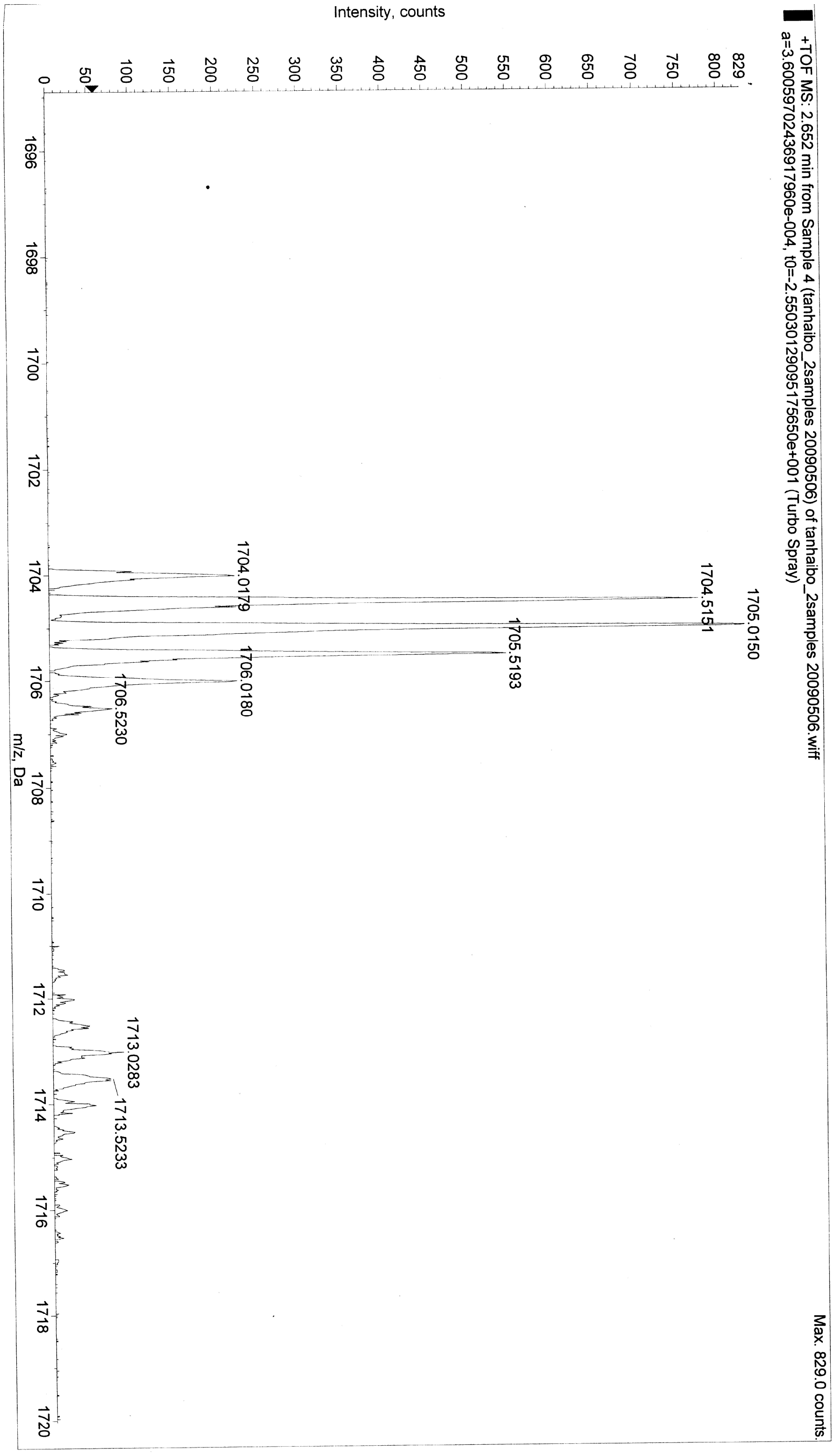


Figure S3. TOF HR Mass spectrum of **1**.

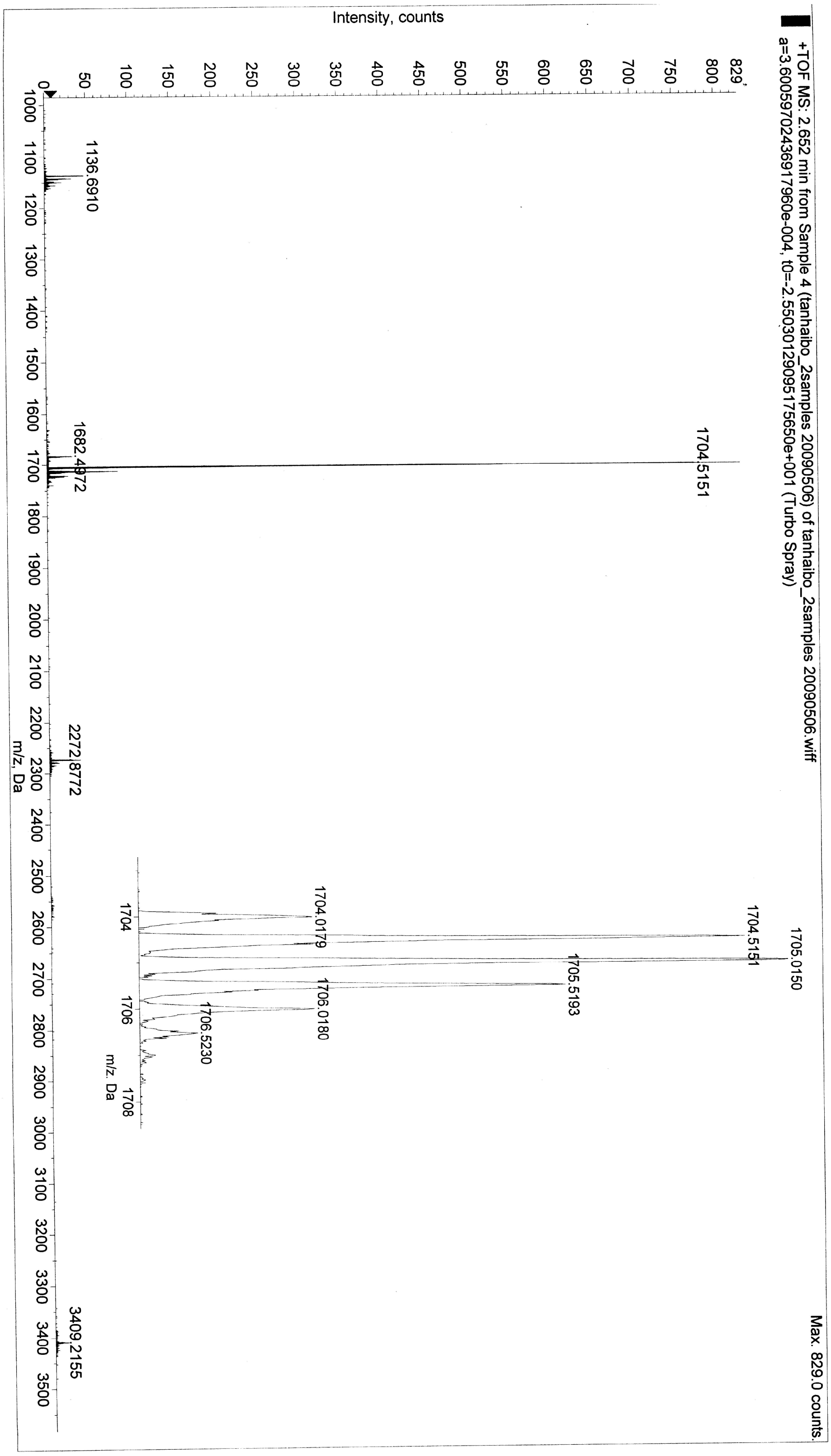


Figure S4. TOF HR Mass spectrum of **1**.

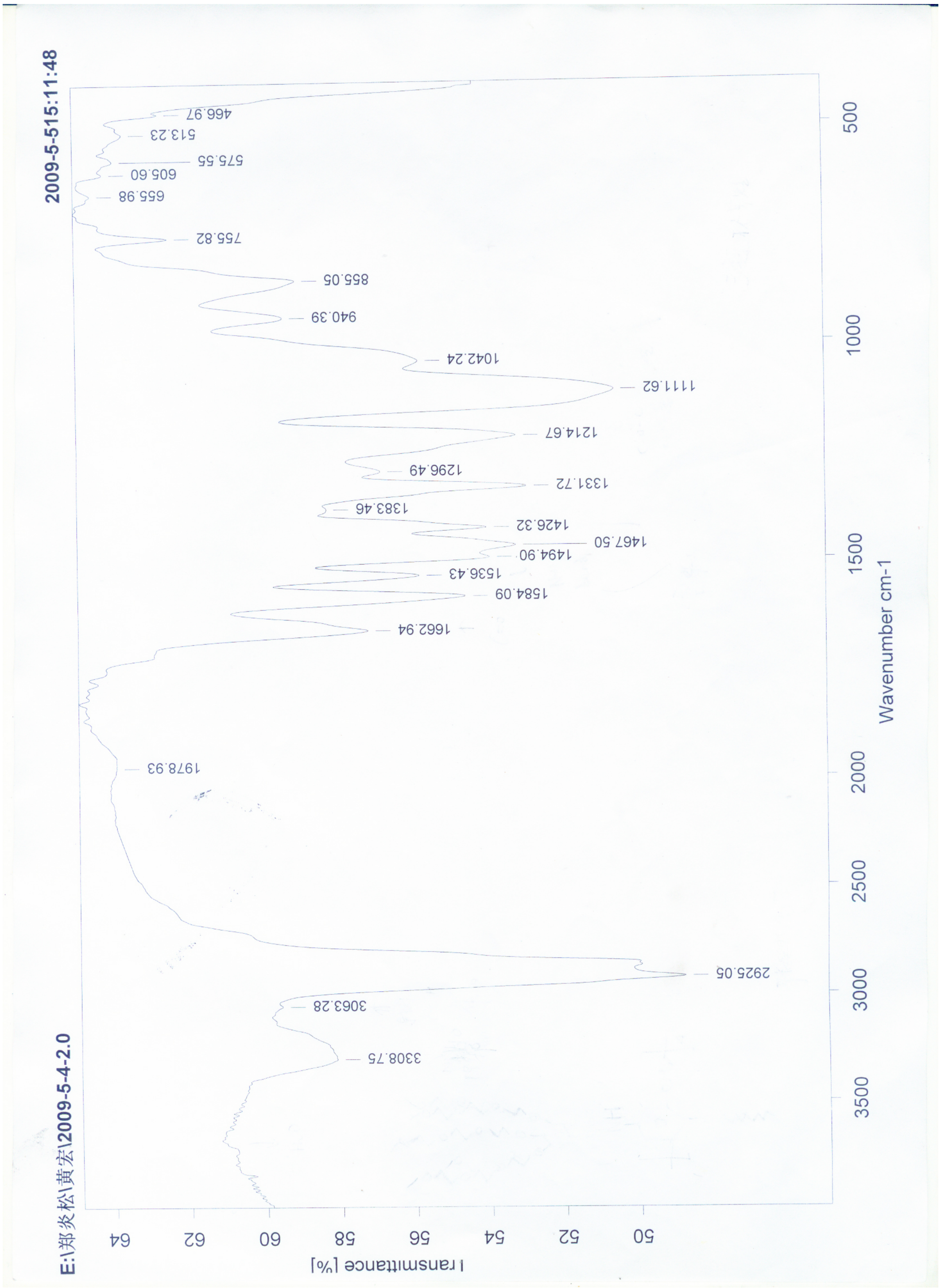


Figure S5. IR spectrum of **1**.

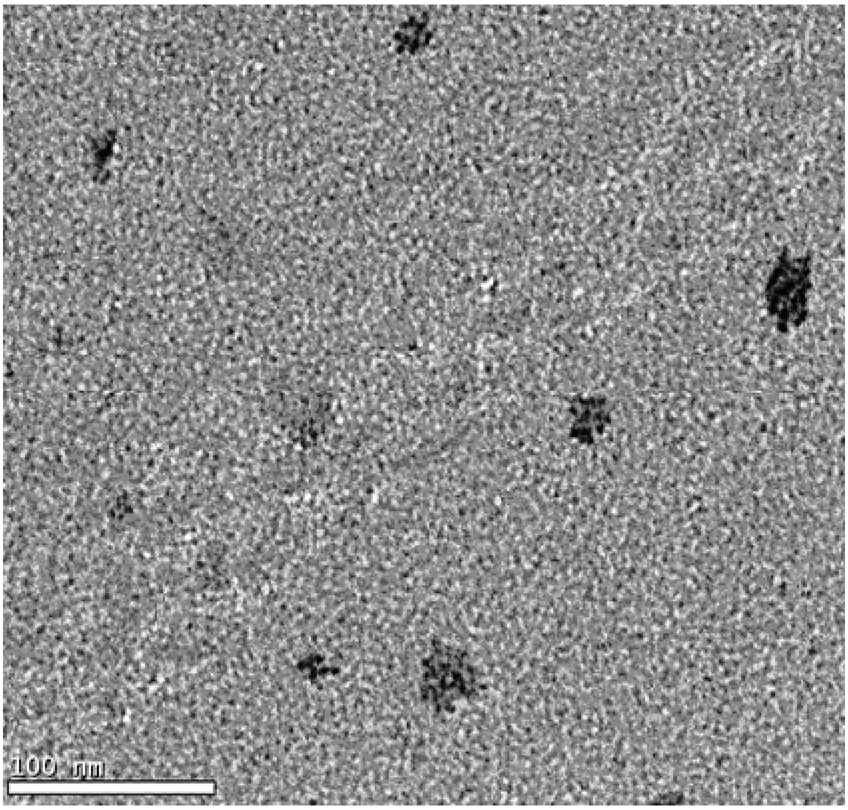


Figure S6. TEM image of solution of **1** in water (0.5 mM).

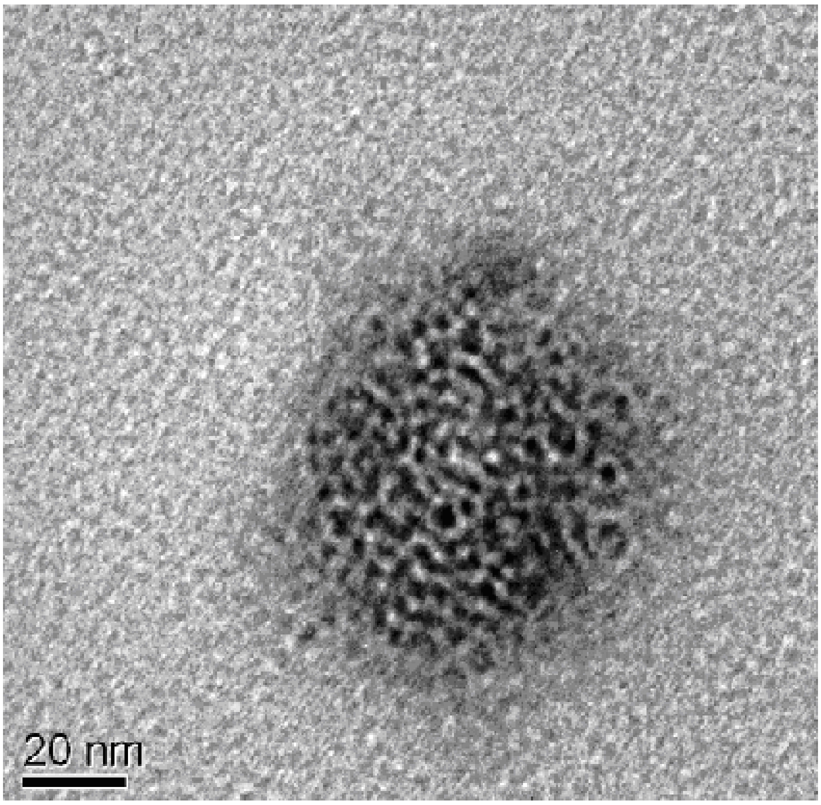


Figure S7. HR TEM image of solution of **1** in water (0.5 mM).

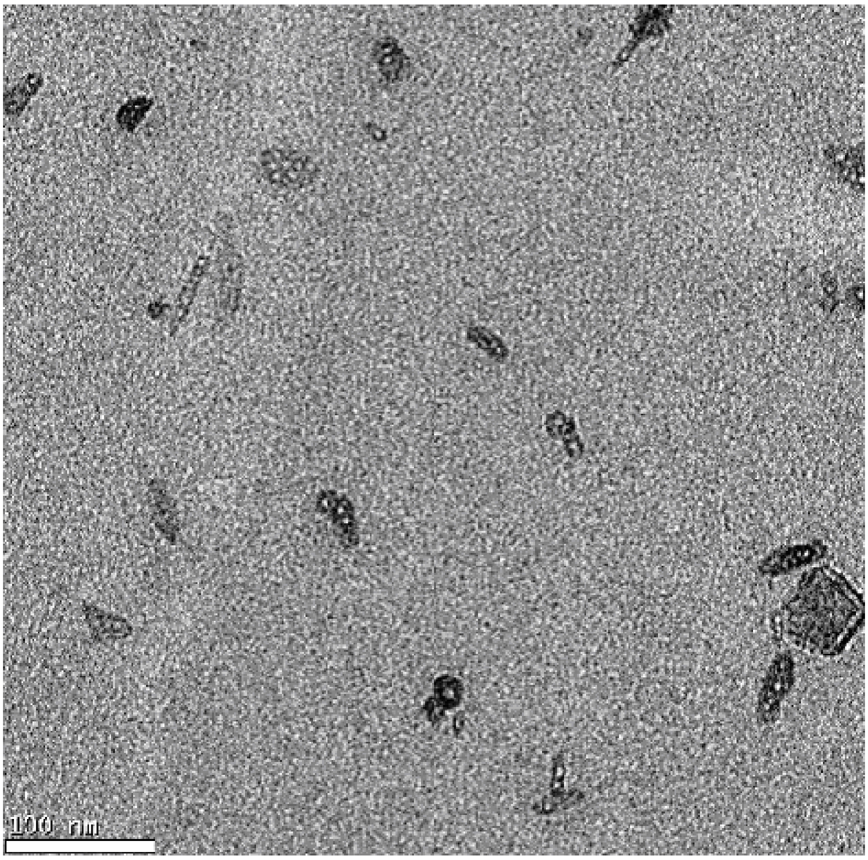


Figure S8. TEM image of mixture of **1** and Naproxen in water (0.5 mM).

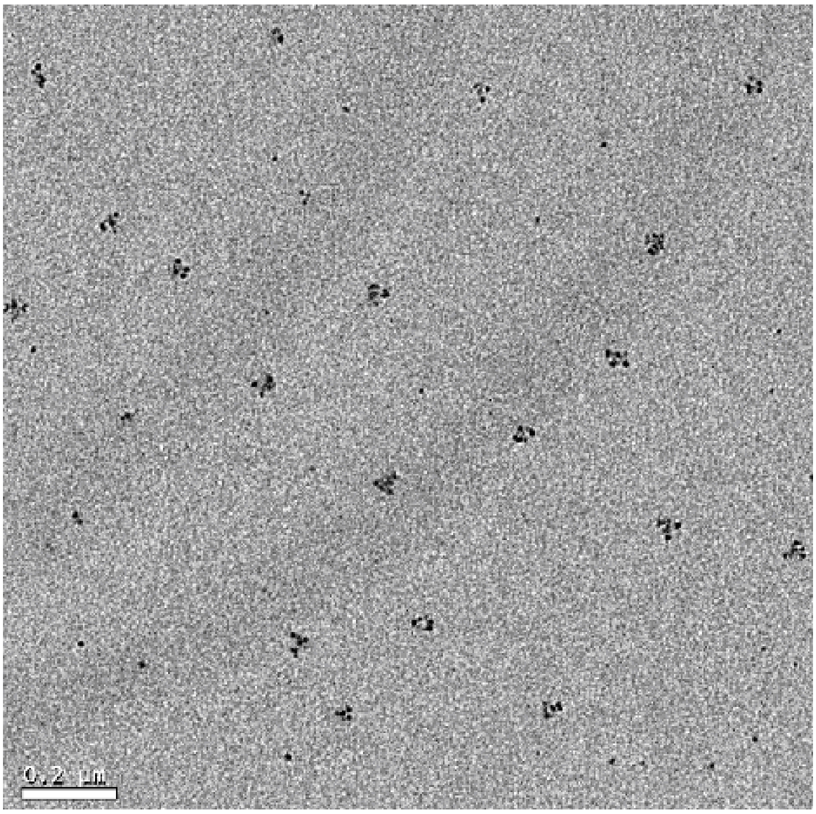
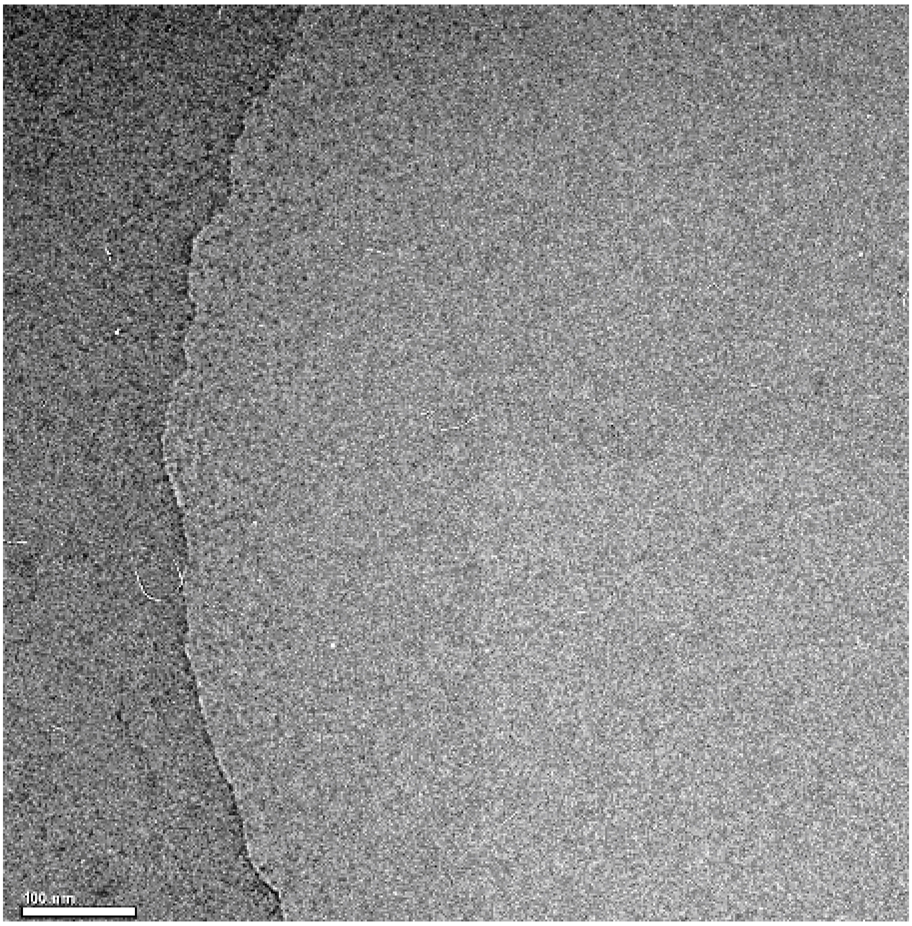
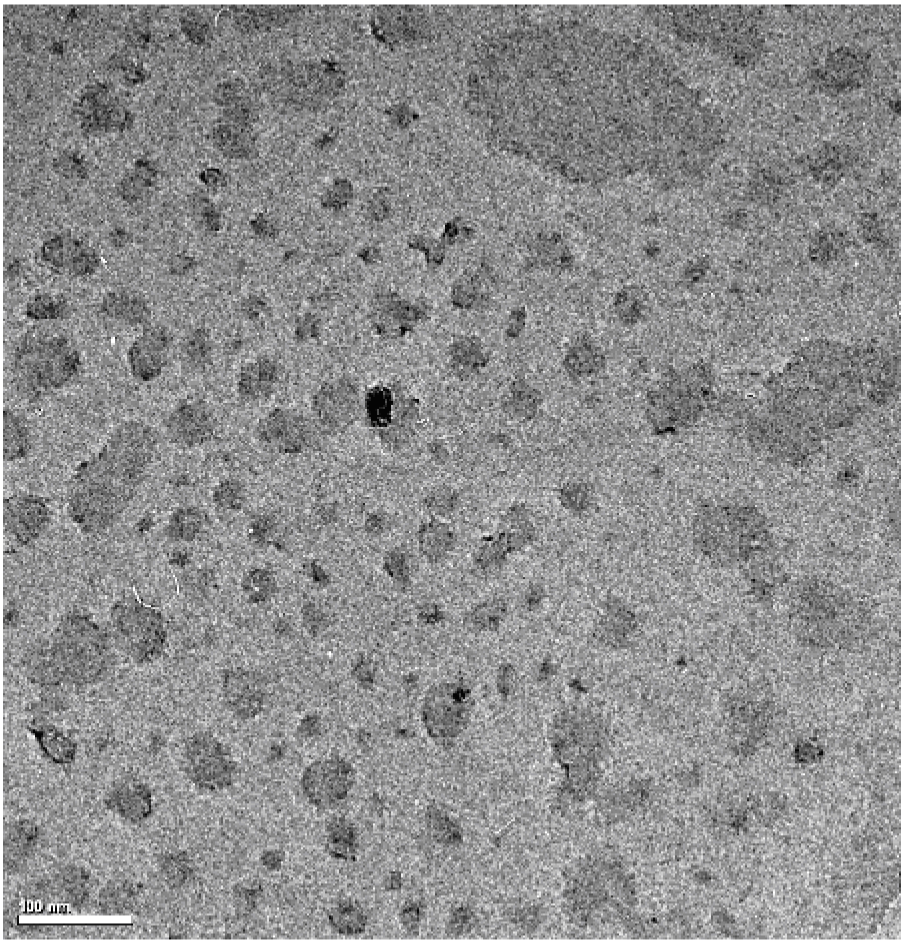


Figure S9. TEM image of mixture of **1** and Ibuprofen in water (0.5 mM).



FigureS10. Cryo-TEM image of solution of **1** in water (1 mM)



FigureS11. Cryo-TEM image of solution of **1** in water (1 mM)

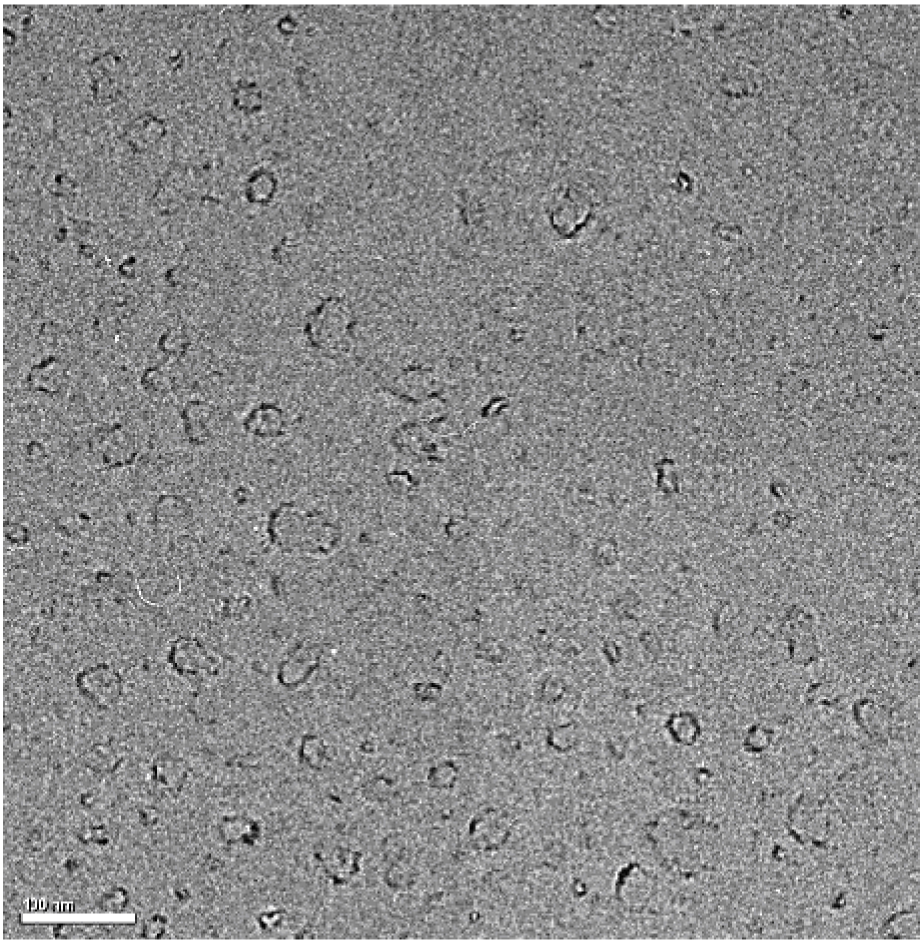


Figure S12. Cryo-TEM image of mixture of **1** and Naproxen in water (1 mM).

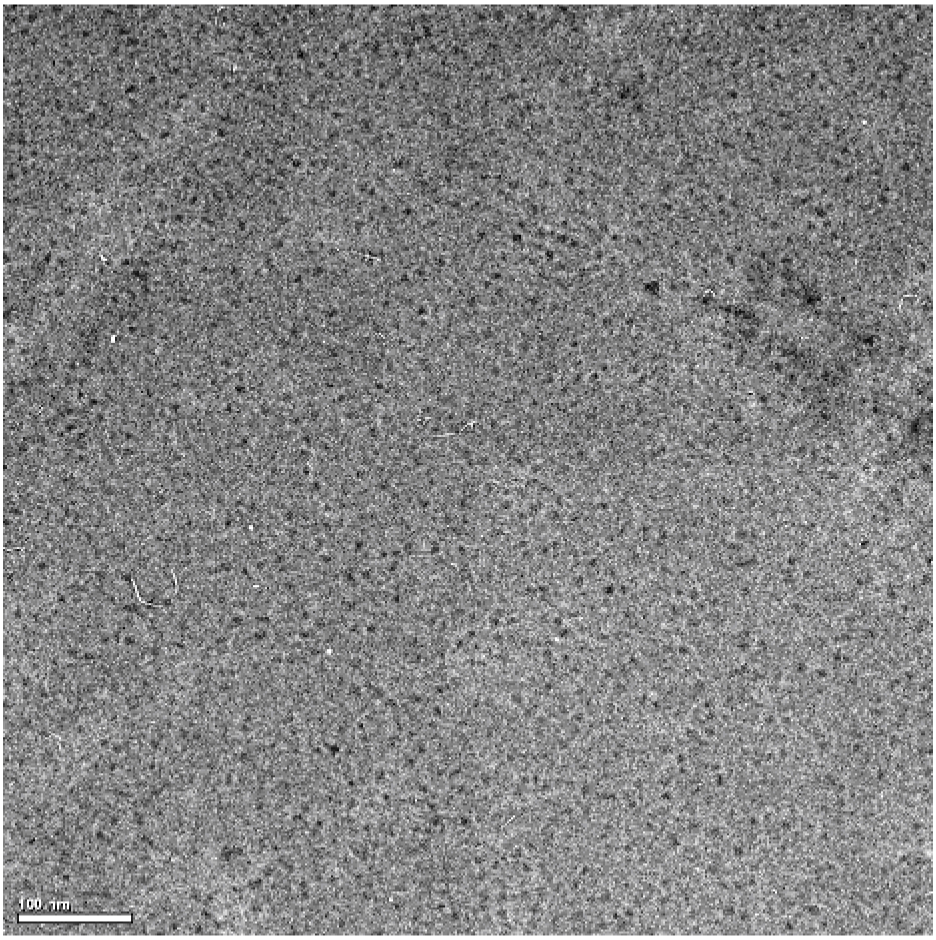


Figure S13. Cryo-TEM image of mixture of **1** and Ibprofen in water (1 mM).

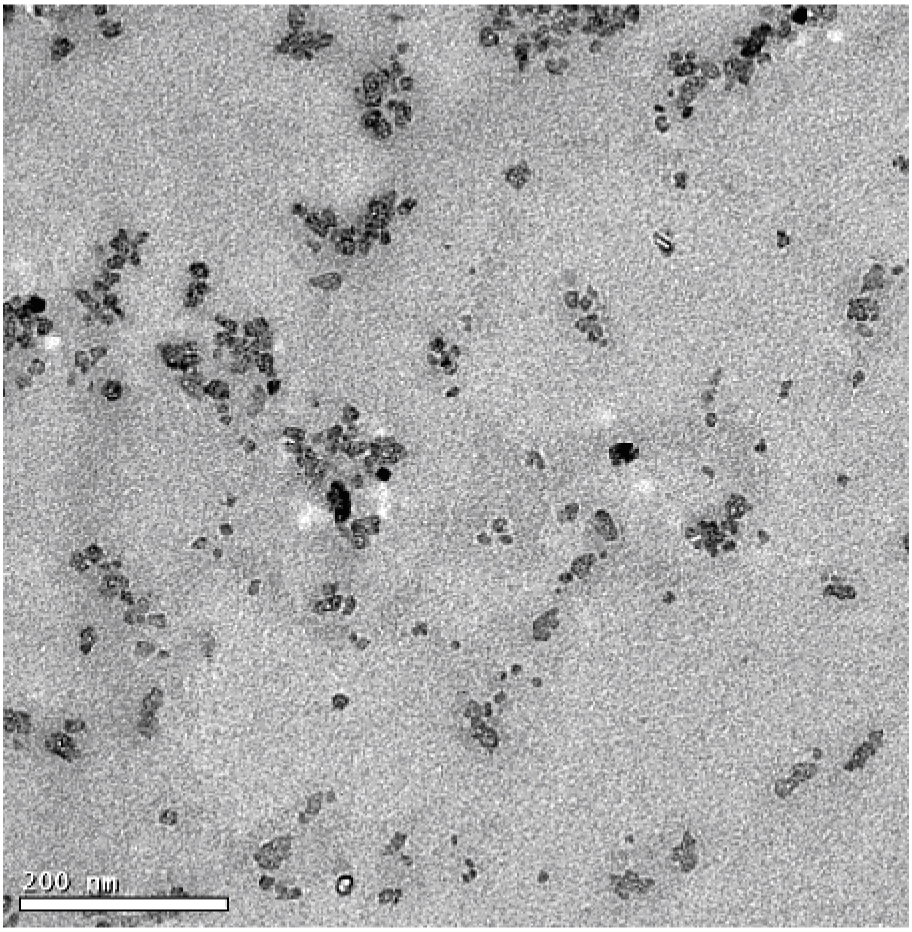


Figure S14. TEM image of mixture of **1** and dodecanoic acid in water (0.5 mM).

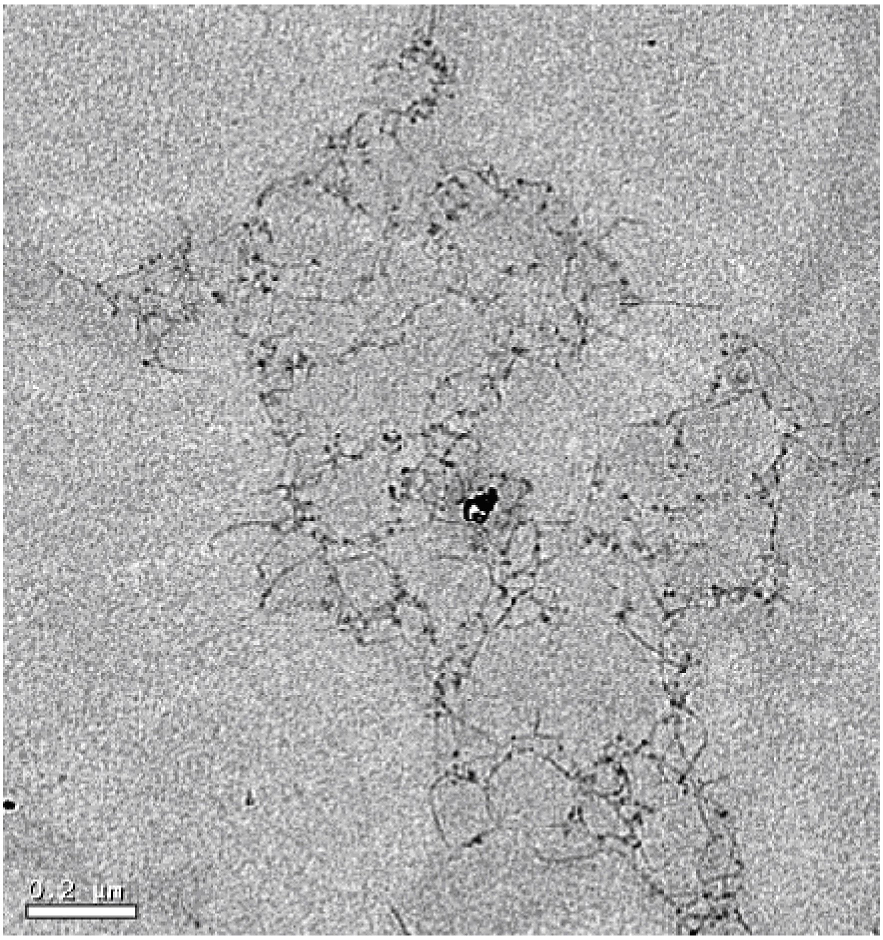


Figure S15. TEM image of mixture of **1** and benzoic acid in water (0.5 mM).

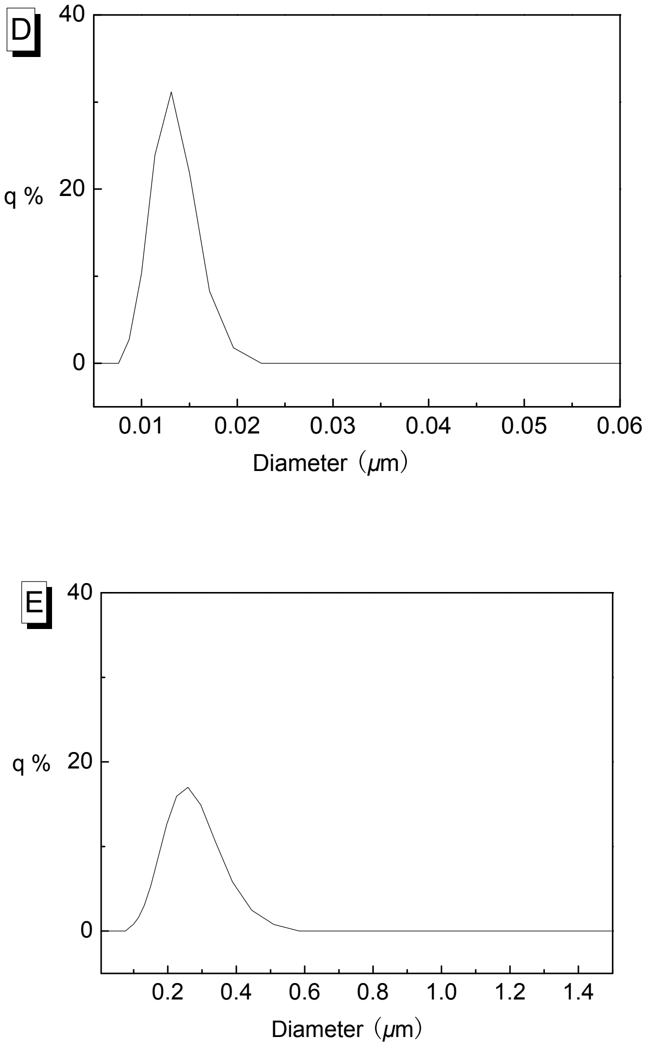


Figure S16. Dynamic light scattering (DLS) diagram of solution of D) of **1** and dodecanoic acid, E) of **1** and benzoic acid in water at 20°C (the concentration of all compounds = 5.0×10^{-5} M, measured as soon as the solution was prepared).