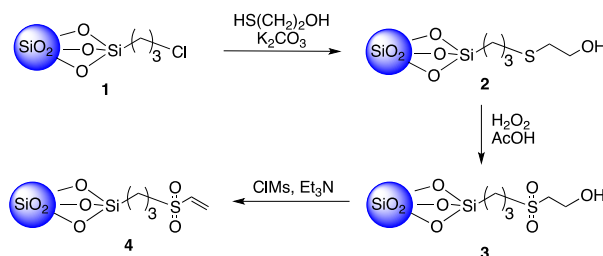


A Bioinspired Hybrid Silica-Protein Material as Antimicrobial Agent by Iron Uptake

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Scheme S11. Synthetic route for the preparation of the vinyl sulfone silica.

Materials and methods

Preparation of mercaptoethanol functionalized silica 2 (Scheme 1). Chloro functionalized silica 1 (5.0 g) was suspended in acetonitrile (40 mL) and then 2-mercaptoethanol (3.5 mL) and potassium carbonate (6.9 g) were added. The magnetically stirred suspension was heated at 50 °C under an Ar atmosphere for 8 h. The reaction mixture was filtered and the white powder washed with hot water (2 x 20 mL) and finally with acetone (2 x 20 mL) and dried under vacuum (1mmHg) at 50 °C for 16 h giving the mercaptoethanol functionalized silica 2 (4.2 g).

Preparation of ethanol sulfone functionalized silica 3 (Scheme 1). Mercaptoethanol functionalized silica 2 (3.0 g) was suspended in acetic acid (6.0 mL) and then hydrogen peroxide 33% (15.0 mL) was added. The magnetically stirred reaction mixture was kept at room temperature for 24 h in the absence of light. After filtration, the white powder was washed with

water (2 x 20 mL), methanol (2 x 20 mL) and finally acetone (2 x 20 mL), and dried under vacuum (1 mmHg) at 50 °C for 16 h giving the ethanol sulfone functionalized silica **3** (2.9 g)

Preparation of vinyl sulfone functionalized silica 4 (Scheme 1). Ethanol sulfone functionalized silica **3** (2.5 g) was suspended in anhydrous dichloromethane (40 mL). The magnetically stirred suspension was cooled at 0 °C by means of an ice bath. Methanesulfonyl chloride (0.9 mL) and triethylamine (3.5 ml) were then added. After the addition of the reagents, the reaction mixture was kept at room temperature for 7 h and then filtered. The white powder was washed with methanol (2 x 20 mL) and acetone (2 x 20 mL), and dried under vacuum (1mm Hg) at 50 °C for 16 h giving the vinyl sulfone functionalized silica **4** (2.4 g).

Proteins. Recombinant H apoferritins were obtained from Molirom and was exhaustively dialyzed against milli-Q water using a Spectra/Por Float-A-Lyzer with a molecular weight cut-off (MWCO) of 300.000 Da. Horse spleen apoferritin and human apolactoferrin were purchased from Sigma and used as received.