

Self-assembled reversed bilayers directed by pnictogen bonding to form vesicles in solution.

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Supplementary Information

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S1 Experimental Details

S1.1 General Methods

The starting materials, antimony(III) trichloride (99%, Strem Chemicals), decanoyl chloride (98+%, Acros Organics), Tris (hydroxymethyl)aminomethane (Trizma® base) ($\geq 99.9\%$, Sigma) were used as purchased. Antimony(III) *tert*-butoxide, $\text{Sb}(\text{OC}(\text{CH}_3)_3)_3$, was prepared as previously reported.¹ Anhydrous tetrahydrofuran was obtained by passing HPLC grade THF over a bed of activated molecular sieves in a commercial (LC Technologies Solutions Inc.) solvent purification system (SPS). Extra dry acetone (99.8%) was purchased from Acros Organics and stored over activated molecular sieves for 72 h under a nitrogen atmosphere prior to preparation of the vesicles. Deuterated solvents, purchased from Cambridge Isotopes Laboratory, were degassed using the freeze-pump-thaw cycles before being transferred onto freshly activated molecular sieves. Air sensitive manipulations were performed in an N_2 purged inert atmosphere box (LC Technology Solutions Inc.) A VWR brand (model symphony) ultrasonic bath with 35 kHz operating frequency and 180W RF power was used for vesicle preparation. All NMR spectra were collected by a JEOL ECS 400 MHz NMR spectrometer. All IR spectra were obtained using a Nicolet iS 5 FT-IR spectrometer equipped with a Specac Di Quest ATR accessory, and CHN analysis were obtained on-site with a Perkin Elmer 2400 Series II CHN Analyzer.

S1.2 Synthesis

S1.2.1 Synthesis of **1** ($(\text{HOCH}_2)_3\text{CNHC}=\text{O}(\text{CH}_2)_8\text{CH}_3$)

The tripodal alcohol **1** was prepared by adapting a reported method.² In a 100 mL round bottom flask, 2.43 g (20.0 mmol) of tris(hydroxymethyl)aminomethane and 3.23 g (80.0 mmol) of magnesium oxide were suspended in a 1:3 mixture of H_2O and THF (4:12 mL). The mixture was stirred for 30 minutes. A solution of 4.78 mL (23.0 mmol) of decanoyl chloride and 4 mL of THF

was added dropwise over the course of one hour. The mixture was stirred at room temperature for 24 hours and then it was filtered through a bed of Celite before removing the volatiles under vacuum. The residual solid was recrystallized from 30 mL of ethanol and colorless crystals were collected, yielding 2.78 g (60%) of pure **1**. mp = 101–104 °C. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 0.85 (t, *J* = 6.8 Hz, CH₃), 1.24 (m, CH₂(CH₂)₆CH₂CH₃), 1.46 (dt, *J* = 6.9 Hz, (CH₂)₆CH₂CH₃), 2.12 (t, *J* = 7.4 Hz, NHCOCH₂(CH₂)₆), 3.51 (d, *J* = 5.7 Hz, (HOCH₂)₃CNH), 4.77 (t, *J* = 5.7 Hz, (HOCH₂)₃CNH), 7.1 (s, CNHCO). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 15.71 (CH₃), 22.64 (CH₂)₆CH₂CH₃, 25.87, 29.10, 29.21, 29.35, 29.45, 31.82 (CH₂(CH₂)₆CH₂CH₃), 36.37 NHCOCH₂(CH₂)₆, 61.27 ((HOCH₂)₃CNH), 62.74 ((HOCH₂)₃CNH), 174.36 (NHCOCH₂). FTIR (ATR, cm⁻¹) 3379 (mb), 3287 (sb), 2917 (s); 1621 (s), 1532 (s), 1025 (s). Anal. Calc. for C₁₄H₂₉NO₄: C, 61.06; H, 10.61; N, 5.09. Found: C, 61.64; H, 11.19; N, 4.91.

S1.2.2 Synthesis of **2** (Sb(OCH₂)₃CNHC=O(CH₂)₈CH₃)

Antimony(III) tert-butoxide (0.341 g, 1.00 mmol) was dissolved in 5 mL of THF. A solution of **1** (0.239 g, 0.87 mmol) in 5 mL of THF was added to the antimony (III) tert-butoxide solution while stirring at room temperature under a nitrogen atmosphere. A white suspension was formed immediately upon mixing. The mixture was stirred overnight before collecting the solid which was rinsed with THF yielding 264 mg (67%) of **2** as a white solid. Samples of **2** were stored under nitrogen. m.p. 154-160 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ=, 0.87 (t, *J*=6.8 Hz, CH₃), 1.25 (m, CH₂(CH₂)₆CH₂CH₃), 1.42 (m, (CH₂)₆CH₂CH₃), 1.98 (t, *J*=7.3 Hz, NHCOCH₂(CH₂)₆), 4.23 (s, Sb(OCH₂)₃CNH), 6.9 (s, CNHCO). ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ= 14.36 (CH₃), 22.54 ((CH₂)₆CH₂CH₃), 25.74, 28.99, 29.08, 29.20, 29.35, 31.73 (CH₂(CH₂)₆CH₂CH₃), 36.20 (NHCOCH₂(CH₂)₆), 57.19 (Sb(OCH₂)₃CNH), 71.19 (Sb(OCH₂)₃CNH), 172.67 (NHCOCH₂).

FTIR (ATR, cm^{-1}) 3412 (m), 2919 (s), 1669 (s), 1509 (s), 491 (s). Anal. Calc. for $\text{C}_{14}\text{H}_{26}\text{NO}_4\text{Sb}$: C, 42.67; H, 6.65; N, 3.55. Found: C, 43.48; H, 6.58; N, 4.30.

Diffraction quality single crystals of **2** were grown by heating a suspension of **2** in DMSO. Heat was applied from the bottom of the flask and single crystals grew on the walls where it was cooler.

S1.3 Crystallography

Data were collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1350 W (50kV, 30 mA) to generate (graphite monochromated) Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Crystals were transferred from the vial and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a M̄TiGen cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100 K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a sphere of data was collected. Omega scans were carried out with a 10 sec/frame exposure time and a rotation of 0.50° per frame. After data collection, the crystal was measured for size, morphology, and color. These values are reported in Table 1.

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX 3.³ A semi-empirical correction for adsorption was applied using the program SADABS.⁴ The *SHELXL-2014*,⁵ series of programs was used for the solution and refinement of the

crystal structure. It was initially determined that eight atoms of carbon alkane tail (C6 < C13) were positionally disordered and were modeled over two sites (A and B). The site occupancies of the two sites A and B were 0.51, respectively. To help model the disordered components, free variable DFIX and SIMU restraints were applied. The average C-C bond distance for the disordered components was 1.514(6) Å. Hydrogen atoms bound to carbon and nitrogen atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. After the hydrogen atoms were positioned, there were a couple significant electron density peaks left in the difference Fourier map. After careful consideration, it was determined that these peaks represented disordered antimony atoms of disordered sheet layers within the crystal. The strongest reflection (Sb2) was included in the final refinement and the Sb1 and Sb2 atom positions were allowed to refine to a total of 1 with an EADP constraint used to keep the Sb2 site reasonable. The resulting refinement showed that this site was occupied 1.5% of the time. However, it was deemed futile to attempt to find the remaining O, N, and C sites that would correlate to this disordered position.

Table S1. Crystal data and structure refinement for **2** (CCDC No. 1843709).

Crystal Color	colorless
Crystal Habit	plate
Empirical formula	$C_{14}H_{26}NO_4Sb$
Formula weight	394.11
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions [Å]	$a = 8.0941(3)$ $b = 43.971(2)$ $c = 8.3622(5)$
Volume [Å ³]	2976.2(3)
Z	8
Calculated density [mg/m ³]	1.759
Absorption coefficient [mm ⁻¹]	1.867
F(000)	1600
Crystal size [mm]	0.480 × 0.450 × 0.016
Theta range for data collection	1.853 to 27.895°
Limiting indices	$-10 \leq h \leq 10$ $-56 \leq k \leq 55$ $-10 \leq l \leq 10$
Reflections collected / unique	33512/3274 [R(int) = 0.0313]
Completeness to theta = 25.242°	99.9%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3274/321/260
Goodness-of-fit on F ²	1.134
Final R indices [I > 2σ(I)]	R1 = 0.0394, wR2 = 0.1081
R indices (all data)	R1 = 0.0413, wR2 = 0.1093
Largest diff. peak and hole [e·Å ⁻³]	1.281 and -2.032

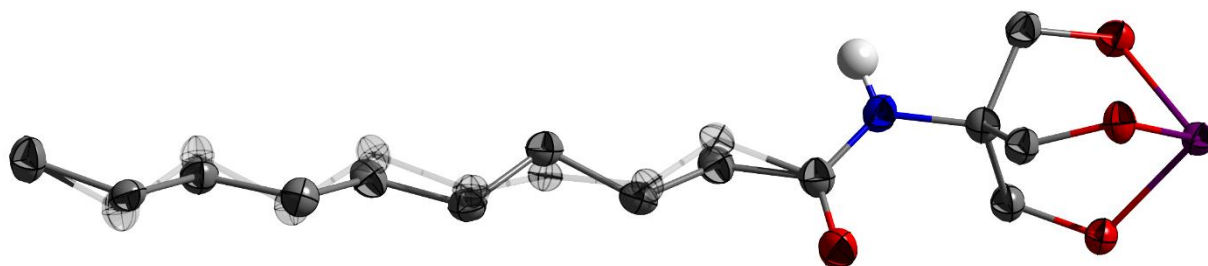


Figure S1. Asymmetric unit of **2** shown with thermal ellipsoids plotted at 50% probability. Alkyl hydrogens were omitted for clarity. The alkyl chain was disordered and the lower occupancy carbons (49%) are shown in a lighter color.

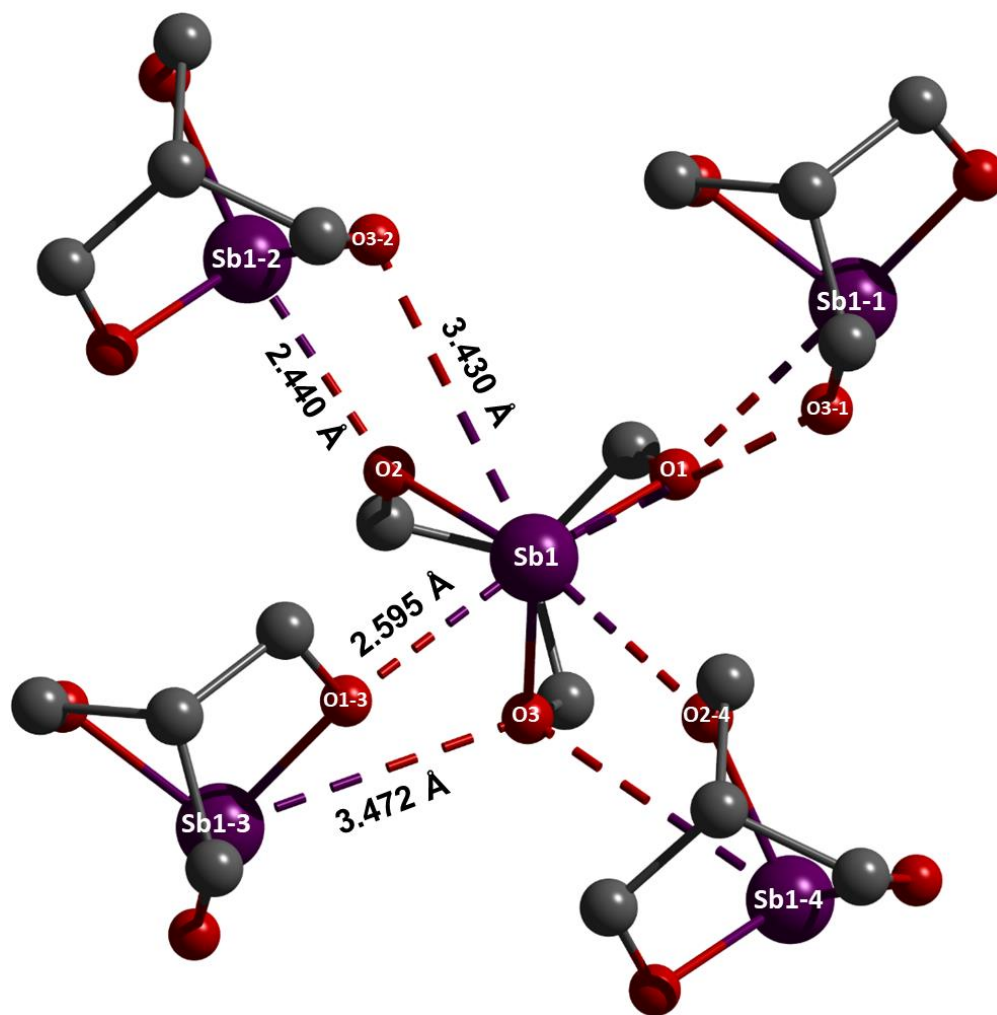


Figure S2. Ball and stick representation of the supramolecular repeating unit of **2** in the solid state (for clarity the tails and hydrogens are omitted).

Figure S2 depicts the asymmetric unit of **2** surrounded by the four symmetry-related molecules that self-assemble through pnictogen bonds. Sb1 bonds to three O atoms with distances of 2.085, 2.005 and 1.974 Å, respectively for O1-O3. These are slightly elongated from non-interacting Sb-O single bonds.¹ The four surrounding molecules are arranged in an antiparallel manner with the tails pointing in the opposite direction of the central molecule. Each pair of molecules is self-assembled through two antiparallel Sb···O pnictogen bonds (one long and one short) to create a non-centrosymmetric virtual four-membered heterocycle. The SBI distances range from 2.440 Å (119% $\sum r_{\text{cov}}$, or 68% $\sum r_{\text{vdw}}$) for Sb1···O2 to 3.472 Å (169% $\sum r_{\text{cov}}$, or 97% $\sum r_{\text{vdw}}$) for Sb1···O3.^{6,7}

Table S2. Crystallographic distances for pnictogen bonds in Figure S2

Pnictogen Bond^a	Distance (Å)	% of $\sum r_{\text{cov}}$⁶	% of $\sum r_{\text{vdw}}$⁷
Sb1···O3-1	3.472	169	97.0
Sb1-1···O1	2.595	127	72.5
Sb1···O3-2	3.430	167	95.8
Sb1-2···O2	2.440	119	68.2
Sb1···O1-3	2.595	127	72.5
Sb1-3···O3	3.472	169	97.0
Sb1···O2-4	2.440	119	68.2
Sb1-4···O3	3.430	167	95.8

^a shading used to denote distances in dimers

S1.4 Dynamic Light Scattering Method

Samples were characterized via Nanotracer Model NPA250 (Microtrac Inc.). All samples were prepared in dry acetone under nitrogen atmosphere. Both time and concentration effect on the

formation of the vesicles were studied. Five different concentrations (0.5, 0.4, 0.3, 0.15, and 0.05 μM) of **2** were prepared in scintillation vials. Vials were taped and sonicated in ultrasound bath for three time variations (10 seconds, 2 minutes, and 5 minutes). All DLS tests were run in triplicates, after sonication time was over the laser was dipped into the solution. To protect the vesicles from hydrolysis, the laser was passed through a scintillation vial screw cap and sealed with Parafilm and vials containing the sample solution were immediately screwed into the cap. For each sample, two 60 s scans were performed. The data was processed with microtrac FLEX 10.3.14 and the size distribution, in percent, of the particles was plotted as a function of the size of the particles in nanometers after averaging the three independent trials.

S1.5 Transmission Electron Microscopy (TEM) Method

Based on the DLS results, 0.1-1.0 mg of **2** was dispersed in 5 mL of dry acetone and sonicated between 2-5 minutes under nitrogen atmosphere. A drop of the prepared solution was cast on a 200 mesh carbon coated copper grid (Ted Pella, inc.) and excess solvent was removed by absorbing it with a filter paper placed under the grid. The prepared sample was characterized with a Hitachi H-8100 scanning transmission electron microscope. Samples were studied under 75 keV accelerating voltage. Image capturing and size measurements were performed with the AMT imaging software.

S1.6 Scanning Electron Microscopy (SEM) Method

To prepare the SEM sample, 0.15 mg of **2** was dispersed in 5 mL of dry acetone and sonicated for 5 minutes under nitrogen. A drop of the solution was cast on a 200 mesh copper grid with carbon coating (Ted Pella, Inc.) and solvent was absorbed with filter paper placed under the grid. Then grid was placed on double sided carbon adhesive tape which was attached to a SEM aluminum pin stub mount. The sample was coated with iridium and the morphology of the

specimen was imaged with a Hitachi S-4300 scanning electron microscope. Imaging individual particles proved difficult due to the fact both TEM and SEM samples were prepared in the same manner most vesicles were well separated which made the adjustments to collect a highly resolved image harder. An aggregate of particles was found and imaged (see Figure S16) not many aggregates were found. Working under low voltages caused the particles to shrink in size and, as a result, the image quality was negatively affected. To enhance the quality of the image, the original image was corrected by gamma 1.6, and the picture was smoothed by 2 pixel averaging.

S2 Spectroscopy and Microscopy Results

S2.1 ^1H NMR

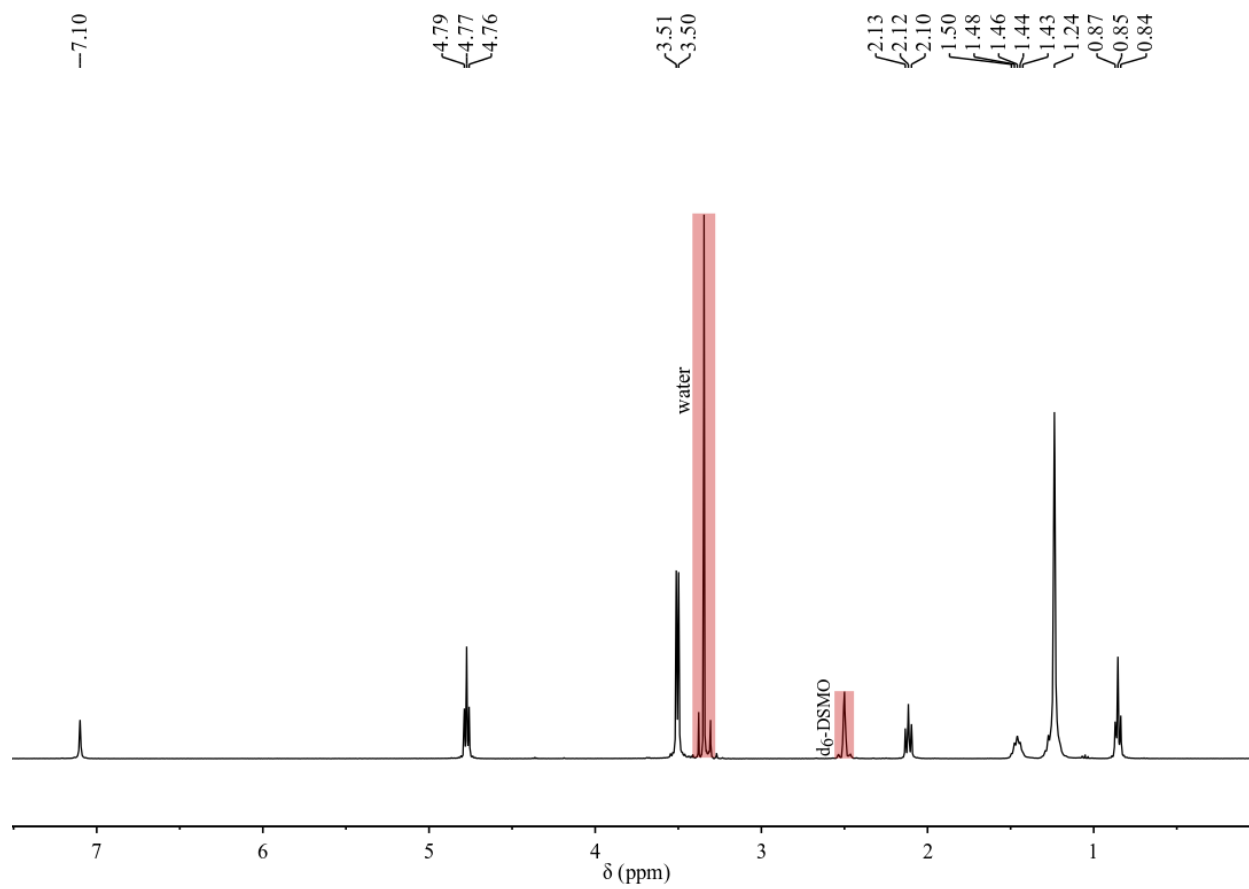


Figure S3. ^1H NMR of **1** in $\text{d}_6\text{-DMSO}$.

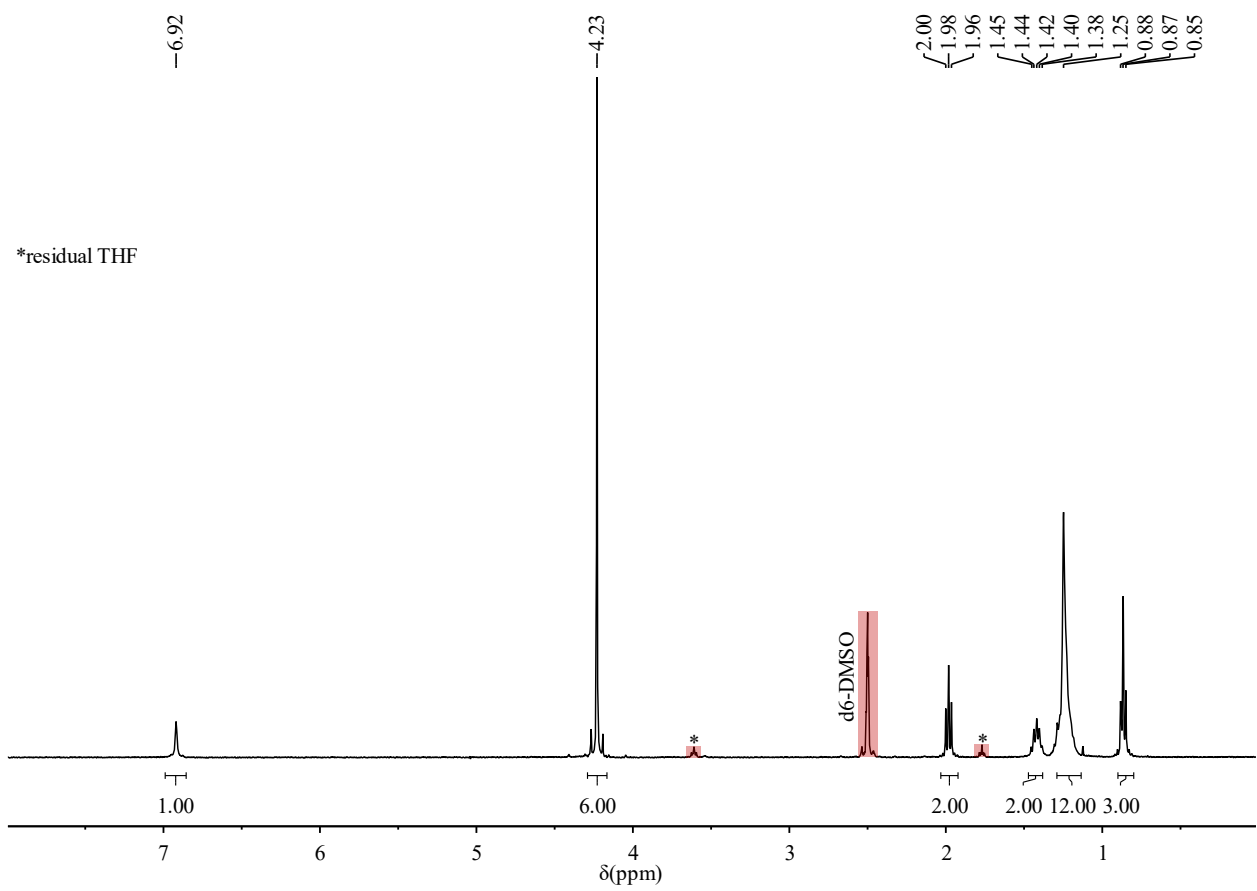


Figure S4. ¹H NMR of **2** in d₆-DMSO.

S2.2 ^{13}C NMR

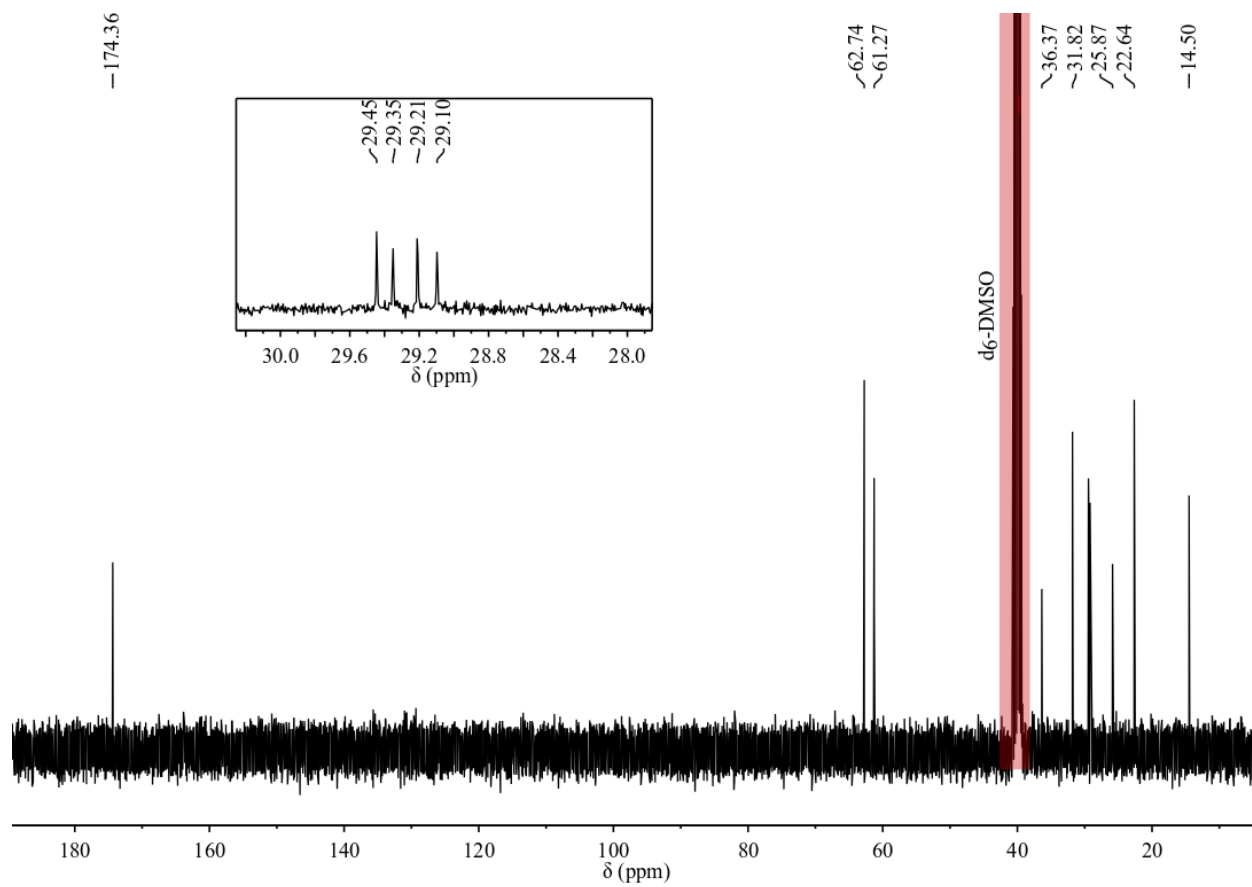


Figure S5. ^{13}C NMR of **1** in $\text{d}_6\text{-DMSO}$.

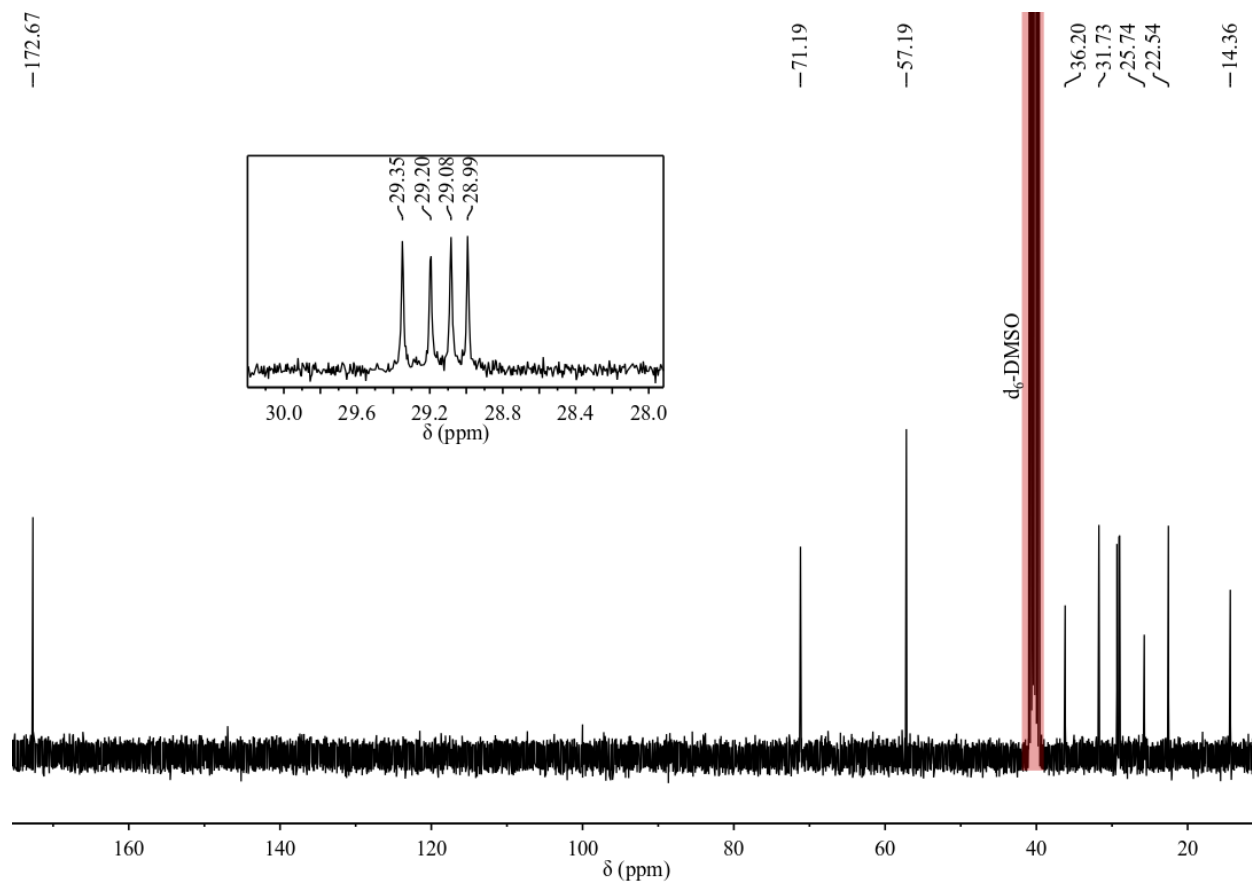


Figure S6. ^{13}C NMR of **2** in $\text{d}_6\text{-DMSO}$.

S2.3 ATR FTIR

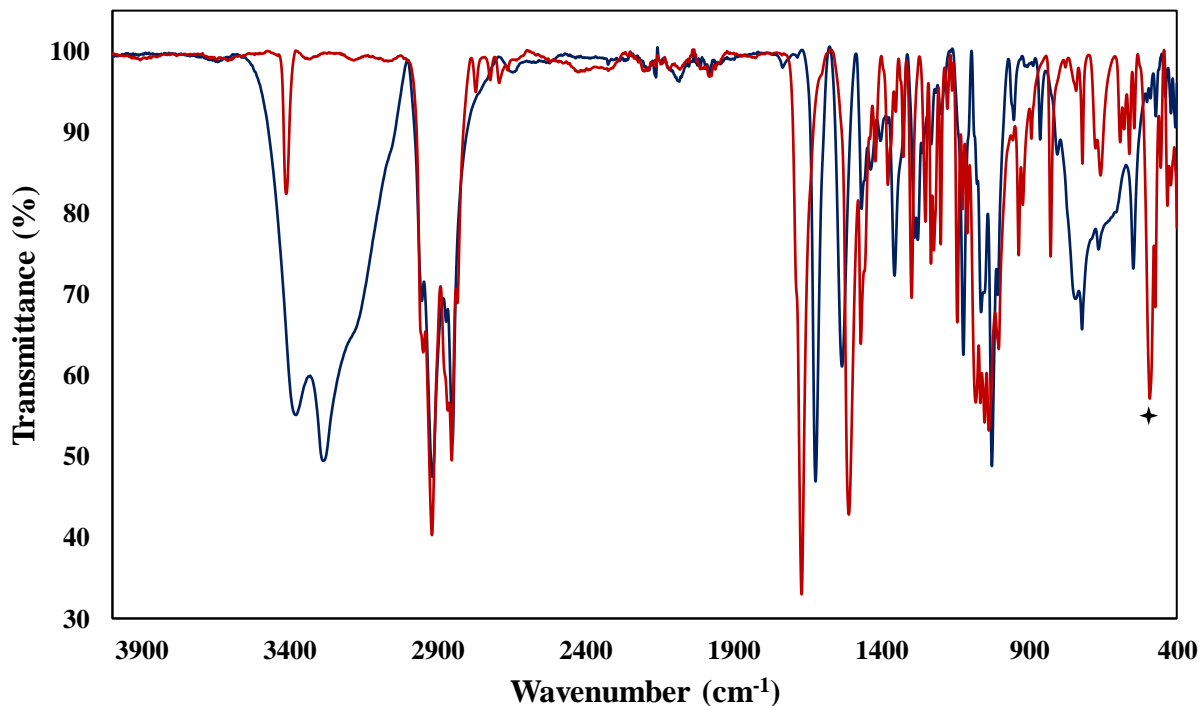


Figure S7. Di-ATR FTIR of **1** (blue) and **2** (red). Sb–O stretch is denoted with a +.

S2.4 Powder X-ray Diffraction

The diffraction patterns for **2** was collected on a Rigaku Ultima III powder diffractometer. X-ray diffraction patterns were obtained by using a 2θ scan with the source fixed at 0° and the detector scanning a θ range of $5\text{--}60^\circ$, step size = 0.02° , and scan time of 16 min/degree. The X-ray source was Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) with an anode voltage of 40 kV and a current of 44 mA. The beam was then discriminated by Rigaku's Cross Beam parallel beam optics to create a monochromatic parallel beam. Diffraction intensities were recorded on a scintillation detector after being filtered through a Ge monochromator.

Crystalline material of **2** was packed inside borosilicate capillary with inner diameter of 0.3 mm and wall thickness of 0.01 mm purchased from Charles Supper Company. Samples were prepared

under an inert atmosphere and the tube was sealed with grease. After sealing, it was mounted on a capillary holder and the data was collected. The resulting diffractogram was processed with the software JADE v9.1. Simulated patterns were obtained from single crystal data of **2** via Mercury 3.9 software.

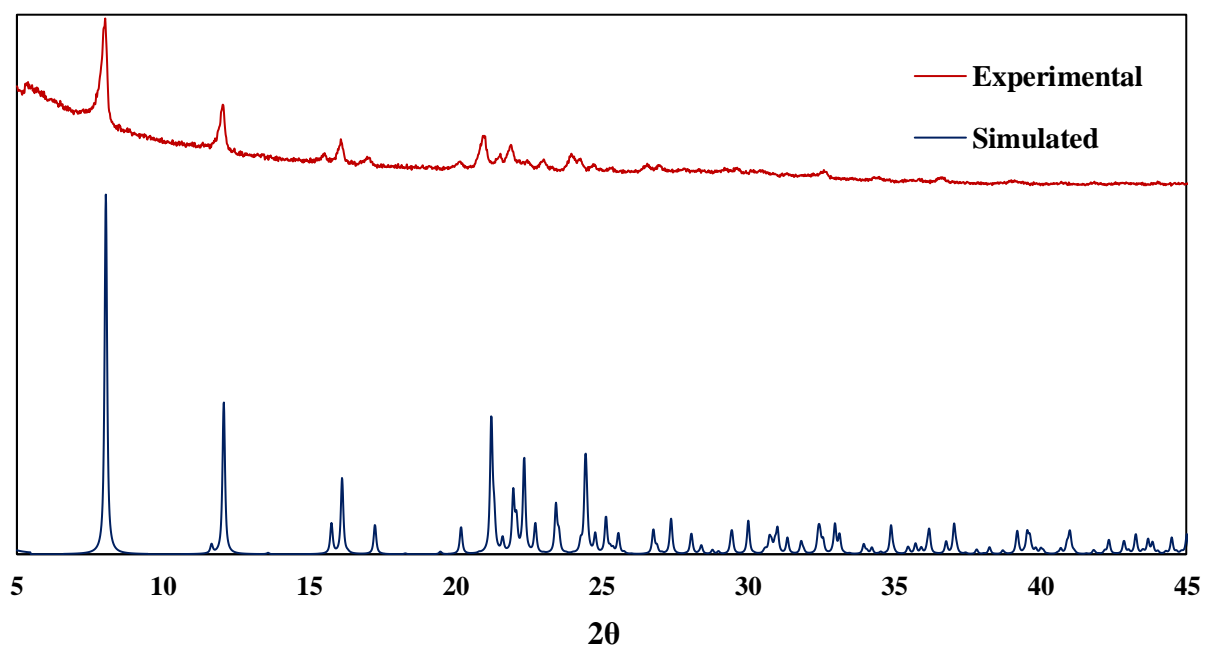


Figure S8. PXRD of **2**.

S2.5 Dynamic Light Scattering (DLS) Results

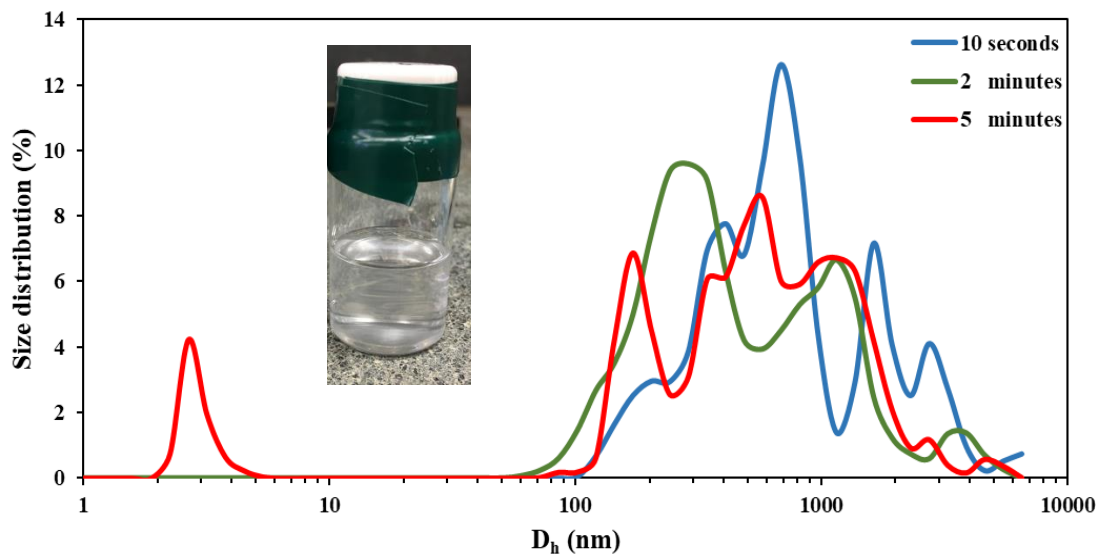


Figure S9. Size distribution of particles in 0.5 μM acetone solution at different sonication times (image of the sample after 5 minute sonication).

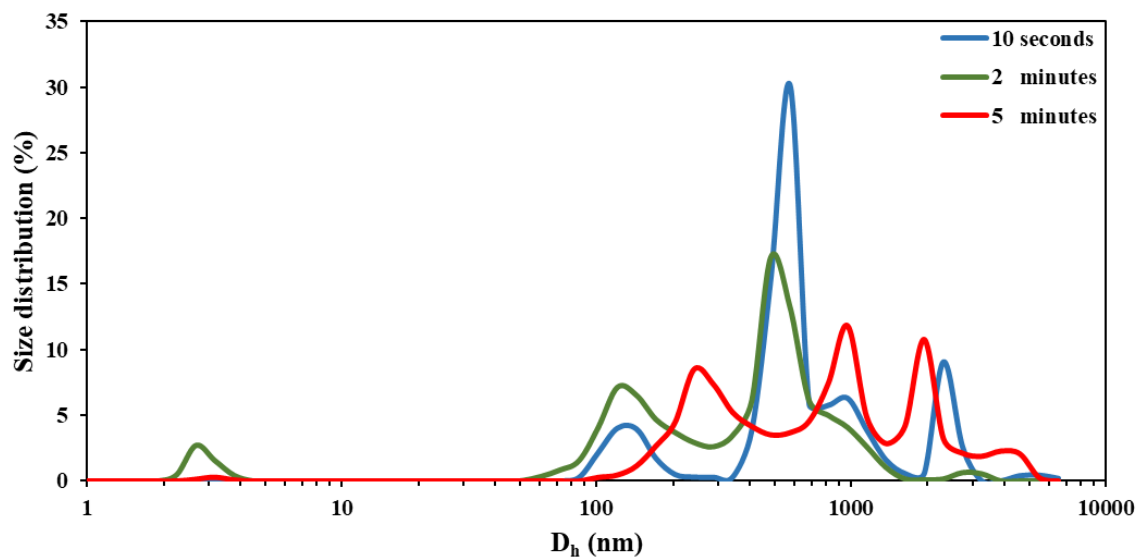


Figure S10. Size distribution of particles in 0.4 μM acetone solution at different sonication times.

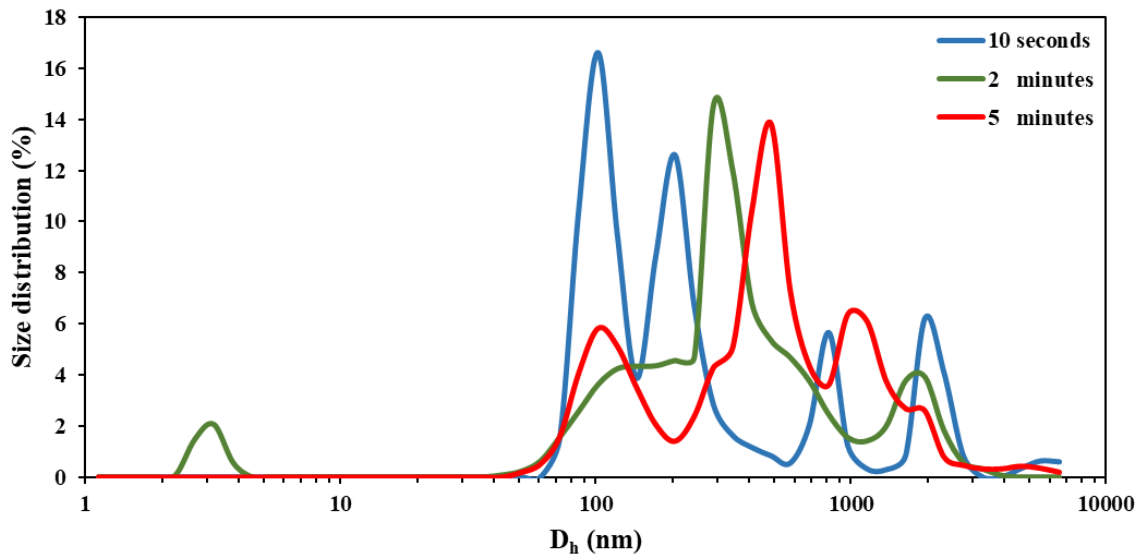


Figure S11. Size distribution of particles in 0.3 μM acetone solution at different sonication times.

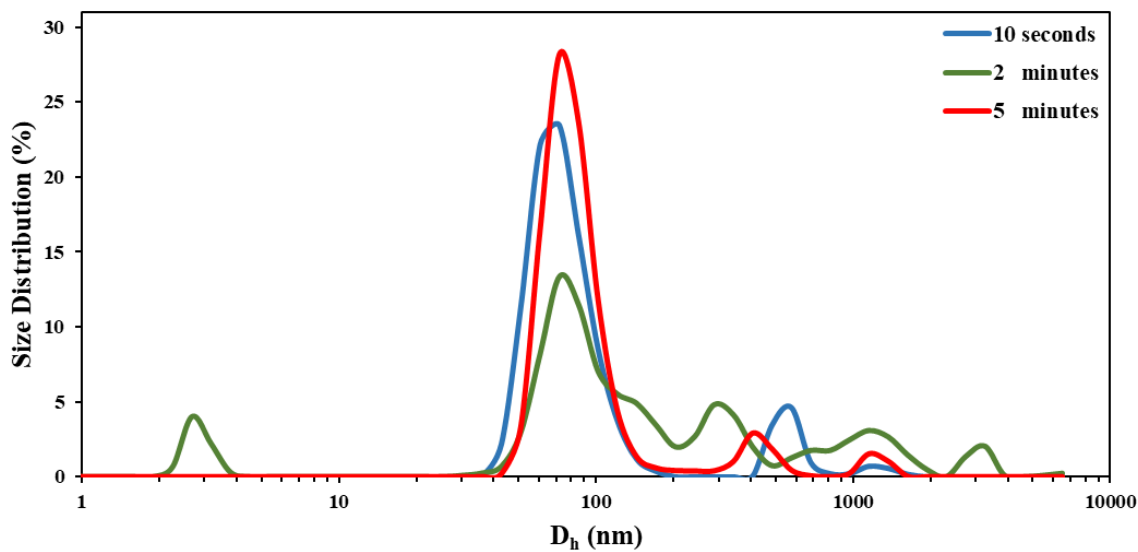


Figure S12. Size distribution of particles in 0.15 μM acetone solution at different sonication times.

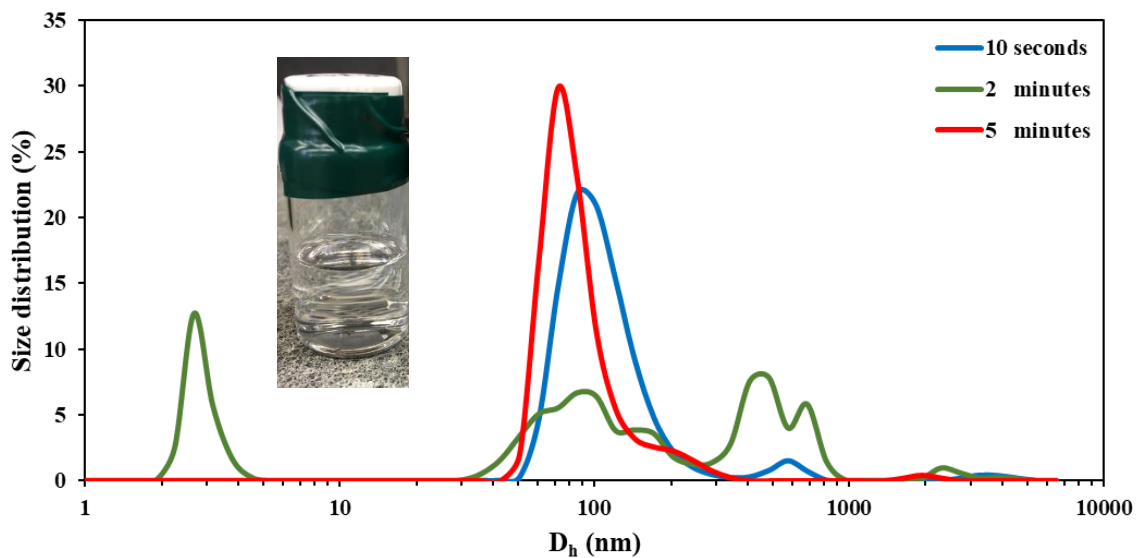


Figure S13. Size distribution of particles in 0.05 μM acetone solution at different sonication times (image of the sample after 5 minute sonication).

S2.6 Transmission Electron Microscope Images

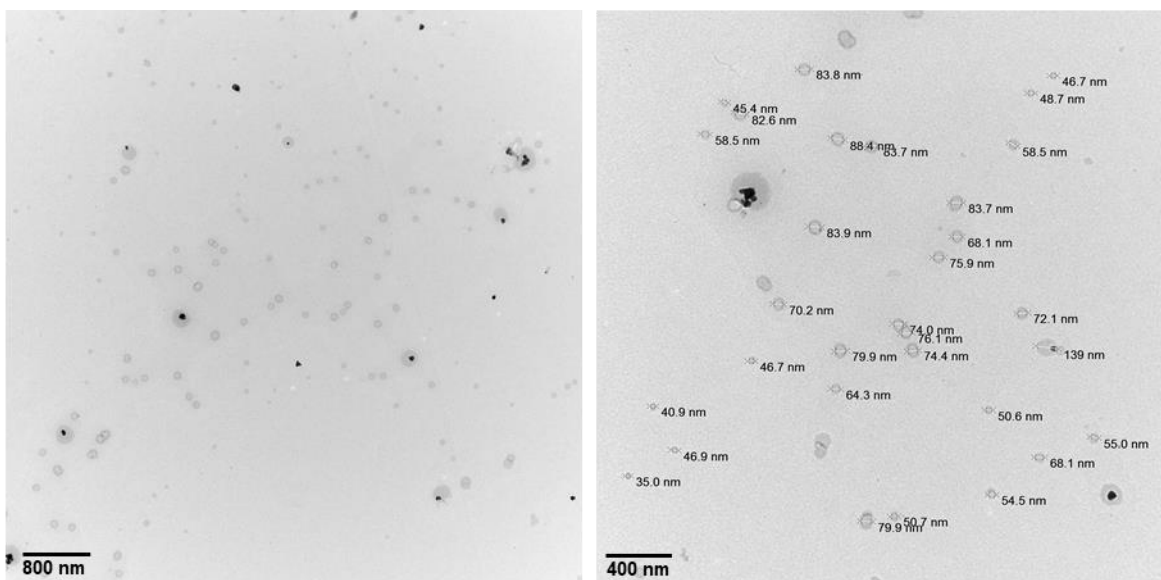


Figure S14. TEM images of **2** prepared in dry acetone (0.075 μM solution sonicated for 5 minutes). Size measurements were performed on these images (See **Figure 5** in manuscript).

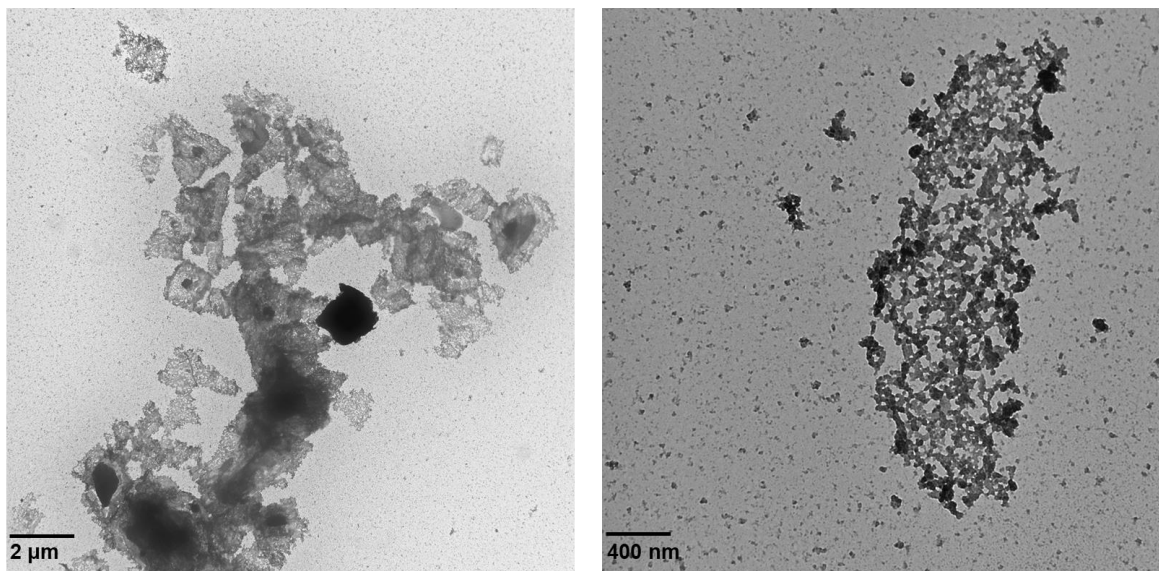


Figure S15. TEM images of **2** prepared in dry acetone (0.3 μM solution sonicated for 2 minutes).

S2.7 Scanning Electron Microscope Images

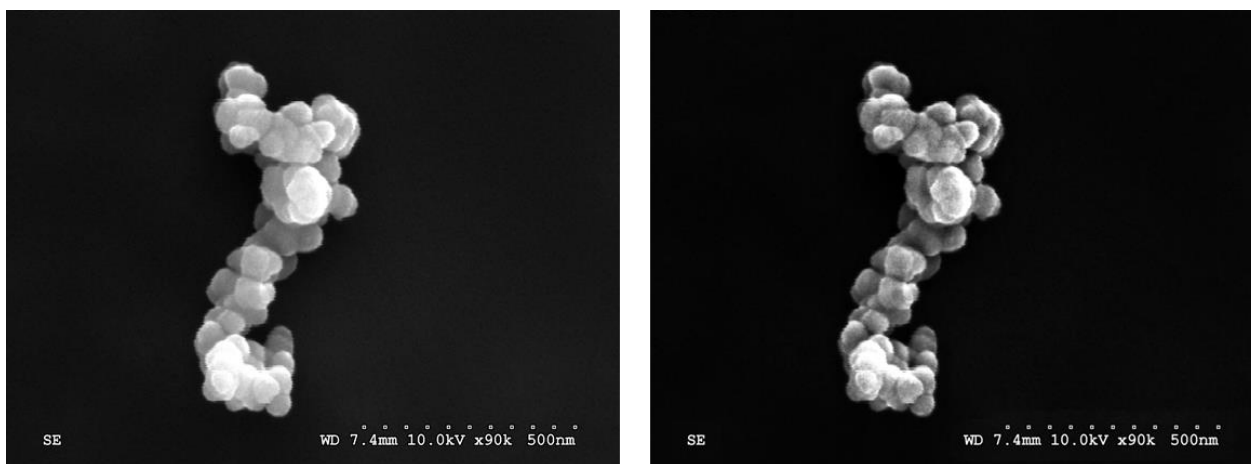


Figure S16. SEM image of **2**. Left: original image. Right: corrected image (gamma correction: 1.6, smoothing: 2 px1 mean).

S3 References

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