Supporting Information

The Self-Assembly of a Macroion with Anisotropic Surface Charge Density Distribution

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Experimental Details

The synthesis one **1** was done earlier according to the literature[1]. 2mg of **1** were dissolved in 10ml solvents consisting of 0, 40, 50, 60, 70, 80(%vol acetone/water mixtures), 50, 60, 70, 80,100(%vol methanol/water mixtures), 100(%vol CH_3OD) and 50(%vol CH_3OD/D_2O mixture) making a concentration of 0.2mg/ml in each sample. Each sample was then filtered using a 200nm filter purchased from Millipore. Methanol, acetone, D_2O were purchased from Sigma-Aldrich and used without further purifications. CH_3OD was purchased from Cambridge Isotope Laboratories and also used without purification.

Instruments used:

a) **Laser Light Scattering (LLS):**
Dynamic and static light scattering measurements were done using a Brookhaven Instrument LLS spectrometer with a solid state laser source operating at 532nm (green laser). The DLS Time Correlation function was generated using a BI-9000AT multi-channel digital correlator. A CONTIN analysis was used to determine the Hydrodynamic Radius.

b) **Transmission Electron Microscopy (TEM):**
One drop of sample was placed on a copper grid, and a JEOL JEM-2000 electron microscope operated at 200 kV was used to search for the images.

c) **pH and Conductivity Measurements:**
pH measurements were done using an Orion pH-meter and the solution conductivity was measured with Oaklon Conductivity meter.

d) **UV-Vis Spectroscopy:**
Stability of **1** was tested using a Shimadzu UV-2101PC Spectrophotometer. A freshly prepared sample was tested and compared with an aged sample (more than 30days).

e) **IR Spectroscopy:**
A Thermo Scientific IR spectrophotometer (NICOLET iS10) was used for further investigating the stability of the cluster.

Stability Studies Using UV-Vis Spectroscopy

0.2mg/ml of 1 in 100% water:

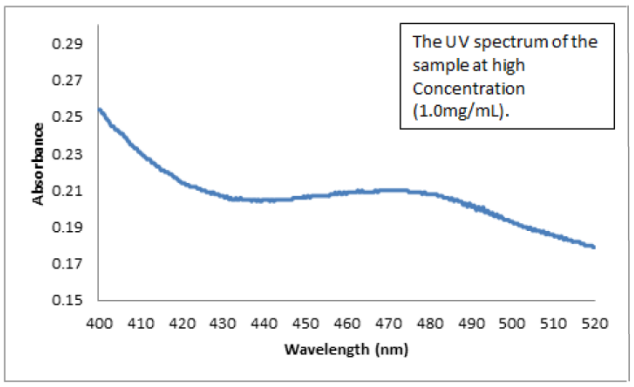

Figure S1. The UV spectrum of 1.0mg/ml sample of **1** in water right after preparation

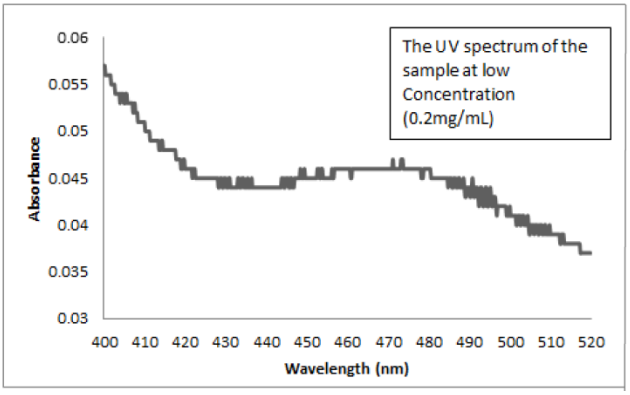

Figure S2. The UV spectrum of 0.2mg/ml of **1** in water right after preparation

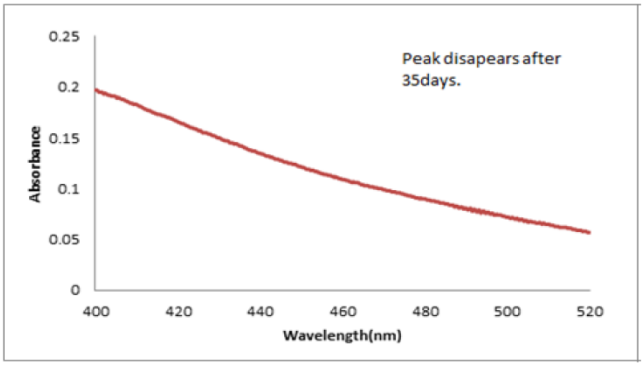

Figure S3. The UV spectrum of 0.2mg/ml of **1** in water after 35 days from preparation. One can notice that the peak disappeared suggesting that **1** is not stable in water

Since the peak disappeared at around 470nm after 35 days along with the sample color changed from clear to yellow. It suggests that **1** is not stable in water.

0.2mg/ml of 1 in (60%vol acetone/water mixture):

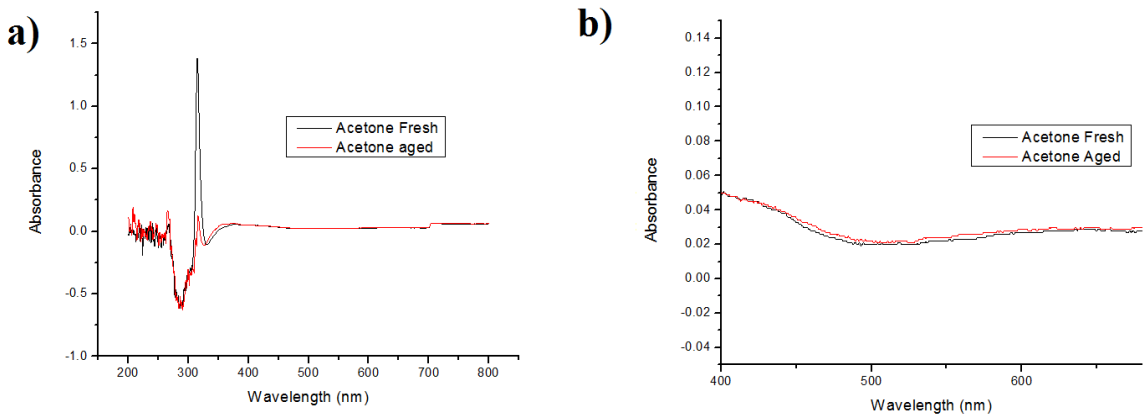

Figure S4. UV-VIS spectra of the sample in 60% acetone/water mixtures. b) Zooming in the spectra at the range of (400-700)

From Figure S4 one can clearly see that **1** is stable in acetone water mixtures. Also the samples did not turn yellow.

0.2mg/ml of 1 in (50%vol methanol/water mixture):

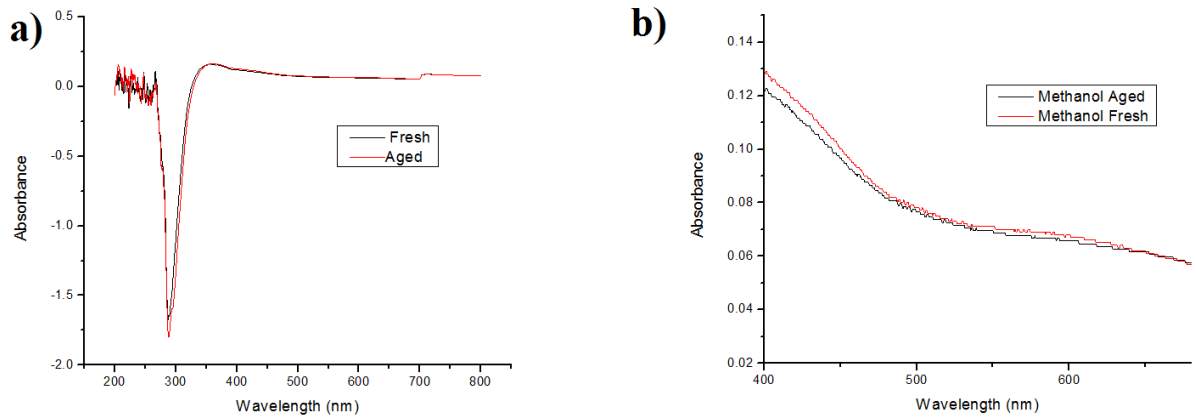

Figure S5. a) UV-VIS spectra of the sample in 50% methanol/water mixtures. b) Zooming in the spectra at the range of (400-700) the plots look very similar to figure S5 and S6 in the ESI.

Since the spectra in figure S5 also look the same and the sample had no color change, it can be concluded that **1** is stable in water methanol mixtures.

TEM images for Acetone/water mixtures

a) 50% acetone

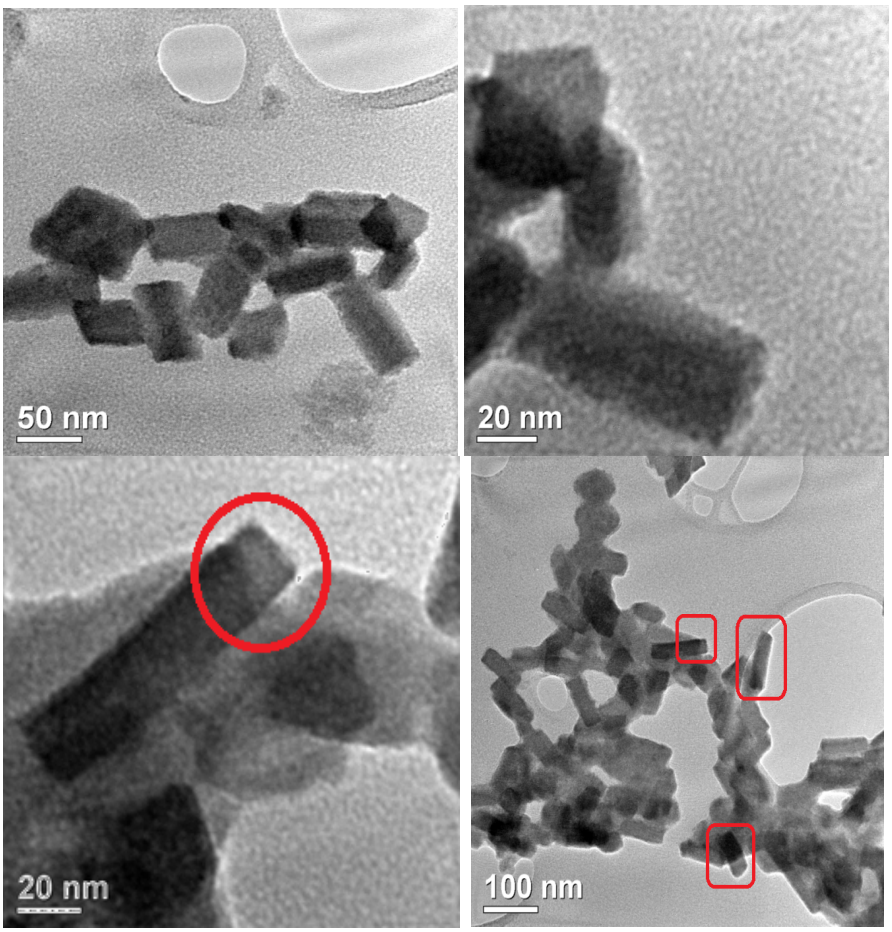

Figure S6. Different TEM images for the 50%acetone/water mixture showing rod like structures. The red color highlights the hollow character of the rods (transparency).

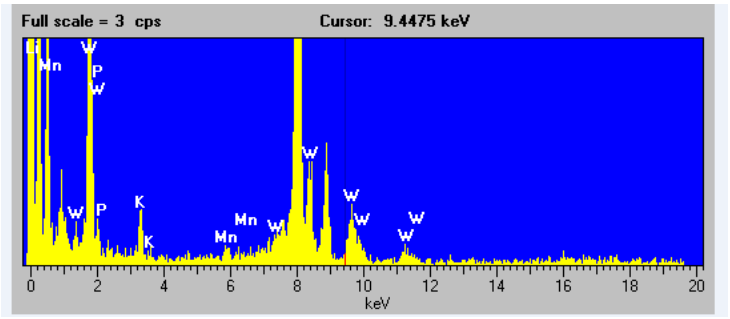

Figure S7. EDS taken under TEM showing various elemental components of 1 in 50%acetone/water mixture

b) 60% acetone

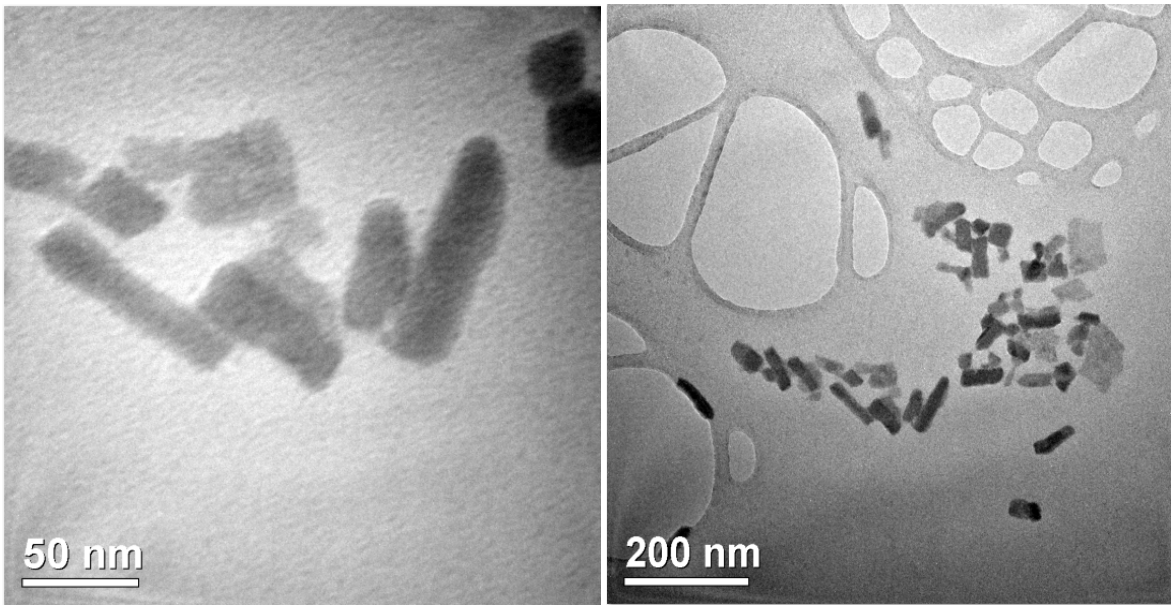

Figure S8. Different TEM images for the 60%acetone/water mixture showing rod like structures

c) 70% acetone

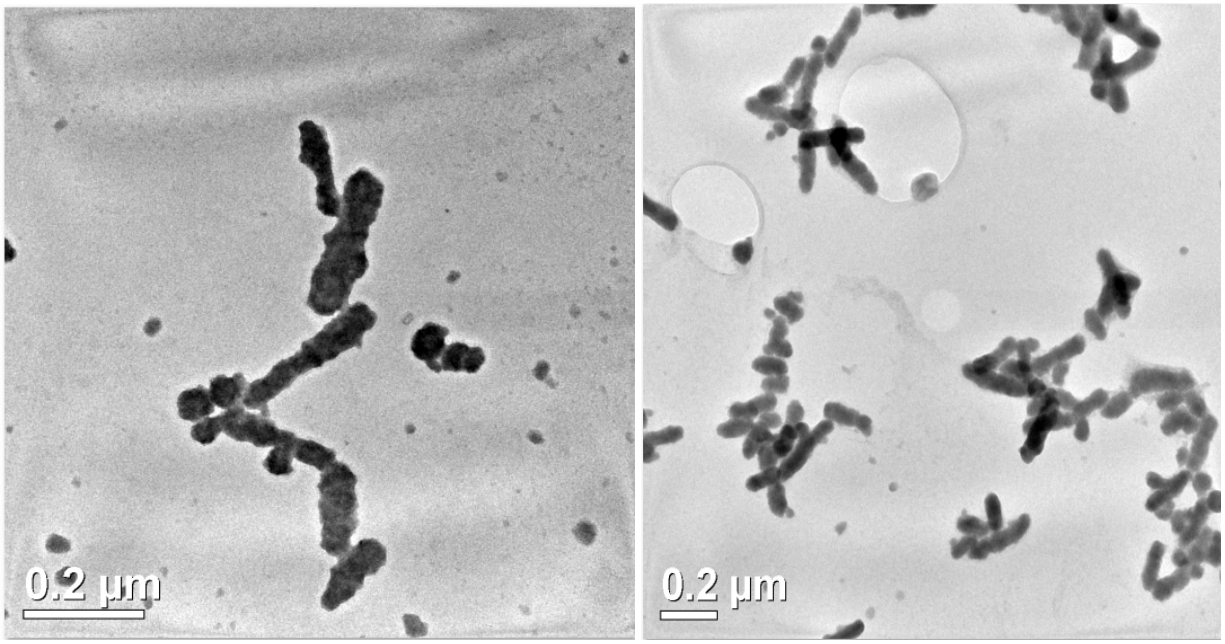

Figure S9. Different TEM images for the 60%acetone/water mixture showing rod like structures

Calculating Radius of gyration from TEM image using ImagJ software[2]

10 different rods were selected from figure S12 and the length and the diameter were measured using ImageJ.

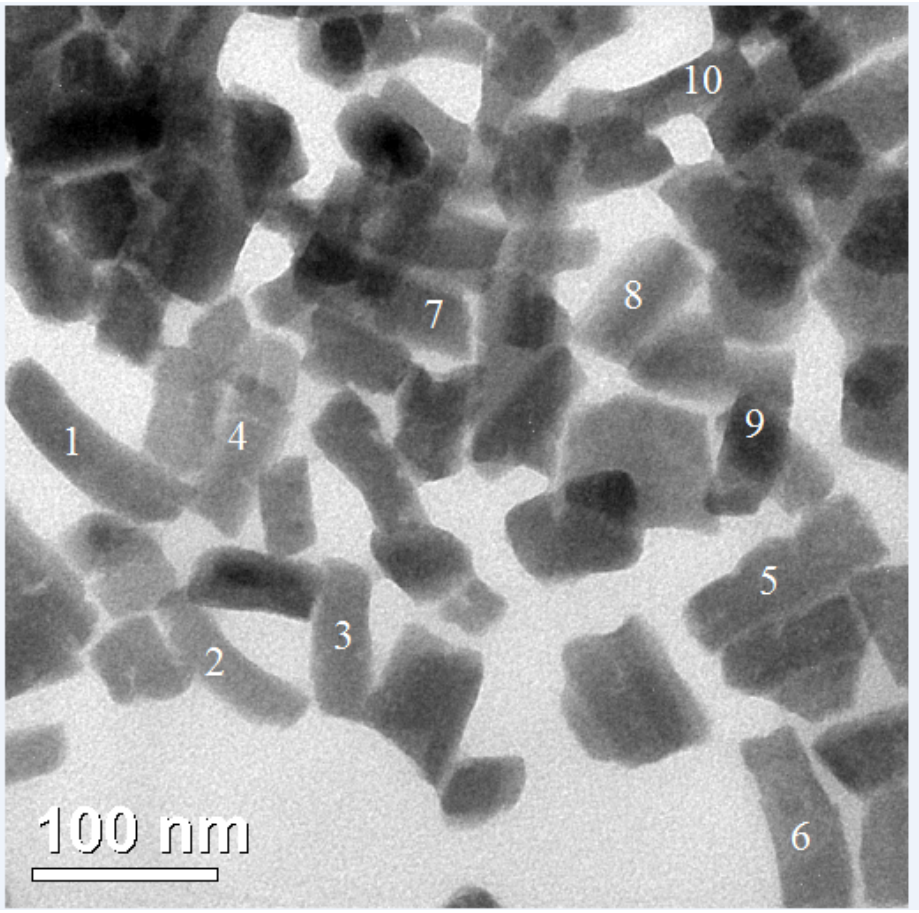

Figure S10. Rods in 50% acetone/water mixture. 10 rods selected for calculations

The average length (l) = (99.91 ± 8.27)*nm*
The average radius (r) = (14.16± 1.22)*nm*

The radius of gyration of a rod can be calculated using equation (1)

$$R_g^2 = \frac{l^2}{12} + r^2 \qquad (1)$$

Substituting r and l in equation 1 and taking the square root results in R_g=32 ± 5*nm*

TEM images for Methanol/Water mixtures

a) 100% Methanol:

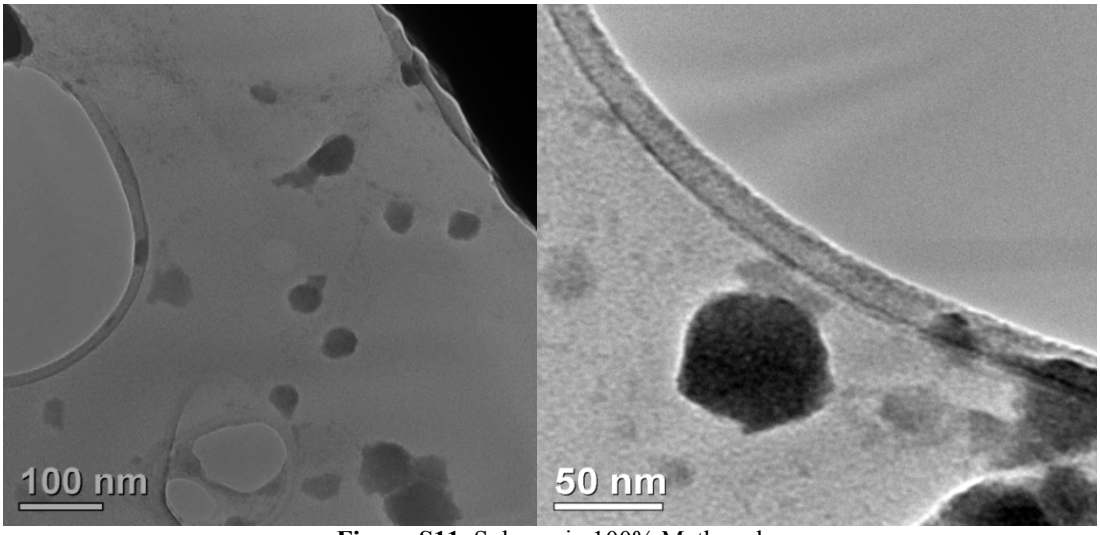

Figure S11. Spheres in 100% Methanol

b) 50% Methanol

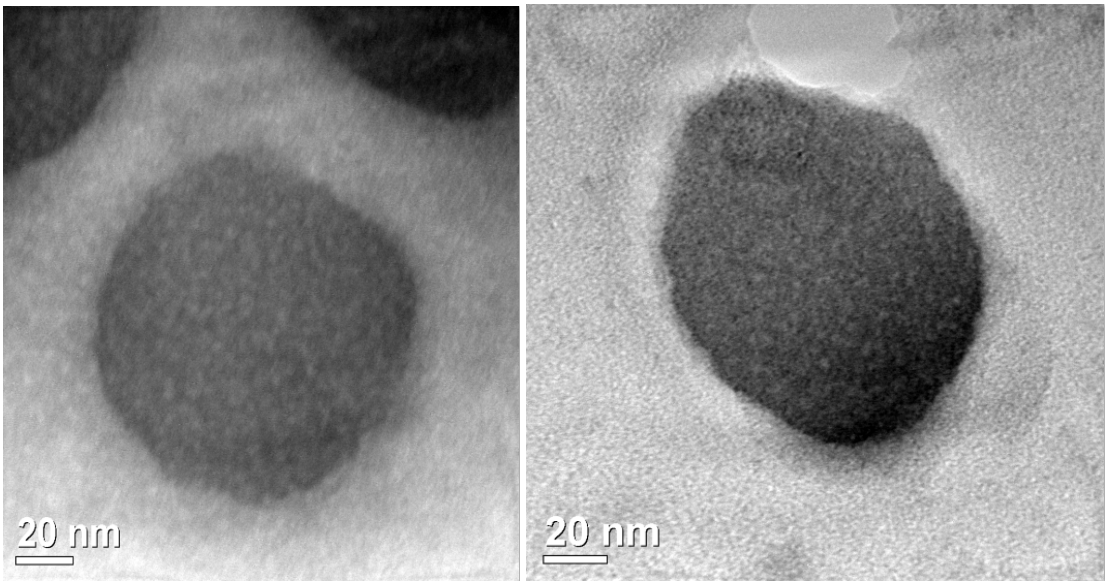

Figure S12. Spheres in 50% Methanol.

TEM images for Samples in 50% CH_3OD/D_2O

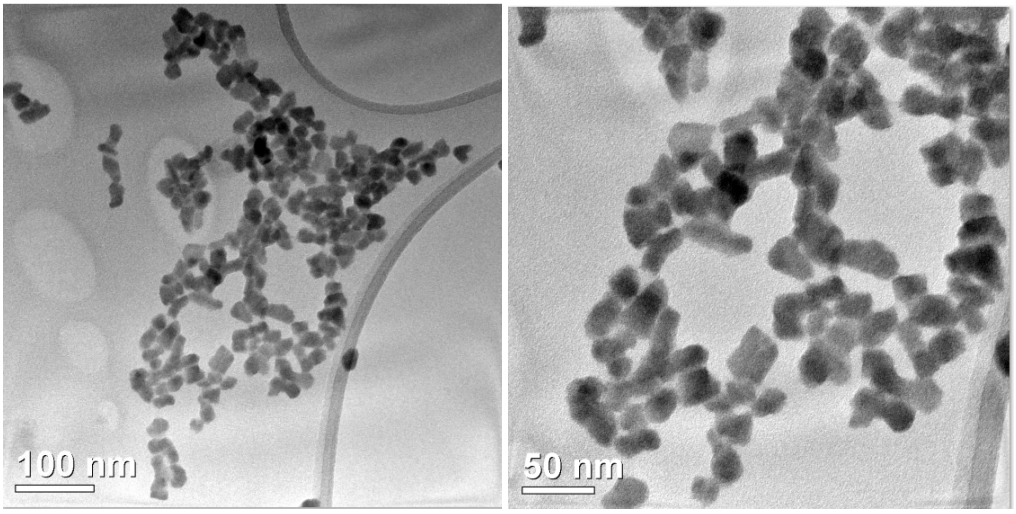

Figure S13. Rods in 50% CH_3OD/D_2O

Anisotropic Surface Charge Density Distribution around the POM:

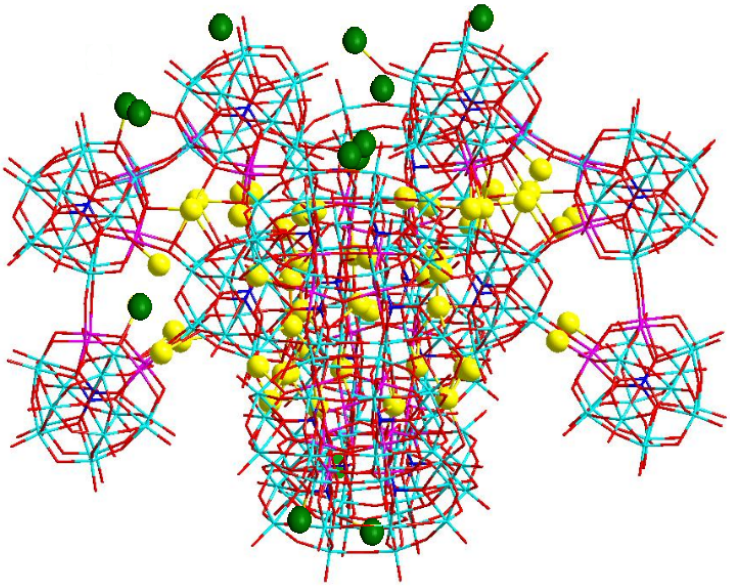

Figure S14. Structure of **1,** showing anisotropic distribution of the potassium (green and yellow) counterions around the POM. The green spheres are counterions distributed on the outer surface of the POM and are essential for self-assembly. The yellow spheres are embedded within the structure and do not contribute to the surface charge density.

It can be seen that the distribution of the potassium counterions (green) is anisotropic.

Static and Dynamic Light Scattering Plots for the Rodlike Structures in 50%Acetone Solution

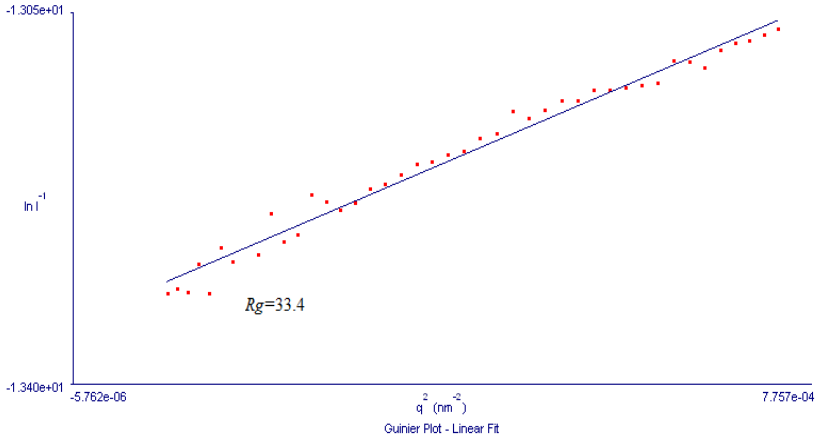

Figure S15. The Guinier plot for the rods in 50% Acetone/water mixtures.

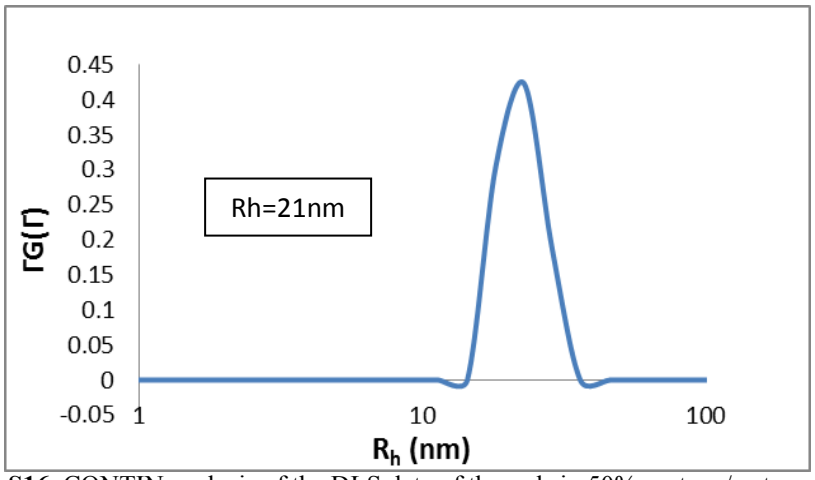

Figure S16. CONTIN analysis of the DLS data of the rods in 50% acetone/water mixture.

IR spectra to further prove stability of the clusters in 80% methanol/water mixtures and 50% acetone water mixtures by comparing freshly prepared sample with a sample that is 6 months old.

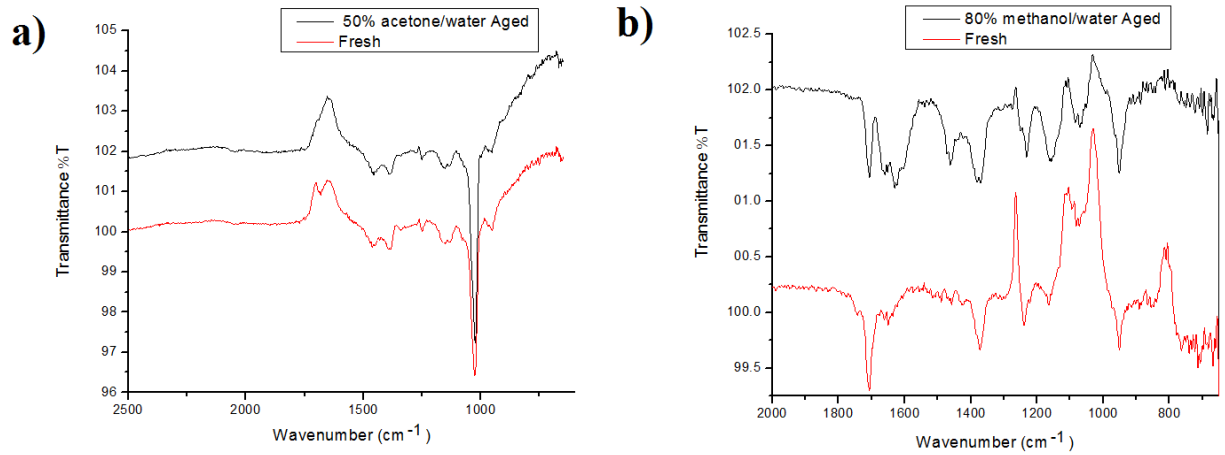

Figure S17. a) IR spectra of 0.2mg/ml POM in 50% acetone water mixture freshly prepared vs. a sample that is 6 months old. b) IR spectra of 0.2mg/ml POM in 80% methanol/water mixture freshly prepared vs. a sample that is 6 months old.

One can see the same features in the IR spectra for the freshly prepared sample and the sample that was prepared six months prior. This indicates that the clusters remain stable in solution.

Diffraction Studies

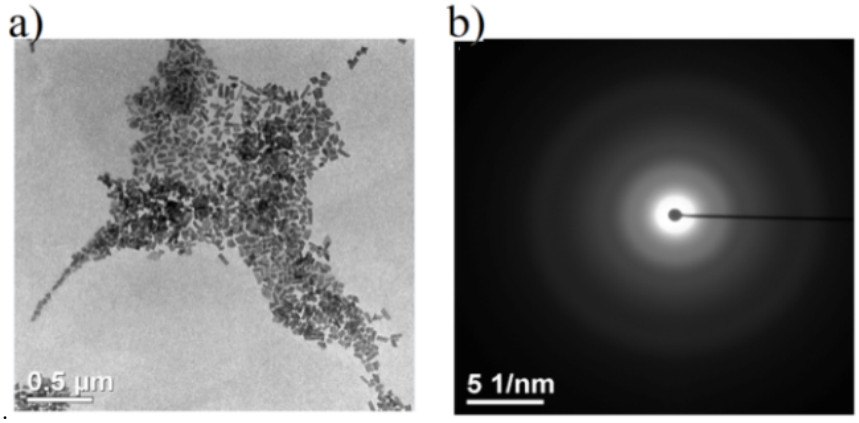

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Fig.S18 a) TEM image showing nano rods in 50% acetone/water mixtures b) Selected area diffraction of the rods indicating that they are not nano-crystals.

REFERENCES

(1) Fang, X.; Kögerler, P.; Furukawa, Y.; Speldrich, M.; Luban, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 5212.

(2) Rasband, W. S. In http://imagej.nih.gov/ij/; U.S. National Institute of Health: Bethesda, Maryland, 1997-2011.