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Supplemental Information

Putrescine Homologues Control Silica Morphogenesis by Electrostatic Interactions and the Hydrophobic Effect

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Experimental Section

To a 30 mM solution of the silicon complex, 15 mM solution of respective diamine were added and the pH was adjusted to ca. 6.8 using a known amount of 2 M HCl in order to dissociate the silicon complex (the undissociated complex was found to be < 2% by ¹H-NMR) as described previously^{S1,S2} and to protonate the diamine. It is noted that previous related studies on silica formation using diatom bioextracts employed higher (often 100 mM) silicon concentrations.^{S3,S4} In addition, for these studies, in contrast to our experiments, the starting material was a mixture of pre-condensed polysilicic acid instead of orthosilicic acid.^{S1} Condensation would be expected to be faster for the model studies performed at higher silicic acid concentrations^{S3,S4} and our experiments were conducted at lower concentrations in order to slow down the process to enable us to separate the processes occurring during silica formation. For kinetic analysis, 10 µL aliquots of the reaction mixture were taken at given time intervals and mixed into molybdic acid solutions, which were then reduced to give blue coloured silicomolybdous acid complex solution; the blue colour was measured at 810 nm using a UV-VIS spectrometer and the corresponding silicic acid concentration was calculated using a calibration curve.^{S1} Aggregation behaviour was monitored over 40 hours using Photon Correlation Spectroscopy (PCS) by preparing samples as described above and filtering through a 200 nm membrane into a 1 cm polymethylmethacrylate cell. Silica samples were isolated by centrifugation after a given time, washed three times with doubly distilled water and lyophilised for further analysis. For SEM and TEM studies, lyophilised samples were dispersed onto sample holders and were sputter coated with gold using argon plasma. Nitrogen gas adsorption/desorption analysis was carried out using a Quantachrome

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Nova3200e surface area and pore size analyser. Samples were first degassed overnight at 150° C under vacuum. Surface areas were then determined *via* the BET method^{S5} where nitrogen is assumed to have a cross-sectional area of 0.16 nm², over the range of relative pressures 0.05 - 0.3 at which the monolayer is assumed to assemble. Pore radii were determined by the BJH method^{S6} using the desorption branch of the isotherm. This method assumes cylindrical pores. Isotherms obtained were typical of type IV with hysteresis loops characteristic of cylindrical pores with possibly some partial closure at the open ends. The entrapped organic material in silica was determined by thermogravimetric analysis under nitrogen as the weight loss between temperatures 500-800 K not attributable to silanol condensation.

S2. C. C. Harrison, N. Loton, J. Chem Soc. Faraday Trans., 1995, 91, 4287.

S4. M. R. Knecht, D. W. Wright, Langmuir, 2004, 20, 4728.

S1. D. Belton, G. Paine, S. V. Patwardhan, C. C. Perry, J. Mater. Chem., 2004, 14, 2231.

S3. N. Kroger, S. Lorenz, E. Brunner, M. Sumper, Science, 2002, 298, 584.

S5. S. Brunauer, P. H. Emmett, E. Teller, J. Am. Chem. Soc., 1938, 60, 309.

S6. E. P. Barrett, L. G. Joyner, P. P. Halenda, J. Am. Chem. Soc., 1951, 73, 373.

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(b) Typical pore distribution data obtained from nitrogen adsorption on lyophilised diamine-mediated silica at 18 h and 7 days.



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(d) Pore size analysis of diamine-mediated silica as a function of time.



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(e) Pore volume data of diamine-mediated silica plotted as a function of time.

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Figure S3 Representative Transmission Electron Microscopy images obtained from selected samples (DA4, DA6, and DA8). EDS spectra are shown for respective samples as inserts. Bars as indicated on figures.



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Figure S4. Representative FTIR data obtained from silica with and without diamines.

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Figure S5 Scanning electron microscopy data from silica samples collected at $t_{1/2}$, 24 h and 7 days in the presence of 1,2 diaminoethane (DA2), 1,4 diaminobutane (DA4), 1,6 diaminohexane (DA6), 1,8 diaminooctane (DA8), 1,10 diaminodecane (DA10) and blank. Bar = 500 nm except 1 μ m for blank and DA2 7 day sample.

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