Qualitative test for supramolecular complexation of C_{60} using a mesoporous silica

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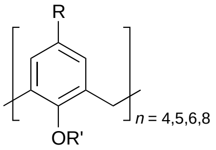
A new form of mesoporous silica with a surface area of 600 m^2 g^{-1}, mean pore radius of 5.4 nm and total pore volume of 1.9 ml g^{-1} uptakes C_{60} in toluene; on removal of toluene or the addition of fullerene complexing agents the C_{60} undergoes aggregation within the silica, identified by an inter-fullerene resonant transition at *ca.* 450 nm.

Complexation of C_{60} has been established for a variety of molecules including some hydrophobic calixarenes **1**[1–3] and cyclotriveratrylenes **2**[4,5] and is determined by the dimensions and shape of the cavity of the complexing agent, the nature of the interactions involving the spherical and otherwise non-polarised fullerene within the supermolecule, solvation effects, and fullerene–fullerene interactions.[5] The primary process in complexation of C_{60} is most likely the formation of host–guest species with the resulting polarised fullerene aggregating as part of micelle-like species with a core of fullerenes surrounded by a sheath of host molecules.[5] The host–guest interactions are inherently weak and may not be evident in solution studies using UV–VIS spectroscopy, and where a discrete complex is not isolable, intimate contact between the two species in solution cannot be ruled out.



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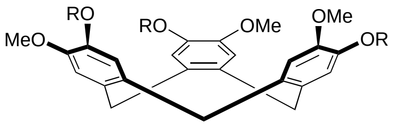

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In addressing the difficulties in identifying and encouraging host–guest interactions, we have developed a new amorphous mesoporous silica ($MPSiO_2$) with sufficient pore size to allow mobilisation of C_{60}, and large enough to accommodate aggregates of fullerenes and associated host molecules, at least for small aggregates where conventional particle size analysis would be difficult. We show that when this material is loaded with C_{60} it offers a qualitative test for supramolecular complexation of the fullerene, and that devoid of C_{60} is a material for uptake of preformed micelles $\leqslant$5.4 nm in diameter. Other noteworthy features of the new mesoporous silica include: (*i*) the material has a narrow range of mesopores, (*ii*) it is prepared using inexpensive template materials; and (*iii*) its ability to allow solid-state diffusion or diffusion from organic solutions for a range of different classes of compounds including iodine at 293 K, ferrocene, nickelocene, and titanocene dichloride at 400 K, and 2-(2,4-dinitrobenzyl)pyridine at 383 K.[6] Mesoporous silicate (and aluminosilicate) materials containing pores in the range 1.6 to 10.0 nm are prepared by taking advantage of the self-assembling properties of liquid-crystal surfactant molecules,[7] and find application in catalysis. MCM-41 for example is effective for the epoxidation of bulky alkenes,[8,9] although the well defined structural arrangement of its mesopores requires relatively large amounts of liquid-crystal template material, which compromises any catalytic conversion of practical value. A zeolite-related microporous aluminophosphate with one-dimensional pores of diameter 12.5 Å can accommodate C_{60}.[10]

$MPSiO_2$ was prepared from sodium silicate, tetraethylammonium bromide, triethanolamine in a mixture of water, dmf and phosphoric acid, with the final product obtained after heating the isolated solid at 823 K:† particle fraction 60–80 mesh, surface area 600 m^2 g^{-1} with a mean pore radius window limit of 5.4 nm with no evidence of microporosity and a total pore volume of 1.9 ml g^{-1}. A sharp IR band at 3740 cm^{-1} shows the presence of silanol groups, which decreased substantially after the adsorption studies. Contact of the magenta toluene solution of C_{60} with $MPSiO_2$ results in magenta colouration of the silica which is retained after air drying, Fig. 1(*a*), but on heating at 320 K to remove the toluene the material changed to yellow, Fig. 1(*b*). This colour change and the associated appearance of a broad new band at 450 nm in the reflectance spectrum, which is ascribed to inter-fullerene resonant transitions, is consistent with disruption of toluene-solvated C_{60} molecules,[11] affording aggregates of C_{60} within the pores of $MPSiO_2$. The band is similar to that found in thin films and aggregates of colloidal C_{60},[11,12] and that for the 1 : 1 complex of C_{60} with **1** (R = Bu^t, R′ = H, n = 8), which has three fullerenes in the core of the micelle.[13] Contact of the yellow material with toluene restored the magenta colour of toluene-solvated C_{60} in the pores.

Addition of toluene solutions of **1** or **2** to the magenta $MPSiO_2$ solid yields brown–yellow material, with representative reflectance spectra shown in Fig. 2. Except for spectrum

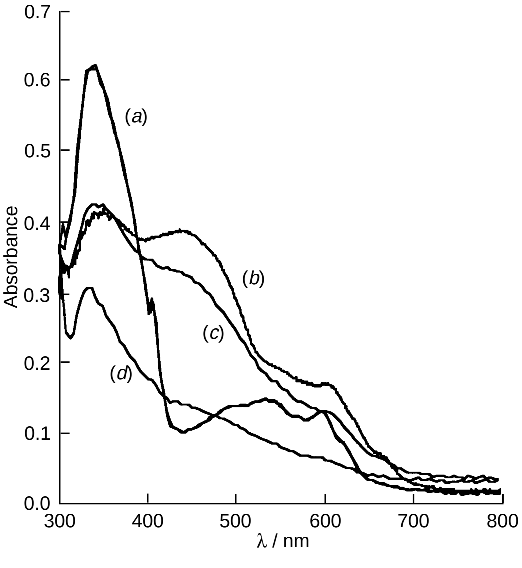

Fig. 1 UV–VIS reflectance spectra of $MPSiO_2$ after (*a*) uptake of C_{60} in toluene, (*b*) removal of toluene from the solid in (*a*), (*c*) treatment with a 1 : 1 mixture of C_{60} : **2** (R = Me) in toluene and (*d*) treatment with a 1 : 10 mixture of C_{60} : **2** (R = Me) in toluene

(*d*), Fig. 2 (see below), they show a similarly broad new band at *ca.* 450 nm, and is likewise consistent with the formation of aggregates of C_{60}, most likely as part of micelle-like structures with the fullerene cores surrounded by host molecules in the pores of $MPSiO_2$. In forming a host–guest interaction the host ligand, L, polarises the fullerene thereby encouraging the formation of aggregates, eqn. (1).[5] The new band is indicative of

$$C_{60} + L \xrightleftharpoons{\text{toluene}} (C_{60})_nL_x \qquad (1)$$

supramolecular complexation of the fullerene in the pores of the silica and is a qualitative test for host–guest interaction. In addition, we note that some molecules of type **1** and **2** failed to yield isolable host–guest complexes, and failed to show any host–guest interaction in solution, unlike in the pores of $MPSiO_2$, *e.g.* **1** ($R = Bu^t$, $R' = H$, $n = 4$), **1** ($R = p\text{-}C_6H_4OPh$, $R' = Me$, $n = 4$), **1** ($R = Ph$, $R' = Me$, $n = 4$) and **2** (R = allyl). However, host–guest interaction is implied by the distinctly different crystal morphology of pure solid C_{60} obtained on evaporation of toluene solutions of the fullerene and host, *e.g.* for **2** (R = allyl) (see below).[5] A toluene solution of C_{70} (red–brown) in contact with $MPSiO_2$ coloured the silica particles red–brown, but in this case there was no marked change in the reflectance spectra on removal of the toluene, or on the addition of host molecules.

Addition of mixtures of C_{60} with a selection of host molecules to $MPSiO_2$ also yielded brown material to varying degrees. A 1 : 1 mixture of C_{60} : **2** (R = Me) gave a similar colour change and spectrum to that of adding the same host to C_{60} already in the pores. However, for a 1 : 10 ratio there was little uptake of fullerene, Fig. 1(*d*), which is consistent with our earlier studies that micelle-like species are being formed under such conditions.[5] The bulk of these must be stable micelles $>$ 5.4 nm in diameter. For **2** (R = allyl) the difference between the 1 : 1 and 1 : 10 mixtures added to the silica is reversed. The 1 : 1 mixture results in little uptake of the fullerene in the pores and thus most of the micelle-like structures are $>$ *ca.* 5.4 nm whereas for the 1 : 10 mixture incorporation of smaller micelles prevails. Electronic spectra of the 1 : 10 solution itself suggests the presence of solvated host–guest species;[5] their intimate contact with the silica in the pores must then encourage fullerene–fullerene interactions.

Unlike other calixarenes, addition of calix[6]arene to the magenta silica results in leaching of the fullerene from the silica, Fig. 2(*d*). However, addition of a mixture of the same calixarene and C_{60} to $MPSiO_2$ gives the inter-fullerene resonant transition. It appears that an excess of the fullerene is required to encourage host–guest interactions/aggregation in the pores and in this context we note that the complex prepared from the calixarene and C_{60} is rich in fullerene, analysing as the 2 : 1 complex.[1] The leaching of the C_{60} by a solution of calix[6]arene may be due to encapsulation of each fullerene by two calixarenes as a toluene-soluble species, and/or the calixarene–fullerene association is more labile than for other calixarenes.

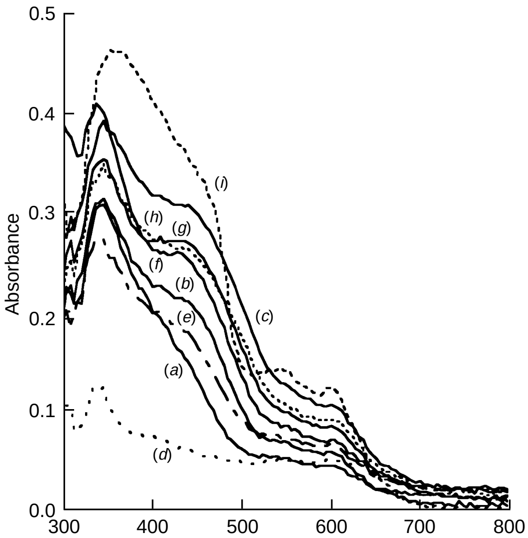

Fig. 2 UV–VIS reflectance spectra of the solid from Fig. 1(*a*), after treatment with a toluene solution of **1**: (*a*) $R = Bu^t$, $R' = H$, $n = 4$; (*b*) $R = p\text{-}C_6H_4OPh$, $R' = Me$, $n = 4$; (*c*) $R = Bu^t$, $R' = H$, $n = 6$; (*d*) $R = H$, $R' = H$, $n = 6$; (*e*) $R = CPh$, $R' = Me$, $n = 4$; (*f*) $R = Bu^t$, $R' = H$, $n = 5$; (*g*) $R = CH_2Ph$, $R' = H$, $n = 5$, (*h*) $R = CH_2Ph$, $R' = Me$, $n = 5$, (*i*) $R = Bu^t$, $R' = H$, $n = 8$

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Footnote

† *Synthesis* of $MPSiO_2$: two solutions were prepared: solution A, which contained 30 ml of a stock solution of sodium silicate (density 1.36 g ml^{-1}; assay Na_2O 8.55% m/m and SiO_2 27.45% m/m) diluted to 100 ml with water containing 2.0 g of tetraethylammonium bromide, and solution B which consisted of 4 ml of triethanolamine in 10 ml of water to which was added 15 ml of dmf and 6 ml of phosphoric acid (85% m/m). Solution B was added to solution A with rapid stirring which was continued through the formation of a gel which formed within minutes and was allowed to stand overnight. Most of the water content was removed by heating the gel at 383 K for 12 h with stirring of the solid material at hourly intervals. The powdered product was washed successively with portions of hot water (5 × 200 ml) and after drying at 393 K was heated at 823 K in a muffle furnace for 48 h. The organic material was removed within a relatively short time with the longer heating period being required to remove coke which finally gives the white powdered product. After grinding, the particle fraction (60–80 mesh) was isolated and used for uptake of the various compounds.

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