Covalent coupling of an organic chromophore into functionalized MCM-41 mesophases by template-directed co-condensation

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An ordered organo-silica-surfactant mesophase containing a covalently-linked chromophore was synthesized with MCM-41-type architecture by template-directed co-condensation of tetraethoxysilane and 3-(2,4-dinitrophenylamino)propyl-(triethoxy)silane: a dye-functionalized mesoporous silica with hexagonal order was produced by surfactant extraction of the as-synthesized material prepared under acidic conditions.

The synthesis and properties of ordered mesostructured and mesoporous inorganic-based materials are currently receiving much attention.[1] The ability to prepare these organized materials depends on the use of surfactant,[2,3] block copolymer,[4,5] microemulsion,[6,7] colloidal[8] or bacterial[9] templates which pattern the deposition of the mineral phase by physical and chemical interactions at the inorganic-organic interface. More chemically complex ordered mesophases are being prepared either by post-synthetic grafting[10,11] or *via* direct routes involving the co-condensation of tetraalkoxysilanes and organo-functionalized trialkoxysilanes.[12–16] Such hybrid materials are intrinsically interesting as new forms of organized matter, as well as being of potential technical importance in catalysis[16,17] metal-ion extraction[18] and adsorption processes.[19]

Previously, we have described the synthesis of a range of organo-silica-surfactant mesophases with MCM-41 architectures containing covalently-linked chemically active groups such as alkyl, aryl, allyl, thiol, amino, epoxy, or imidazole moieties.[12,13] Here we extend this approach and show that an intact chromophore can be covalently incorporated into the MCM-41 mesostructure by direct chemical synthesis involving co-condensation of tetraethoxysilane (TEOS) and 3-(2,4-dinitrophenylamino)propyl(triethoxy)silane (DNPTES) in the presence of hexadecyl(trimethyl)ammonium bromide (C_{16}TMABr) micelles. Although a previous report has described the synthesis of phthalocyanine-doped MCM-41, the chromophore was present as an additive within the surfactant micelles.[20] Post-synthetic grafting of a Schiff-base moiety to the surface of MCM-41 silica produced a mesoporous material which showed a characteristic absorption spectrum for the organic ligand.[21] Thus, to the best of our knowledge, the work reported here is the first example of the direct synthesis of an ordered mesoporous silica containing covalently linked organic chromophore functionalities.

A silica-surfactant mesophase was synthesised from either an alkaline or acidic mixture containing the following molar composition, respectively: C_{16}TMABr:NaOH:TEOS:DNPTES:H_2O = 0.12:0.5:0.9:0.1:130 and C_{16}TMABr:HCl:TEOS:DNPTES:H_2O = 0.12:9.2:0.9:0.1:130.‡ In both methods, small-angle X-ray powder diffraction (SAXRD) of the bright yellow as-synthesized materials gave peaks corresponding to hexagonally-ordered organo-silica-surfactant mesophases with unit cell parameters of 4.55 (basic mixture) and 4.31 nm (acidic mixture)§ (Fig. 1). The product prepared under basic conditions showed sharper reflections than the analogous material synthesized at low pH. Acid extraction of the C_{16}TMABr surfactant template from the latter was achieved
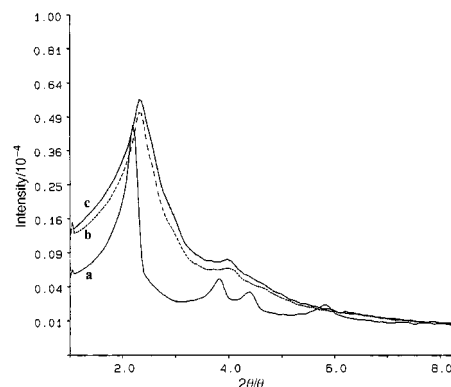

Fig. 1 SAXRD profiles for dye-functionalized ordered silica mesophases: (a) as-synthesized material prepared at high pH, (b) as-synthesized material prepared at low pH, and (c) after surfactant-extraction of material prepared under acidic conditions

without loss of the hexagonally ordered MCM-41 structure or contraction in the unit cell parameter (Fig. 1), to produce a dye-functionalized inorganic replica with channel-like mesopores.§ In contrast, similar treatment of the product prepared at high pH resulted in a disordered organo-silica hybrid. TEM images, which showed hexagonal sets of lattice fringes, as well as parallel fringes corresponding to side-on projections of the mesostructure (Fig. 2), were consistent with the long range order parameters determined by SAXRD.

Nitrogen adsorption studies confirmed that surfactant extraction of the dye-functionalized material produced under acidic conditions was predominantly mesoporous. A type IV isotherm, with a distinct capillary condensation step that was characteristic of a MCM-41 mesoporous material with a relatively large pore size distribution, was observed. The BET surface area was 760 $m^2 g^{-1}$, with an average BJH pore diameter of 2 nm. These values are less than those typically reported for pure MCM-41 silicas. As no significant lattice contraction was observed by
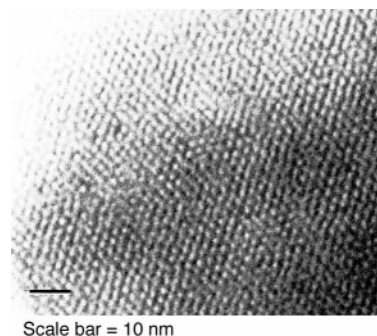

Scale bar = 10 nm

Fig. 2 TEM image of as-synthesized dye-functionalized MCM-41 material showing hexagonally ordered mesostructure. Scale bar = 10 nm.

SAXRD, we attribute this reduced porosity to pendent chromophore moieties that extend into the channel spaces.

^{29}Si DP MAS NMR spectroscopy showed distinct resonances for siloxane [$Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 2$–4] and organosiloxane [$T^m = RSi(OSi)_m(OH)_{3-m}$, $m = 1$–3] centres in both the as-synthesized and surfactant-extracted materials.¶ The predominance of T^3 compared with T^2 and T^1 organosiloxane centres indicated that condensation of the organo-functionality in the MCM-41 wall structure was extensive. ^{13}C CP MAS NMR spectroscopy indicated that the dinitrophenylaminopropyl chromophore was covalently linked into the mesophase as an intact unmodified moiety both before and after surfactant extraction.|| This was consistent with FTIR spectra of the as-synthesised and surfactant-extracted materials which showed characteristic Si–O–Si framework vibrations [1050 (large band), 1200 (shoulder), 480, 750 and 900 cm^{-1}], a Si–C band at 1150 cm^{-1}, as well as vibrations indicative of the chromophore (1338, 1621, 2880–2980, and 3365 cm^{-1}). The intensities of these vibrations were equal in the as-synthesised and surfactant-extracted materials, suggesting no disintegration or loss of the dinitrophenylaminopropyl functionality during the solvent extraction procedure. CHN analysis indicated that *ca.* 20 mol% of the dye functionality was incorporated into the MCM-41 structure.

Diffuse reflectance UV–VIS spectroscopy of the as-synthesised materials showed two broad absorbance bands at 317 and 417nm. These bands were characteristic of the *o-* and *p*-nitro groups, respectively, of the chromophore,[22] and indicated that the optical properties of the dye moiety were maintained when covalently linked into the MCM-41 structure. Extraction of the surfactant resulted in a shift in the position of the band with highest intensity from 317 to 341nm, indicating that the dinitrophenylaminopropyl groups were preferentially located in the pore spaces rather than internalized within the mineral walls. This band was observed at 350 nm for both an acetone solution of non-hydrolysed DNPTES and a sol-gel film of amorphous silica containing hydrolysed DNPTES, suggesting that the blue shift observed for the as-synthesized MCM-41 mesophase was due to specific interactions of the organic moiety with the surfactant micelles. As the infrared spectra of the surfactant-extracted and as-synthesized materials were unchanged, protonation of the chromophore can be ruled out as a cause of the shift in the absorption band.

Our results suggest that it should be possible to incorporate a range of organic chromophores into surfactant-silica mesophases and corresponding mesoporous replicas without extensive modification of the optical properties. Although further work is required, the covalent attachment of dye molecules into ordered or semi-ordered porous MCM-type materials could be of general importance in a number of areas. In principle, the organic moieties can be dispersed and isolated from each other, which for some systems, for example with rhodamine derivatives, should minimize intermolecular quenching of fluorescence properties. Furthermore, the combination of mesoporosity and optical properties should give rise to interesting materials, particularly when host–guest interactions are being examined. Similarly, covalently linked chromophores could be used as sensors in separations technologies to detect molecules within the channel-like pores of MCM-41 phases fabricated in the form of thin membranes. Finally, as the optical properties of the chromophore can be highly sensitive to the local environment, such moieties could be used to probe the internal structure and dynamics of silica mesophases in general.

Notes and References

‡ In a typical preparation under alkaline conditions, C$_{16}$TMABr (0.40 g, Aldrich) was dissolved in a solution containing 1.0 M NaOH (5.0 g) and distilled, deionised H$_2$O (17.55 g). TEOS (1.5 g, Aldrich) and DNPTES (0.31 g, Apollo Sci. Ltd) were added, and the mixture stirred for 24 h at room temperature. The solid product was filtered, washed with H$_2$O and dried for 10 h in air. Extraction of the surfactant was performed by stirring a suspension of the solid product (0.99 g dm^{-3}) in 1.0 M HCl in EtOH at 75 °C for 24 h. The extracted material was filtered, washed with EtOH and dried for 10 h at 100 °C *in vacuo.* CHN analysis gave 6.9% (N), 19.2% (C) and 2.8% (H). For preparations under acidic conditions, TEOS (3.43 g) and DNPTES (0.71 g) were added to acetone (1.34 ml) and co-hydrolysed by addition of 3.85 M HCl acid (0.33 ml) (TEOS:DNPTES:acetone:HCl = 0.9:0.1:1.0:1.0). The mixture was stirred for 15 min at room temperature, and the resulting sol added with stirring to 42.8 ml of a solution of C$_{16}$TMABr (18.7 mg ml^{-1}; 51.3 mM) in 3.85 M HCl. The final solution was stirred and heated at 90 °C overnight (16 h). The yellow precipitate was filtered, washed repeatedly with distilled H$_2$O and EtOH, and dried in an oven at 70 °C. Surfactant extraction was performed as described above.

§ SAXRD *d* spacings (*hkl*): DNPTES-MCM (as-synthesized, high pH): 3.95 (100), 2.30 (110), 1.99 (200) and 1.51 nm (210); DNPTES-MCM (as-synthesized, low pH): 3.74 (100), 2.15 (110) and 1.98 nm (200); DNPTES-MCM (surfactant-extracted, low pH): 3.76 (100), 2.20 (110) and 2.00 nm (200). Unit cell parameter, $a = 2d_{100}/\sqrt{3}$.

¶ ^{29}Si DP (direct polarization) MAS NMR data (60 MHz, TMS, 20 °C) for DNPTES-MCM (as-synthesized, high pH): δ -50.9 (T^1, 3.1%), -58.1 (T^2, 4.7%), -66.7 (T^3, 12.5%), -90.3 (Q^2, 7.5%), -98.7 (Q^3, 34.4%), -108.6 (Q^4, 37.9%). For DNPTES-MCM (surfactant-extracted, high pH): δ 58.9 (T^2, 5.0%), -66.9 (T^3, 11.4%), -91.5 (Q^2, 5.9%), -100.6 (Q^3, 37.6%), -109.3 (Q^4, 40.1%).

|| ^{13}C CP MAS NMR data for DNPTES-MCM (as-synthesized, high pH): δ 11.2, 23.0, 46.7, 115.5, 123.1, 129.4, 135.4, 148.6. For DNPTES-MCM (surfactant-extracted, high pH): δ 10.2, 22.6, 46.3, 115.0, 123.4, 129.8 135.5, 148.5.

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