Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Synthesis and grafting of CAN-derived tetravalent cerium alkoxide silylamide precursors onto MCM-41

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Experimental Details

Synthesis of Periodic Mesoporous Silica MCM-41 (Parent Material).

Surfactant $C_{16\text{-}3\text{-}1}$ was recrystallised from a hexane/methanol mix before use. CTMABr (4.27 g, 11.70 mmol) and $C_{16\text{-}3\text{-}1}$ (5.51 g, 10.34 mmol) were dissolved in a mixture of distilled water (280.76 g, 15.6 mol) and Me_4NOH (23.56 g, 67.88 mmol). This mixture was stirred vigorously by an overhead stirrer for 20 mins. TEOS (27.04 g, 129.78 mmol) was added dropwise at ambient temperature over 10 mins. The reaction mixture was stirred for a further 40 mins. This mixture was then filtered under vacuum and the residue resuspended in 350 ml of distilled water. This white solid was hydrothermally annealed at 100 °C for 6 days. This mixture was filtered, dried and calcinated at 450 °C for 24 hr. This as-synthesised material was dehydrated *in vacuo* (270 °C, 10^{-4} Torr 8 hr). The molar composition of the synthesis gel was 0.08:0.08:0.5:120:1 CTMABr:$C_{16\text{-}3\text{-}1}$:Me_4NOH:H_2O:TEOS.

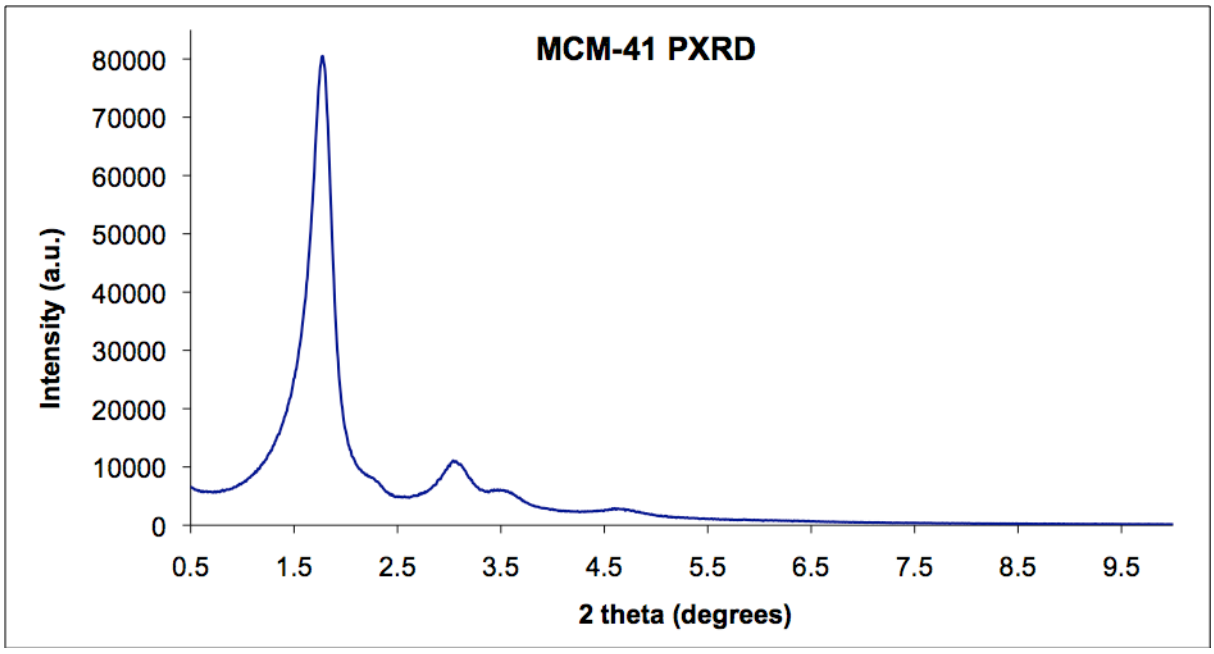

Figure S1. Powder XRD pattern of the parent material MCM-41

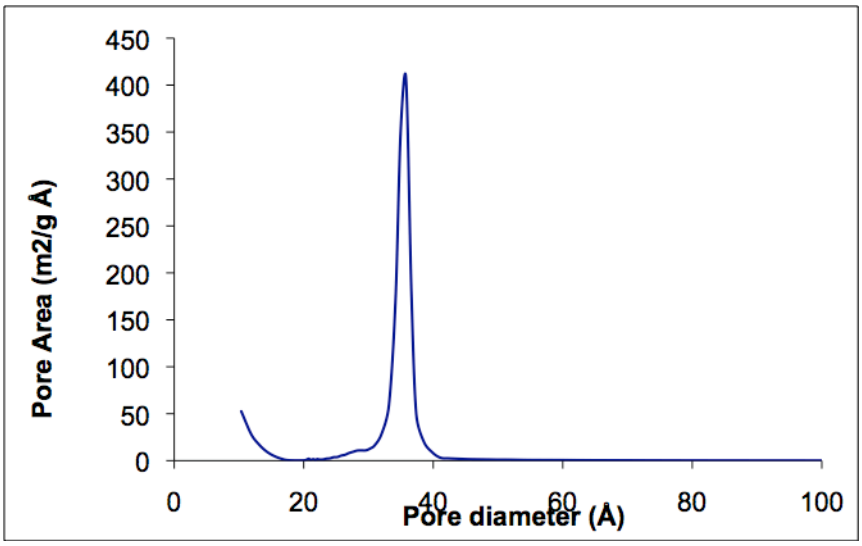

Figure S2. BJH pore size distribution of the parent material MCM-41

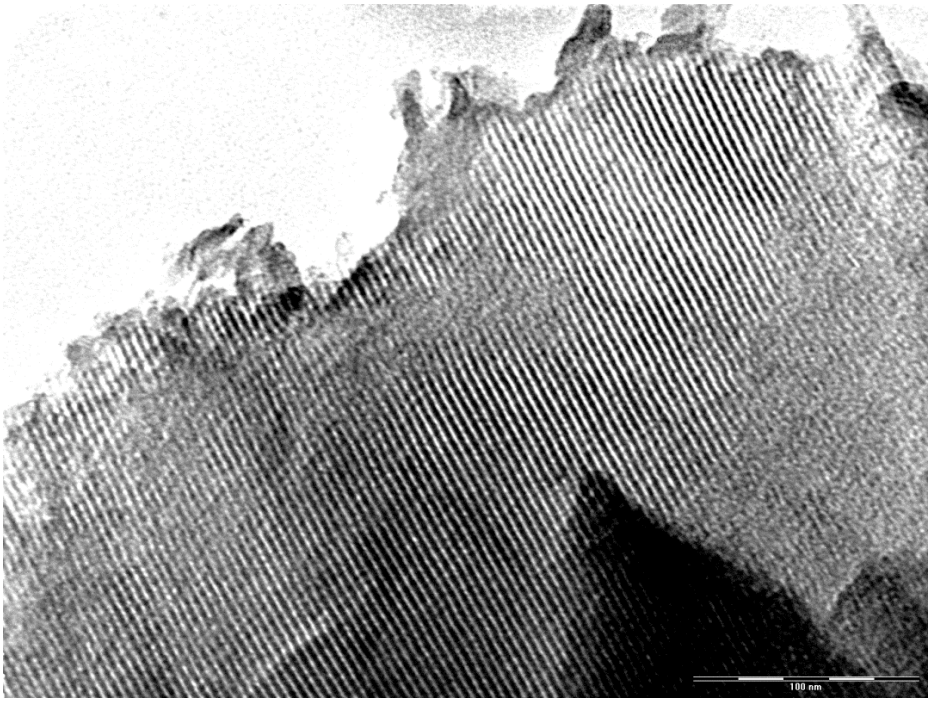

Figure S3. TEM image of the parent material MCM-41

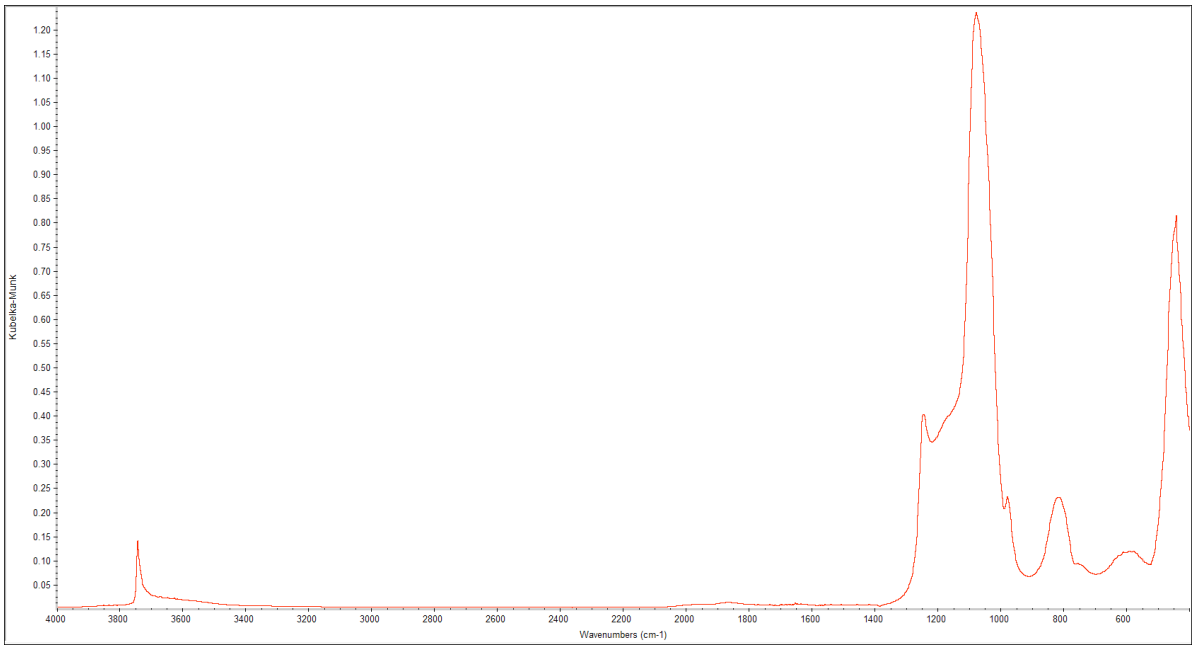

Figure S4. IR spectrum (DRIFT) of the parent material MCM-41 in the range 400-4000 cm^{-1}.

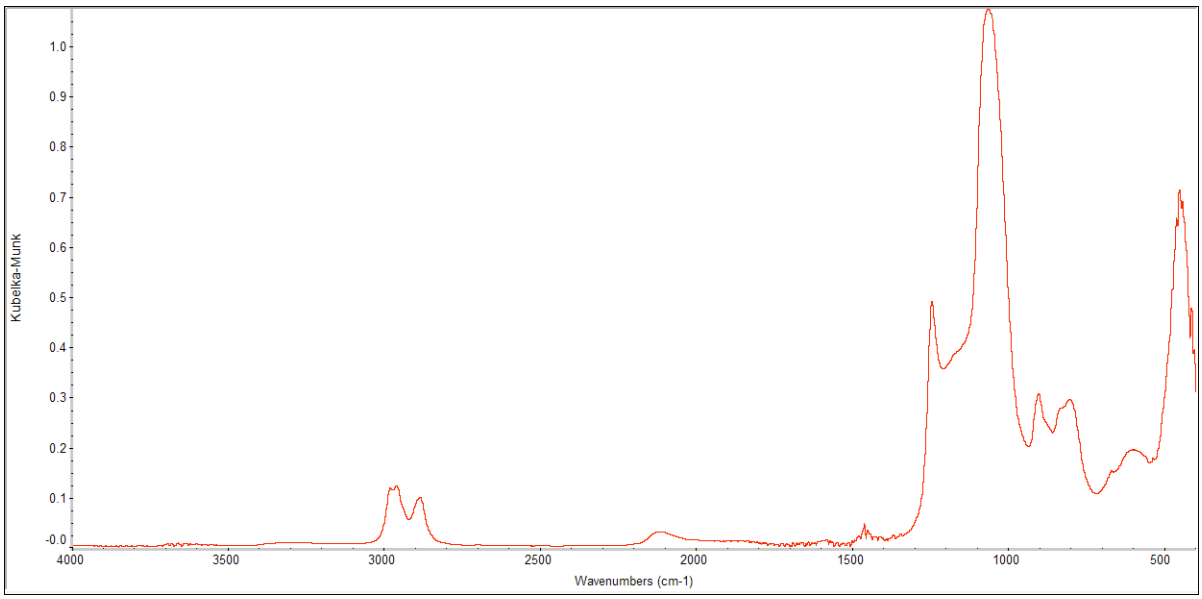

Figure S5. IR spectrum (DRIFT) of the material $Ce[N(SiHMe_2)_2]_4$@MCM-41 (**5**) in the range 400-4000 cm^{-1}.

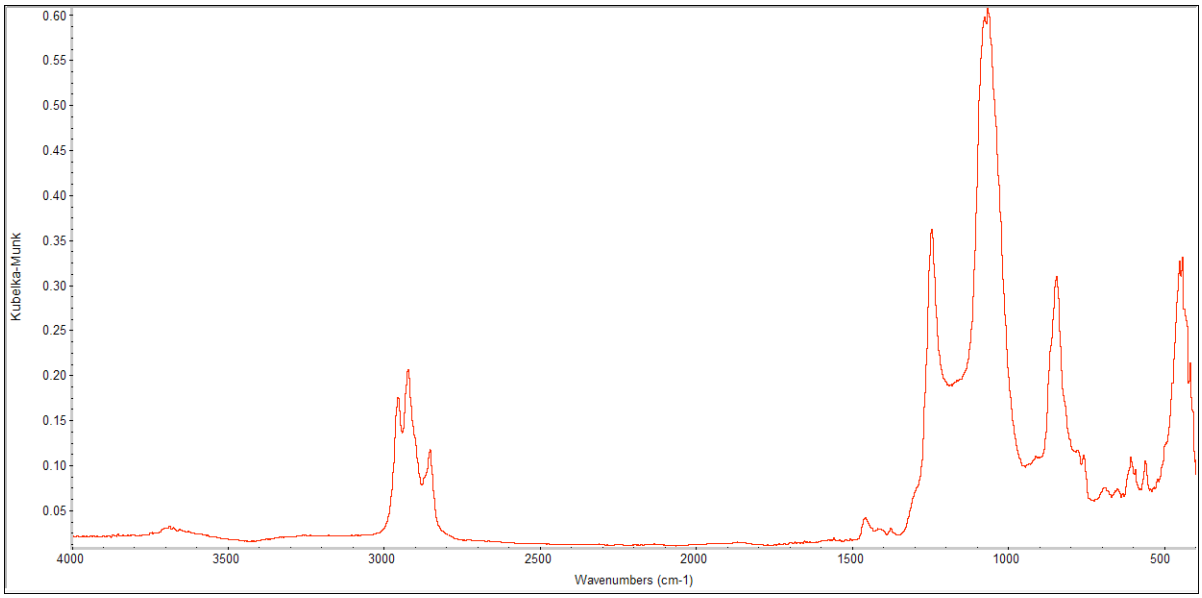

Figure S6. IR spectrum (DRIFT) of the material $Ce[N(SiMe_3)_2]_3Cl$@MCM-41 (**6**) in the range 400-4000 cm^{-1}.

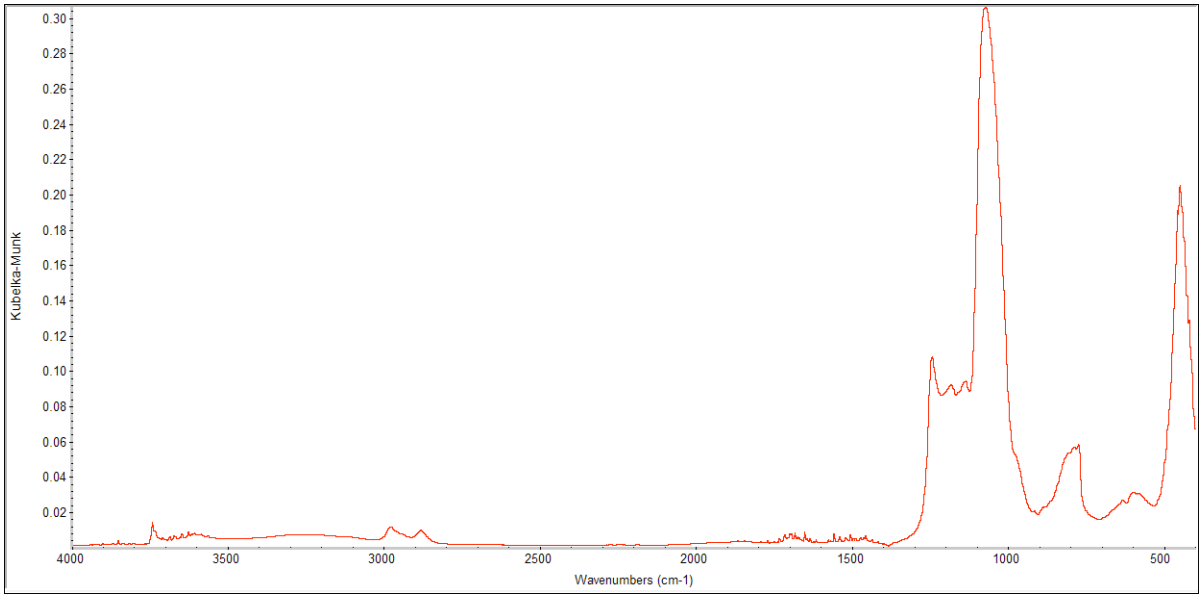

Figure S7. IR spectrum (DRIFT) of the material Cp_3CeCl@MCM-41 (**7**) in the range 400-4000 cm^{-1}.