Supporting Information

Visible Light Induced Synthesis of Fluorescent Silver Clusters in Reverse Micelles

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1. Experimental procedure for synthesis of the Ag clusters:

SDBIL surfactant was synthesized in the laboratory following the reported procedure.¹ For the preparation of nanoclusters, silver acetate (CH₃COOAg, 50 mg) was added to a previously prepared solution of SDBIL (33 mg) in 100 ml of dichloromethane. The mixture was than exposed to visible light and stirred under nitrogen atmosphere for 24 hours at room temperature ($\sim 25^{\circ}$ C). The color of the solution changed from colorless to orange-red indicating formation of Ag clusters. The UV-Vis spectrum of the as-prepared Ag clusters (Fig. 1) exhibits well defined stepwise absorption bands at ~ 366 , 408, 460, 580 and 630 nm. The Ag cluster solution was than centrifuged at 15000 rpm for 15 minutes to remove the excess CH₃COOAg (sparingly soluble in dichloromethane). The UV-Vis spectrum of the Ag clusters after centrifugation does not change (including relative intensity of 408 nm peak) after centrifugation suggesting that small Ag clusters are exclusively formed during the synthesis. To remove the organic impurities (excess SDBIL and byproducts if any), dichloromethane was removed in a rotary evaporator and the dried sample was washed with acetonitile twice. The purified clusters were then redispersed in either dichloromethane or toluene.

2. Materials and Methods

All the chemicals and reagents were purchased from Aldrich and used as received. Nanopure water (resistivity 18.2 MU cm) was produced with a Barnstead NANOpure DI water system. All glassware was thoroughly cleaned with aqua regia (HCl : HNO_3 3 : 1 vol%), rinsed with copious amounts of Nanopure water, and then dried in an oven prior to use.

All UV-vis absorption spectra were recorded in the range of 190–1100 nm using a Hewlett-Packard (HP) 8543 diode array spectrophotometer. Fluorescence spectra and fluorescence lifetime were measured in a FluoroLog TCSPC Spectrofluorometer (Horiba). Mass spectrometry analyses were performed in

electrospray ionization (ESI) mode with an Agilent electrospray (ESI)-TOF mass spectrometer. Transmission electron microscopy (TEM) imaging of Ag nanoclusters was performed with a H7100 Hitachi TEM microscope operated at 75 kV. ¹H and ¹³C NMR spectra were recorded in a 400 MHz NMR Spectrometer (Bruker) using CDCl₃ solvent. Size of the reverse micelles was measured using dynamic light scattering (DLS) technique by Zetasizer Nano ZS instrument (Malvern).

3. Reference:

1. A. Mohanty, J. Dey, Langmuir, 2007, 23, 1033.



Figure S1. Emission spectra of Ag₁₀ clusters in CH₂Cl₂ at different excitation wavelengths.



Figure S2. Absorption and emission spectra of pure SDBIL and absorption spectrum of Ag_{10} Cluster in CH_2Cl_2 solvent.



Figure S3. Emission spectrum of Ag_{10} cluster before and after addition of 1N HCl in CH_2Cl_2 solvent. Inset: Photograph of the Ag_{10} cluster solution before and after HCl addition.



Figure S4. Fluorescence intensity decay profile of Ag_{10} clusters. Inset: residuals of the fittings.



Figure S5. Size distribution of SDBIL reverse micelles in dichloromethane measured by dynamic light scattering technique.



Figure S6. ¹H NMR spectra of the side products produced (blue) during Ag_{10} synthesis and pure SDBIL (red).





Figure S7. ¹H NMR (A) and ¹³C NMR (B) spectra of Ag_{10} clusters showing broadening (A, encircled) and suppression (B, encircled) of peaks adjacent to carbonyl carbon.