Supporting Information

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SI Text

The homologous propylamines were synthesized and characterized in accordance with published procedures (1). Homologous ethyleneamines, spermidine (SPN), spermine (SPDN), and *N*,*N*′-(di-3-aminopropyl)-1,3-diaminopropanes (C3N3-0, C3N3-1, and C3N3-4) were purchased from Sigma Aldrich and used without further treatment. Dipotassium tris(1,2-benzenediolato-O,O′)silicate was purchased from Sigma Aldrich and recrystallized from methanol before use. Reagents for the molybdenum blue assay [ammonium molybdate·$4H_2O$, oxalic acid, 4-methylaminophenol sulfate, sodium sulfite, hydrochloric acid (35%) and sulfuric acid (98%)] were purchased from Sigma Aldrich, Fisher, or Acros Chemicals and used without further treatment.

We prepared 30 mM solutions of monosilicic acid by the dissociation of dipotassium tris(1,2-benzenediolato-O,O′)silicate with 2 M hydrochloric acid. At reduced pH, aqueous solutions of dipotassium tris(1,2-benzenediolato-O,O′)silicate rapidly dissociate to give monosilicic acid and no other silicate species. Also, at the concentration chosen, the condensation of these solutions is slow enough to allow us to monitor the early third-order kinetic stage and to reach the equilibrium state within 24 h. The polyamines were added at a maintained Si/N ratio of 1:1 to compare the effects of the amine functionality. The level of acid addition was predetermined to take into account the basicity of the polyamines added to give a final pH of 6.8 ± 0.05, unless otherwise stated. The rate of condensation was determined by the well established molybdenum blue spectrometric assay method (2–4). Photon correlation spectroscopy (PCS) of amine microemulsions was carried out by using a Coulter N4 plus photon correlation spectrometer with a He–Ne (632.8 nm) laser supply. Polyamine solutions were prepared at 30 mM relative to amine content in filtered deionized water, and pH adjustments were made with dilute hydrochloric acid. Ionic strength was maintained throughout at 0.06 molal by the use of potassium chloride. All PCS measurements were carried out in a 1-cm cuvette at an angle of 90° and at 293 K. Measurements obtained were averages of the data collected over intervals of 5 min. The stability of the droplets was assessed in terms of percent error of the data from the average measured diameter. Rapidly changing or coalescing and breaking droplets, that is, less cohesive ones (on the millisecond scale) would be expected to show a greater error margin than those that remain relatively unchanged during the measurement process.

The siliceous products were isolated by centrifugation, water washing (three times), and finally lyophilized after rapid cooling with liquid nitrogen. For scanning electron microscopy (SEM) analysis the lyophilized samples were placed on a double-sided sticky carbon tape mounted on aluminum sample holders and then sputter-coated with gold; the analysis was performed by using a JEOL JSM-840A. Samples for transmission electron microscopy (TEM; JEOL 2010) were prepared by dipping sample holder grids in ethanolic suspensions of lyophilized powders followed by drying under air. Nitrogen gas adsorption/desorption performed by using a Quantasorb NOVA 3200e surface area and pore size analyzer used BET (5) analysis to determine the surface areas and BJH (6) analysis for the porosity measurements. Low partial-pressure adsorption is assumed to be caused by microporosity, but because of the limitations of the nitrogen gas adsorption technique, actual pore dimensions could not be determined (7). Samples were heat-treated to remove organic content in a muffle furnace at a heating rate of 20°C min^{-1} for 1 h at 650°C. The SPARC online pK_a tool was used to predict theoretically the protonation behavior of amine molecules under consideration (http://ibmlc2.chem.uga.edu/sparc) which was compared with experimentally derived pK_a data for the amines used. Agreement between the SPARC theoretical data and the experimentally derived potentiometric data were within 2% for all systems studied (data not shown).

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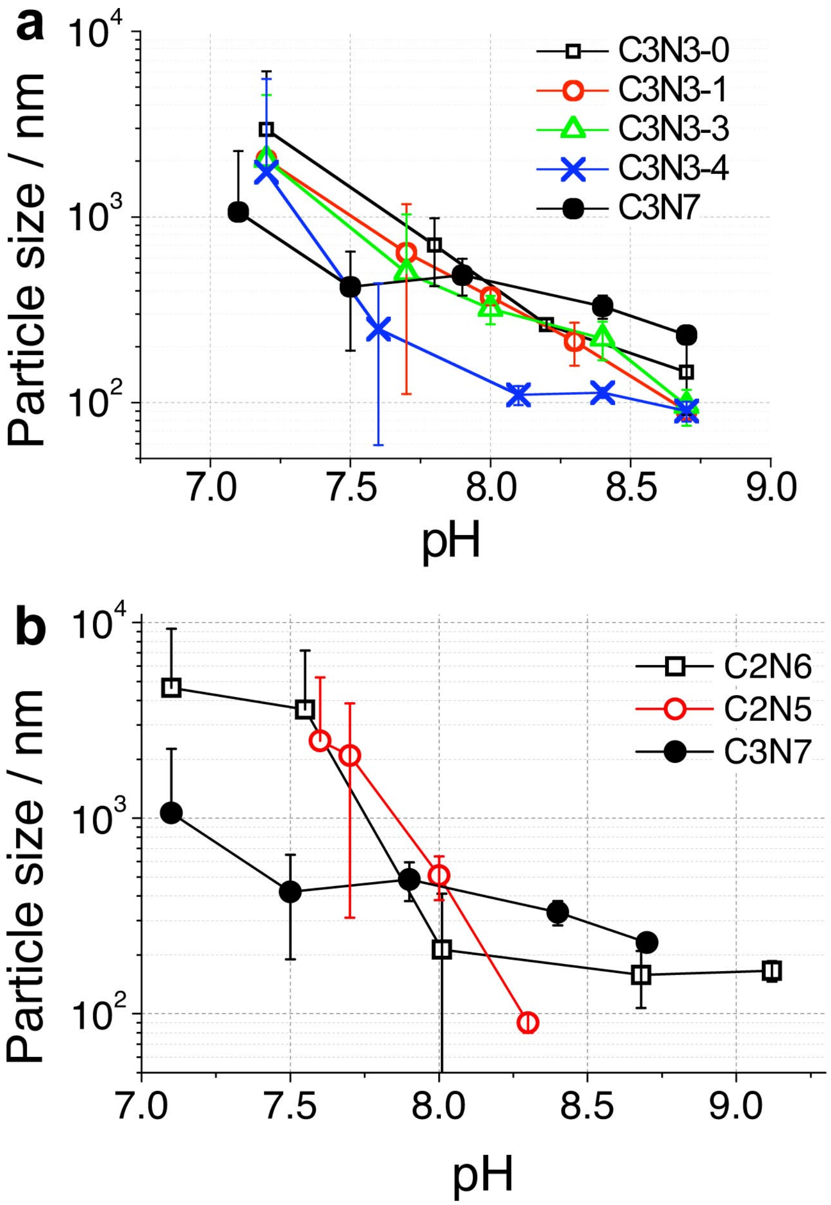

Fig. S1. Microemulsion droplet size determined by dynamic light scattering on solutions of methylated C3N3s (*a*) and C3 series (*b*). C3N7 is plotted in both graphs for comparison with Fig. 5.