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Synergy in macrocycle/SiO_2 sol–gel nano-composites†

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Sol–gel (*SG*) processing of tetraethylorthosilicate is shown to produce porous SiO_2 nano-composites and coatings that contain a variety of adsorbed-impregnated and encapsulated macrocycles. Their texture, cation uptake and spectroscopic properties have been probed. Consideration has been given to whether this technology can be combined to form a sensitive sensor for ions in aqueous solution. The synergy and interaction between the guest and host in these nano-composites will have to be fully explored if this technology is to achieve its full potential in medical and environmental fields.

Introduction

While retaining their chemical character, organic and biomolecules can be trapped inside porous inorganic oxide sol–gel (*SG*) matrices[1,2] from which they are not leached into H_2O or CH_3OH at 298 K[3] (although inward fluid diffusion occurs[4]). Avnir[2] showed that the Si–OH silanol and Si–O–Si siloxane environment within a porous silica *SG* host was less polar than that in aqueous solution. 18-Crown-6 adsorbs onto SiO_2 surfaces from chloroform solutions and is then held coplanar to the surface by hydrogen bonding between surface ≡Si–OH silanols and Os in the adsorbate polyether ring;[5] therefore the adsorbent surface modifies the complexing properties of the guest chelator. Others[6,7] found leaching of guests from *SG*s with hot CH_3OH[7] and so favoured covalent binding of the chelators to the host gel surface, even though this also induced a heterogeneity of sites of different cation binding selectivity[8] (as the *local* geometry and chemistry of the host affected the strain and distortion of the bound chelator[9]).

There is a growing need for rapid, simple and selective analysis of trace metals in aqueous environments (industrial and medical).[10] *SG* nano-composite devices are attractive if they are more selective than those based on zeolites. For example, although zeolite A has been used for Pb, Cd and Zn[11] cation removal from waste waters, Na4A (Si/Al = 1.00) and NaY (Si/Al = 2.00) show almost equally good uptake of $Cu^{2+}{}_{(aq)}$, $Zn^{2+}{}_{(aq)}$, $Pb^{2+}{}_{(aq)}$ and $Cd^{2+}{}_{(aq)}$. Since *SG* hosts can incorporate crown ethers,[6,9,12-14] azacrowns,[15] cyclams[16] and other selective macrocycles[17] there is analytical interest in the design of new *SG* nano-composites as components of ion-sensors, where ion-active centres are entrapped in a porous *SG* inorganic oxide host (such as SiO_2).[18] These can be films of controlled thickness ($1 < \tau < 6$ μm)[17] ensuring a fast response for nano-engineered analytical devices.[12-16] In addition to selectivity and responsivity, the beauty of macrocycle/*SG* nano-composites is their ease of design and synthesis. Here, following the successful application to Sr^{2+} detection of crown ethers simply physically encapsulated in *SG*s[19] with minor (13%) leaching, the authors have tried to retain the cation selectivity of free macrocycles, when these were adsorbed in silica *SG* hosts[16] that permitted optical signal transduction.[17] It was hoped that this might be the first step in the design of nano-sensors of cations in aqueous solutions (and heterogeneous catalysts) using alkoxide molecular precursors to *SG*-encapsulate chosen ion-selective macrocycles.

Experimental

Preparations

Some of the authors have previously prepared *SG* materials,[20] organically-modified *SG*s[21] and aeroglasses.[22] The samples given in Table 1 were prepared.[23] *SG*36 for example was prepared by mixing CH_3OH (4.05 cm^3; 99.8% AnalaR; BDH), H_2O (1.44 cm^3) and HCl (1.0 cm^3; 1 M HCl; Aldrich Chemicals) in a polypropylene vessel and then slowly adding tetrethylorthosilicate (TEOS; 4.45 cm^3; 98%; Aldrich Chemicals) with agitation to give a final TEOS : CH_3OH : H_2O molar ratio of 1 : 5 : 4 (*i.e.* the CH_3OH : TEOS molar ratio (R_A) was 5 and the H_2O : TEOS molar ratio (R_W) was 4). The product sol was refluxed for 16 h at 328 K. Complete gelation occurred in 1–8 weeks. Aerogels were dried supercritically at 10–15 MPa and 573 K to remove pore-held organic fluids, although FTIR still revealed some traces remaining. Xerogels were therefore produced subcritically to avoid ligand extraction into the supercritical CO_2. *SG*s in Table 1 were synthesised in the presence of HCl (in preference to HNO_3 which would have caused too rapid a gelation[24]).

Ligands (L) of different cation selectivity[25] (Aldrich, Priton Labs and Parish) (*i.e.* 15-crown-5 and 18-crown-6 (*crown*) with exclusively O donor atoms, 18-azacrown-6 (*azacrown*), 1,4,8,11-tetraazacyclotetradecane; ([14]aneN_4; *cyclam*[26]), 1,4-dithia-18-crown-6 (*dithia*) and 1,4,8,11-tetrathiacyclotetradecane ([14]aneS_4; *tetrathia*[26])) were incorporated in the above gels at a 10 wt% loading (or 5 wt% for the *azacrown*/*SG*) at the start of the *SG* formation ($t = 0$; *sol* method) or after gelation by adsorption/impregnation (*adsn-imp* method) without solvent in the case of 15-crown-5 or using a suitable solvent (*i.e.* diethyl ether for 18-crown-6 or methanol) that was removed by evaporation.

For comparison with earlier work[2] rhodamine 6G chloride was also introduced to a SiO_2 *SG* by the *adsn-imp* method.

Uniform xerogel coatings of 3-day old SiO_2 *SG*36 (primary particle size 8 nm; filtered to 0.2 μm) 500 nm thick or

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Table 1 Properties[a] of *SG*s prepared

SG	TEOS/H_2O/CH_3OH (cm^3; moles)	S_{BET}/m^2 g^{-1}	MFPD/nm	PV/cm^3 g^{-1}	%wt loss 353–423 K
4	4.45/7.52/1.62; 1.0/7.0/2.0	747	14.6	2.70	11
16	8.91/1.44/3.24; 2.0/4.0/4.0	912	8.6	1.90	6
17	4.45/1.62/3.65; 1.0/4.5/4.5	476	17.6	2.06	3
18	2.67/1.69/3.81; 0.6/4.6/4.7	356	34.2	3.05	4
24	4.45/2.88/0.81; 1.5/8.0/1.0	492	17.8	2.20	8
36	4.45/1.44/4.05; 1.0/4.0/5.0	618	11.8	1.95	5
37	3.56/1.15/4.86; 0.8/3.2/6.0	663	15.3	1.78	4
44	8.91/1.08/4.05; 2.0/3.0/5.0	802	7.2	1.45	7

[a] S_{BET} is the total surface area, MFPD is the most frequent pore diameter (*i.e.* the median of the pore size distribution) and PV is the total pore volume. *SG*35 was also prepared at a TEOS/H_2O/CH_3OH (cm^3; moles) ratio of 6.68/2.16/2.03; 1.5/6.0/2.5.

tetrathia/*SG*36 (410 nm thick) were spin-coated onto BK7 (2.5 cm diameter; pre-cleaned with Decon 90, distilled water and then C_2H_5OH) at 2000 rpm.

Methods

Some *SG*s and *SG* nano-composites were investigated by FTIR (Nicolet 710). N_2 adsorption at 77 K was measured (Micromeritics 2010) after outgassing for 16 h and this led to values of total surface area (S_{BET}/m^2 g^{-1}), most frequent pore diameter as defined in Table 1 (MFPD/nm) and total pore volume (PV/cm^3 g^{-1}). Coatings were characterised by UV-vis reflectance (Perkin-Elmer Lambda 9).

Ion uptakes by 0.01 g of each free ligand in 5 cm^3 C_6H_6 in contact at 298 K with 25 cm^3 of a 100 ppm aqueous solution of a K, Pb or Cu sulfate for 60 min were determined by AA (Perkin-Elmer 2380). Uptakes were also measured on *SG*s or nano-composites (0.1 g) agitated for 60 min in 25 cm^3 of aqueous solutions of 100 ppm K, Pb or Cu sulfate at 298 K at $5.49 < pH < 6.59$; solution samples were analysed by AA. Leaching from 0.01 g of a nano-composite such as *tetrathia*/*SG*36 was followed by UV analysis of the solution (25 cm^3 of 1000 ppm of $CuSO_4$ in H_2O) at 388 nm.

Results

Characterisation

Table 2 shows that the SiO_2 *SG* host lowered the melting points of the guest ligands by some 8–25 K compared to their free state. This suggests that some $\equiv$Si–OH···L interaction has occurred, for example, by hydrogen-bonding.[5] The weight loss of the nano-composites (1–13% at 353–423 K in Table 1) was due to water and organics removal, but ligand loss followed at higher temperature.

Outgassing prior to N_2 adsorption was at a temperature designed to avoid ligand melting but remove pore fluids (see weight losses in Table 1). All N_2 adsorption–desorption isotherms at 77 K on *SG*s and nano-composites prepared by ligand adsorption-impregnation (see Fig. 1–3) were of type IV with H1 hysteresis loops. Fig. 1–3 show that the total surface areas and pore volumes of the host decreased on ligand adsorption-impregnation, but that the isotherm type and the *SG* host pore structure was *not* dramatically changed. Hence (as suggested by the depression of the ligand melting points in Table 2) there must be some L···HO–Si$\equiv$ interaction causing a blocking of host *SG* pore entrances even at the modest ligand loadings used here (*i.e.* 2.5 ligands per nm^2 or about one ligand per two surface *OH*s). Fig. 4 shows how increased CH_3OH dilution of TEOS at low R_W causes (a) a broad increase in the MFPD calculated from the desorption branch of the N_2 isotherm at 77 K and (b) a decrease in the total surface area of the resultant SG.

Table 2 Melting points (K) of free L and *SG*-hosted L[a]

	Free L	L/*SG* nano-composite
18-crown-6	315–319	—
azacrown	384–387	—
cyclam	457–459	433
dithia	330–332	323
tetrathia	391–394	383

[a] Those not given were obscured by solvent loss.

However, Table 3 shows that when the *dithia* ligand (or even the diethyl ether solvent alone) was encapsulated at $t = 0$ (by the *sol* method; see Fig. 3c), mesoporosity, pore volume and total surface area were significantly lost. This may be an extension of the effect of CH_3OH dilution seen in Fig. 4. There are then advantages in simple ligand adsorption-impregnation into a mesoporous *SG* host in terms of subsequent N_2 accessibility.

Ion uptake

Rhodamine 6G chloride constrained in SiO_2 *SG* (see Fig. 5) shows a maximum absorption in the UV-vis at a wavelength 4.5 nm above that for its free solution, because it is experiencing less freedom in its *SG* cage. There was also evidence of *SG*–ligand host–guest interactions in the ion uptakes seen here for *SG*-held macrocycles. Table 4 and Fig. 6 show that the ratio of $K^+_{(aq)}$/$Pb^{2+}_{(aq)}$ ion uptakes is *higher* for the *crown*/*SG* and *azacrown*/*SG* nano-composites than for these ligands in free solution, but is *lower* for the *tetrathia*/*SG* nano-composite than the free ligand. Certainly the ligand is modified in its ion chelation characteristics by the *SG* host. The *SG*s alone under the conditions in Table 4 gave $K^+_{(aq)}$/$Pb^{2+}_{(aq)}$ ion uptake ratios of 1.04–1.11. Despite the fact that the point of zero charge of SiO_2 is at $pH = 2$[27] and so its surface charge at relevant pHs is negative, (i) the solution pH on ion uptake by *SG*2 rose from 5.72 to 6.24 and from 5.49 to 5.91 in $K^+_{(aq)}$ and $Pb^{2+}_{(aq)}$ experiments respectively and (ii) the *SG* raised or lowered $K^+_{(aq)}$/$Pb^{2+}_{(aq)}$ with different ligands. Hence, it is unlikely that non-discriminating cation uptake by the *SG* (*via* their interaction with surface OH groups[28]) could be responsible for the substantial changes in $K^+_{(aq)}$/$Pb^{2+}_{(aq)}$ uptake ratio seen here. The host–macrocycle interaction is we assume more complex.

The ligands encapsulated in microporous *SG* silica *via* a *sol* method showed no measurable cation uptake from aqueous solution: presumably because cation entry was kinetically or thermodynamically unfavourable into the dominant micropores. On the other hand such samples showed no ligand leaching.

Fig. 7 shows UV absorption at 388 nm for the $Cu^{2+}_{(aq)}$ solution surrounding the mesoporous *tetrathia*/*SG*36 nano-composite at 298 K. This increased with time to a meagre extent. Nevertheless, there must have been some ligand leaching from the mesoporous *SG*36-based nano-composite over a period of some hours. Even this modest leaching (which did not remove all adsorbed ligand) will need to be overcome in a real sensor prototype. Reflectance spectroscopy (see Fig. 8a, b) showed

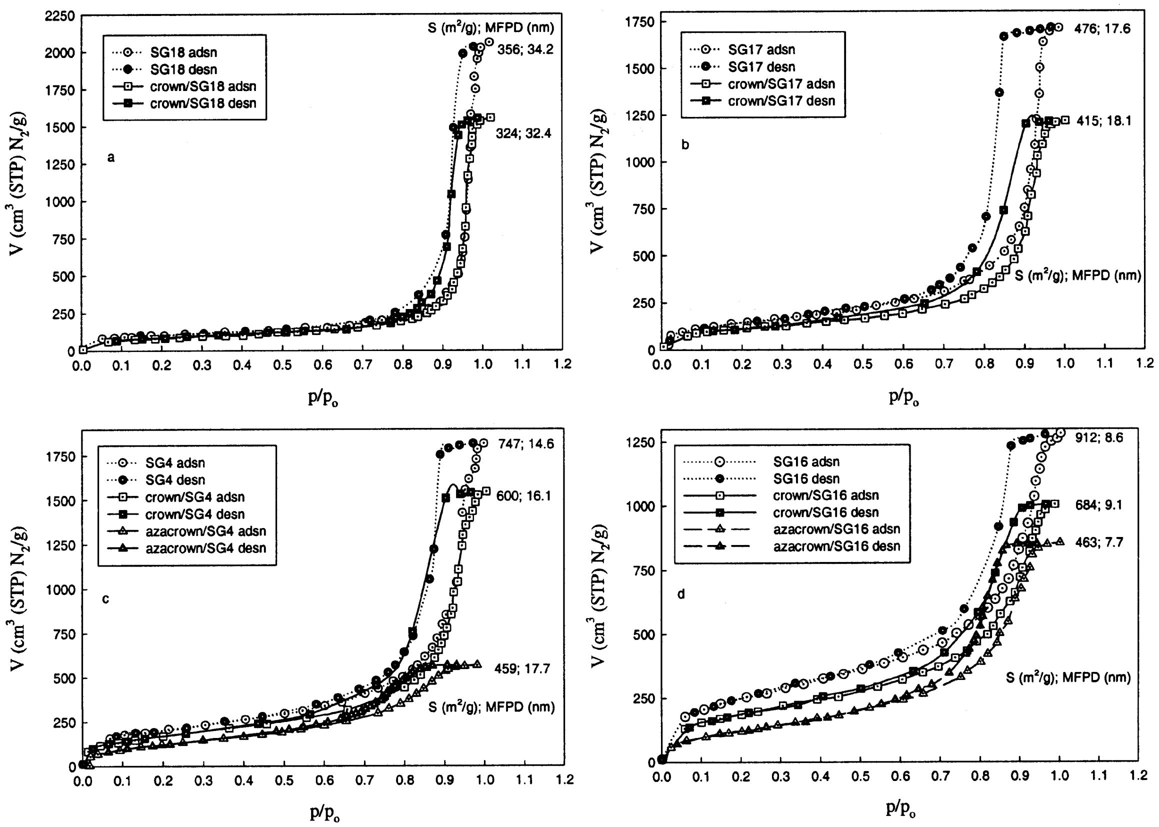

Fig. 1 N_2 adsorption–desorption isotherms at 77 K on nano-composites derived by ligand adsorption-impregnation onto *SG*18 (a), *SG*17 (b), *SG*4 (c) and *SG*16 (d).

that mesoporous *SG*36 coated well onto BK7 (or quartz) to a thickness defined by the positions of the maxima and minima in reflectance, but for *tetrathia*/*SG*36 the coating was thinner, presumably because it was denser and less porous. More importantly, however, τ *decreased* when the nano-composite film came into contact with a $Cu^{2+}_{(aq)}$ solution. This contraction of the nano-composite on $Cu^{2+}_{(aq)}$ complexation could be used as the basis of a fibre-optic distortion-based ion-sensor. Consider now information in the IR. Fig. 8c shows a highlighted peak at 1400–1500 cm^{-1}, which can be assigned to a CH_2 deformation in the CH_2–S bond. This is not present for the host SiO_2 *SG*36 and only weakly present for the parent *tetrathia*/*SG*36 nano-composite. However, it increases in intensity especially when 100 ppm $Pb^{2+}_{(aq)}$ is complexed by the composite, but was less intense when 100 ppm $Cu^{2+}_{(aq)}$, $Ni^{2+}_{(aq)}$ or $K^{+}_{(aq)}$ were available. The uptake of $Pb^{2+}_{(aq)}$ (56.1%) was greater than that of $K^{+}_{(aq)}$ (2.6%), which is consistent with the low (0.05) value of $K^{+}_{(aq)}/Pb^{2+}_{(aq)}$ seen in Table 4, but is even higher for $Cu^{2+}_{(aq)}$ (72.5%). Hence it could be that the IR absorption bands at 1400–1500 cm^{-1} for a *tetrathia*/*SG*36 coating on an optical-fibre core are the basis of a potential $Pb^{2+}_{(aq)}$ selective sensor.

Conclusions

SG solids are made from colloidal building blocks[29] with control of total surface area and average pore sizes possible (see Fig. 4); organic–inorganic nano-composite gels[30] can be so produced. Indeed *SG*s are the gateway to a variety of new nano-structured materials[31] with unusual mechanical, optical and magnetic properties relevant to a wide range of advanced analytical[32] technologies. Here the first steps towards nano-engineered ion sensors have been taken.

Microporous macrocycle/*SG* nano-composites exhibit no ligand leaching, but no cation uptake either. *Mesoporous* macrocycle/*SG* nano-composites, on the other hand, have guest ligands in *SG* cages[33] with (i) modified thermal stability, (ii) meagre leaching,[32], (iii) modified absorption maxima, and (iv) modified cation (*e.g.* $K^{+}_{(aq)}/Pb^{2+}_{(aq)}$) uptakes while the *SG* host has a moderate guest-induced lowering of its total surface area and porosity. This is not surprising since encapsulated chelators may induce new structures and porosity in the *SG* host.[34] Cation complexation by these mesoporous nano-composites (that is now being optimised) caused the appearance of IR absorption bands and composite expansion, both of which could be the basis of a new ion-sensor technology applicable to environmental, industrial and medical fields. Nevertheless, even at this preliminary stage these macrocycle/*SG* nano-composites are more selective than traditional zeolites.[11,35]

It was hoped that the *adsorbed* macrocycle would be simply hydrogen-bonded[5] to the surface of the *SG* host and would hence retain the ion selectivity of the native species in solution, but Fig. 6 shows that this is not the case. Fig. 9 shows the full FTIR spectra of the *tetrathia*/*SG*36 nano-composites before and after cation complexation. It is clear that the ligand binds with the *SG* surface sufficiently strongly to affect even the Si–O–Si bands. If this is the case (and it is surprising) then it is to be expected that the distortion of the chelator ring will be immense. Therefore most of the ligand (but not all, since there is some initial leaching) must be strongly adsorbed in the *SG* pores.

$K^{+}_{(aq)}$ and $Pb^{2+}_{(aq)}$ were chosen because the former is too small and the latter is too large for the *tetrathia* cavity, but the ligand does form stable complexes with d^9 Cu^{2+} in two conformations: *anti*[26] (with four donor sulfur atoms coplanar, trimethylene bridges lie on opposite sides of the central plane, with two axially coordinated anions/solvent molecules completing the tetragonal coordination and S lone-pairs above and below the plane) and *syn*. Both conformations may co-exist in solution, but will that be true within *SG* cages?[33] The average

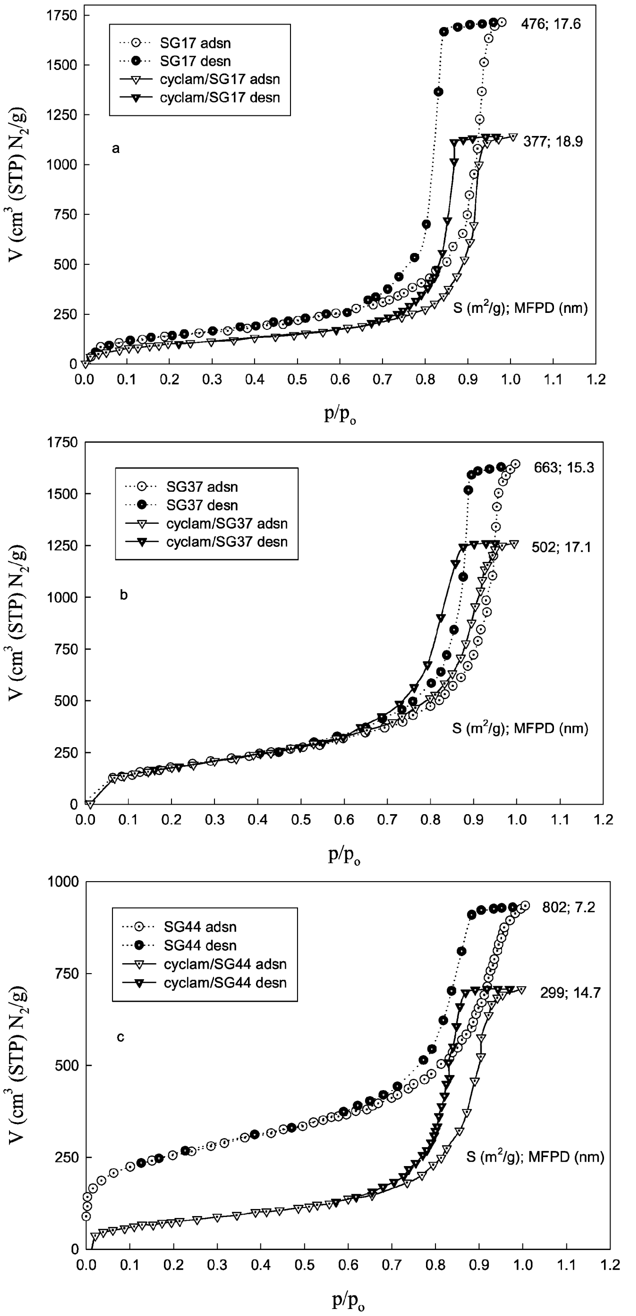

Fig. 2 N_2 adsorption–desorption isotherms at 77 K for nanocomposites derived by ligand adsorption-impregnation onto *SG*17 (a), *SG*37 (b) and *SG*44 (c).

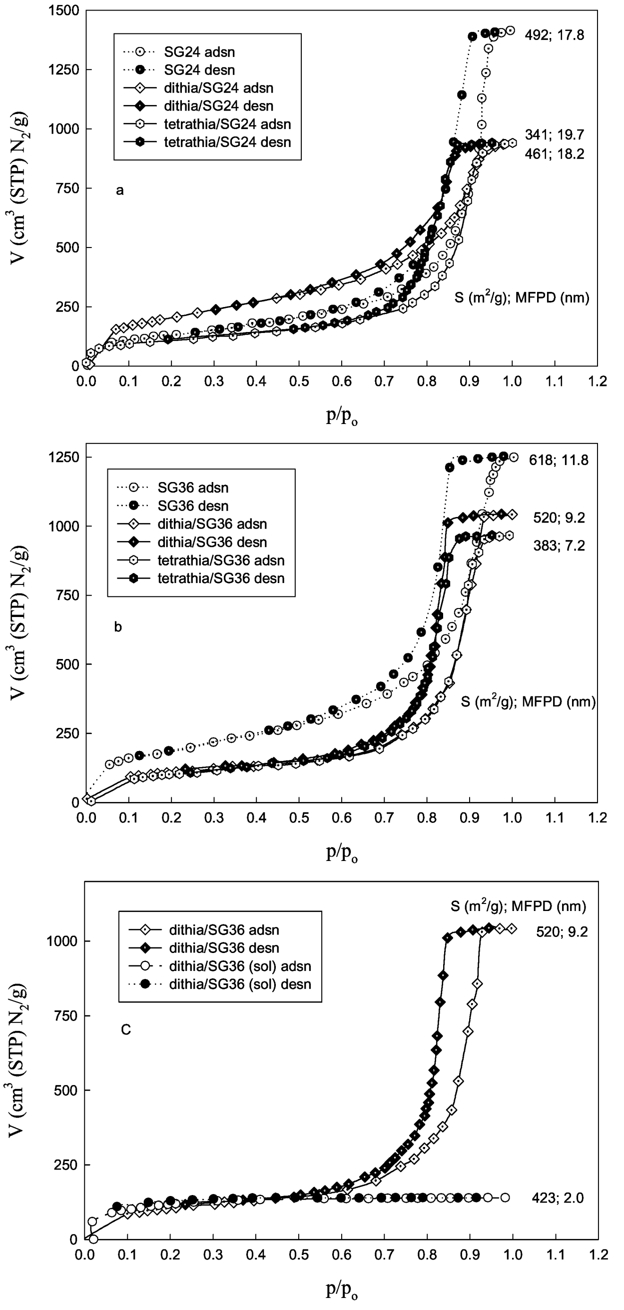

Fig. 3 N_2 adsorption–desorption isotherms at 77 K for nanocomposites derived by ligand adsorption-impregnation onto *SG*24 (a), *SG*36 (b) and *SG*36 (c). Dithia/*SG*36 (*sol*) was derived by encapsulating the ligand at sol $t = 0$ stage (*sol* method) and for this the isotherms were of type I.

Cu–S distance was 0.2303 nm in the solid tetrathia–Cu^{2+} complex,[26] while the S_1–Cu–S_2 angle was 89.9–90.1°, but to what extent will these be different for the *tetrathia/SG* nanocomposites? UV-vis absorption[36] (*e.g.* $S_{(\pi)} \rightarrow Cu^{2+}$, $S_{(\sigma)} \rightarrow Cu^{2+}$, *etc.*), ESR,[37] EXAFS and XPS[38] are needed to unravel the full detail of *tetrathia/SG*–$Cu^{2+}_{(aq)}$. Not surprisingly, in the light of the present data, others[16] have studied the binding of Cu^{2+} by covalent-held *cyclam/SG* composites (S_{BET} = 370 $m^2\ g^{-1}$; <30 nm pore diameters) and noticed that the coordination chemistry seen is *not* the same as in solution.

Initial ion complexation experiments with the free ligand have indicated ion selectivity trends comparable to those seen in the literature:[33] (i) for simple crown ethers $K^+_{(aq)} > Pb^{2+}_{(aq)}$; (ii) for *azacrowns* there was an increased affinity for $Pb^{2+}_{(aq)}$; and (iii) for *cyclams*, *dithias* and *tetrathias* $Cu^{2+}_{(aq)} > Pb^{2+}_{(aq)}$. The properties of macrocyclic ligands for cation binding depend on their thermodynamics of chelation,[39] which in turn depend on their relative ring size, cavity size, rigidity, and number/type of donor atoms. Control of these parameters allows their fine-tuning by those with supramolecular expertise to bind specific cations, such that the ligand satisfies the solvation/coordination preferences of the cationic solute. However, anions also place their own limitations. There may well be a need for anion acceptance in conjunction with cation entry into the macrocycle. For example, if X^{x-} is Cl^-, SO_4^{2-}, NO_3^-, *etc.* and the macrocycle is a crown ether (CE) one may have

$$M^{x+} + q\mathrm{CE} + mX^{x-} = M(\mathrm{CE})_q{\cdot}X_m$$

Simultaneous cation *and* anion acceptance is certainly more effective than either separately.[40] Synergism exists, as in other areas of chemistry, in chelation.[41] For the present nanocomposites it is important to remember that acid-catalysed *SG*s

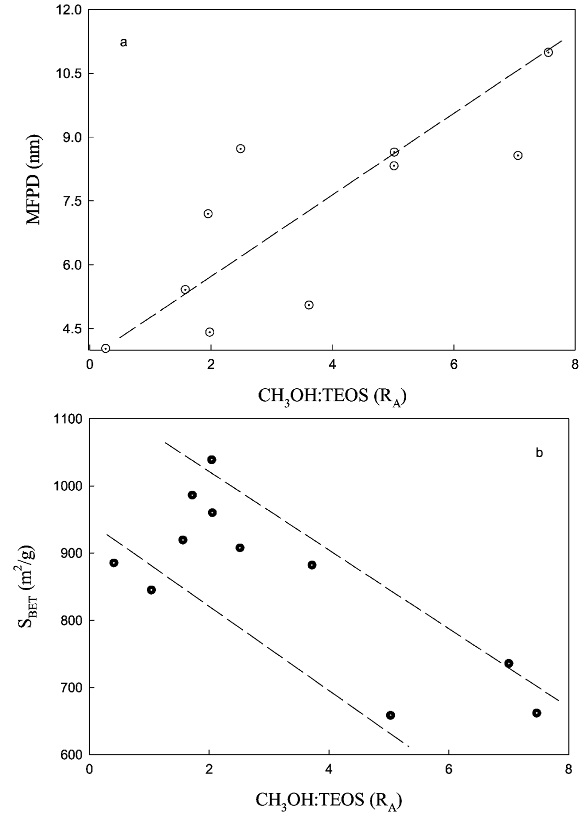

Fig. 4 Effect of CH_3OH : TEOS ratio (R_A) at low R_W on the most frequent pore diameter (a) and total surface area (b) of the silica *SG* produced.

Table 3 Textural effect of different modes of 10% *dithia* incorporation into *SG*36

	S_{BET}/m^2 g^{-1}	MFPD/nm	PV/cm^3 g^{-1}
*SG*36	618	11.8	1.95
dithia/*SG*36 (*adsn-imp*)	520	9.2	1.52
dithia/*SG*36 (*sol*)	423	2.0	0.20
diethyl ether/*SG*36 (*sol*)	428	2.4	0.24

can be rich in catalyst-derived H^+ and anions (Cl^- here) that will affect the guest ligand, the SiO_2 *SG* surface and their combined uptake of $K^+_{(aq)}$, $Pb^{2+}_{(aq)}$ and $SO_4{}^{2-}_{(aq)}$. Since lauryl sulfate anions do not adsorb on bare SiO_2, except in the presence of octadecyldimethylsilane,[42] do organic residues in *SG*s also affect cation–anion uptakes? This potential synergy needs to be investigated *in-situ*. Sensor design will require a detailed knowledge of this synergy if they are to be sufficiently selective, sensitive and stable. It will not simply be the synthesis of new ligands or *SG* materials that alone will provide the basis for a whole realm of new opportunities.

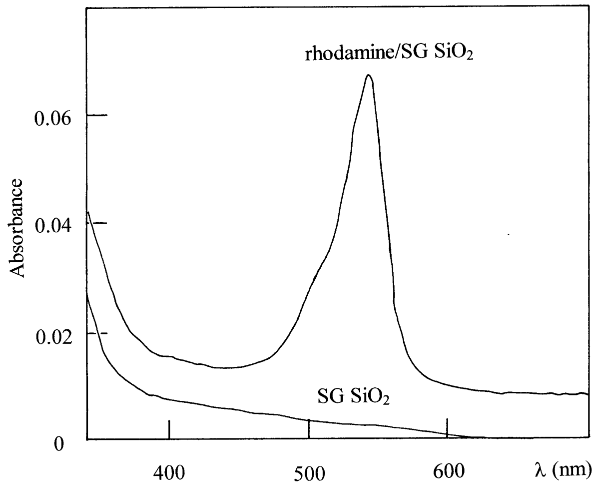

Fig. 5 UV-vis absorption spectra of SiO_2 *SG* and rhodamine 6G chloride/SiO_2 *SG*.

Table 4 The relative ion uptakes by 0.01 g of the ligands (L) in 5 cm^3 benzene or 0.1 g of 10%L/*SG* nano-composite in contact with 25 cm^3 of a 100 ppm aqueous solution of a metal sulfate at 298 K and 60 min. Data for *crown* and *azacrown* nano-composites are given in Fig. 6

	$K^+_{(aq)}$/$Pb^{2+}_{(aq)}$
tetrathia	0.33
tetrathia/*SG*36	0.05
tetrathia/*SG*24	0.04
tetrathia/*SG*35	0.03

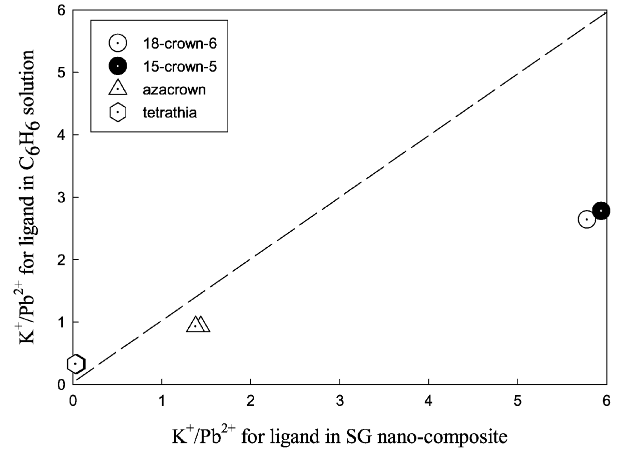

Fig. 6 Relative ion uptakes of K^+/Pb^{2+} by free ligand in 5 cm^3 C_6H_6 compared to 0.01 g ligand/*SG* nano-composite at 298 K and 60 min when both are agitated with 25 cm^3 of an aqueous solution containing 100 ppm of one ion or the other added as the metal sulfate. For the 18-crown-6 in solution $K^+/L = 1.1 \pm 0.1$ and $Pb^{2+}/L = 0.001$.

For the moment it seems clear that in the future there will be a $Ba^{2+}_{(aq)}$,[43] $Pb^{2+}_{(aq)}$[43] or $Cu^{2+}_{(aq)}$[10] sensor based on a *SG* containing an immobilised chelator with output *via* IR or UV absorption or *via* displacement. Medical-industrial sensors so designed will be stable in the environments (pH, *T* and salinity) in which they operate. The *SG* host could be SiO_2–TiO_2[2] and the guest ligand could be one of a myriad of evolving molecular macrocycles.

The authors look forward to the time when *SG*s[44] and macrocycles will be designed *as one* such that sensor users will

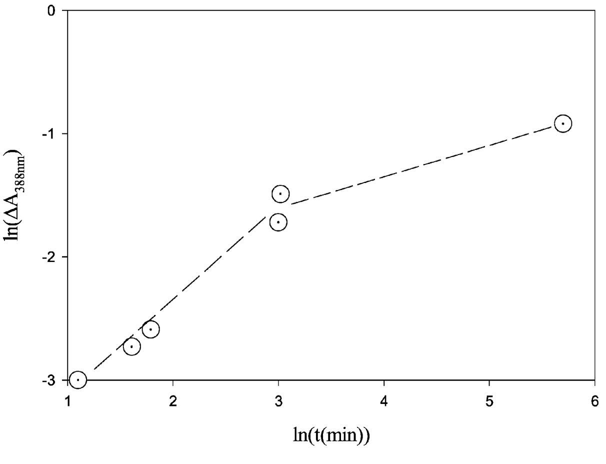

Fig. 7 Change in absorbance at 388 nm when 10 mg of *tetrathia*/*SG*36 was immersed in 25 cm^3 of 1000 ppm of $CuSO_4$ aqueous solution at 298 K.

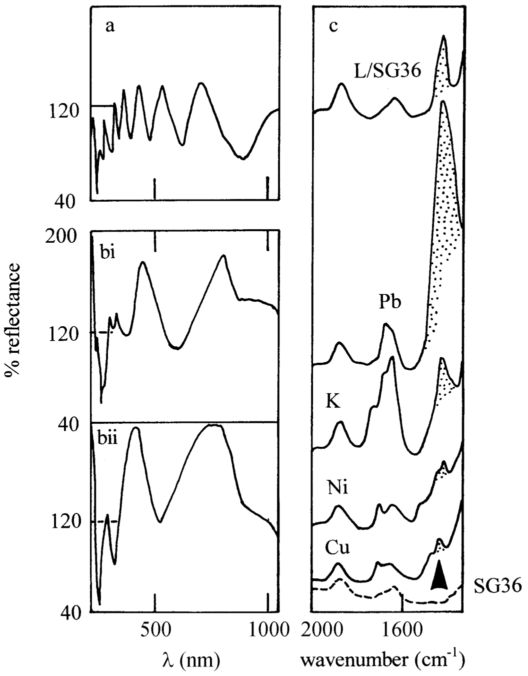

Fig. 8 UV-vis reflectance spectra for *SG*36 (a) and *tetrathia*/*SG*36 coatings on BK7 before (bi) and after (bii) immersion in $Cu^{2+}_{(aq)}$ (100 ppm). (c) IR spectra of *SG*36, *tetrathia*/*SG*36 and *tetrathia*/*SG*36 after complexation of $Cu^{2+}_{(aq)}$, $Ni^{2+}_{(aq)}$, $K^{+}_{(aq)}$, and $Pb^{2+}_{(aq)}$.

note that they have 'received an honoured guest'[45] (*i.e.* ppm levels of aquated cations) for sensing[46] and imaging[47] that are of medical[48] or environmental importance. Chelators are abundant;[49] chelation within constrained systems is important in plants and animals[50] (*e.g.* spectral and redox properties of Cu^{2+}/*tetrathia* are similar to those found for blue Cu-proteins[36]). There is an interface between supramolecular chemistry and *SG* chemistry that needs to be exploited in environmental and bio nano-sensing.[51]

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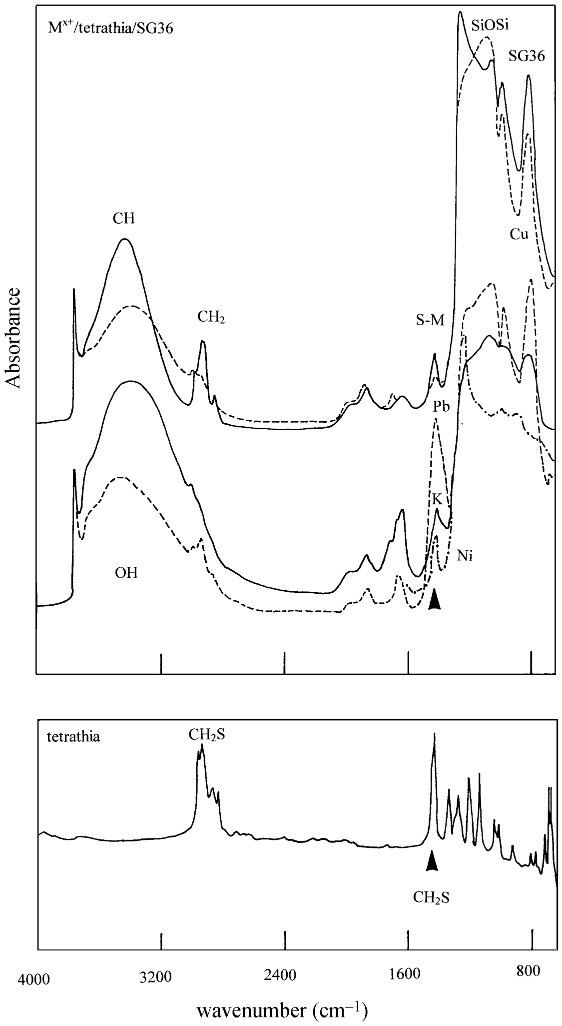

Fig. 9 FTIR spectra of *tetrathia* ligand, *SG*36 and *tetrathia*/*SG* nanocomposites before and after complexation of $Ni^{2+}_{(aq)}$, $K^{+}_{(aq)}$, $Pb^{2+}_{(aq)}$ and $Cu^{2+}_{(aq)}$.

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