Covalent incorporation of an alkoxysilyl-substituted [60]fullerene derivative in sol-gel matrices

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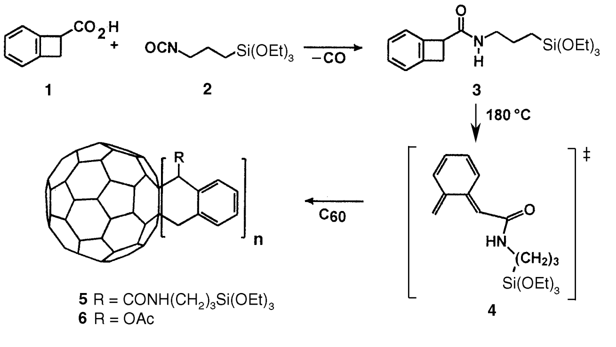
A [60]fullerene adduct bearing a reactive triethoxysilyl functional group has been synthesized. The high solubility of this adduct in polar solvents enables its covalent incorporation into a sol-gel silica matrix. In comparison to the conventional admixing of 'naked' fullerene to silica sols, this approach has the following distinct advantages: (i) even with an adduct content of up to 2 wt% (related to SiO_2), the reaction mixture remains homogeneous during the entire sol-gel process, and (ii) the covalently attached fullerene adduct is fixed in the silica matrix and therefore cannot migrate.

The promising electrochemical and optical properties of [60]fullerene and [60]fullerene adducts have prompted their use in, for example, photovoltaic cells,[1,2] filters (laser safety glasses),[3] and non-linear optical devices.[4–6] The prerequisites for the application of these properties are (i) the processibility of the [60]fullerene containing material, and (ii) the protection of [60]fullerene against oxygen (especially in the presence of light). This can be achieved by encapsulating the fullerene in a matrix which is impermeable to oxygen and resistant to irradiation and ageing. For this purpose, incorporation in silicon dioxide matrices by sol-gel processing seems to be the method of choice.[3,7,8] This versatile technique allows the preparation of glasses doped with organic compounds at low temperatures (*ca.* 100 °C). By variation of the reaction conditions, the morphology and the structural and mechanical properties of these glasses can be tailored. Furthermore, the sol can be processed into coatings, monoliths or powders. The preparation of glasses with admixed fullerenes or fullerene adducts has already been accomplished.[7–9] The disadvantages of this approach are that (i) precipitation of the fullerenes during the sol-gel process can occur, yielding an inhomogeneous material, and (ii) the mobility of the fullerenes in the silica matrix may cause migration out of the matrix. The latter problem has recently been confirmed by Zerda *et al.*[9] We reasoned that this problem could be effectively suppressed by covalent incorporation of the fullerene moieties into the silica matrix. Herein we describe the synthesis of the triethoxysilyl substituted fullerene adduct **5** and its incorporation into a silica matrix *via* the sol-gel process.

Starting from cyclobutabenzene-1-carboxylic acid **1** and (3-isocyanatopropyl)triethoxysilane **2**, which are both commercially available compounds, *N*-(3-triethoxysilylpropyl)cyclobutabenzene-1-carboxamide **3** was obtained in nearly quantitative yields. Heating of **3** to 180 °C in 1,2-dichlorobenzene led to the *in situ* generation of the corresponding *ortho*-quinodimethane **4** which, in the presence of [60]fullerene, afforded the Diels–Alder adducts **5** (Scheme 1).[10,11] The amount of bis-adduct **5** ($n=2$) could be reduced drastically by using an excess of [60]fullerene. Due to the reactivity of **5**, the separation of the adducts **5** ($n=1$) and **5** ($n>1$) was not possible by conventional chromatographic methods with stationary phases like silica gel or alumina. However, pure monoadduct could be isolated by chromatography on polystyrene gel with THF as the mobile phase. Since traces of bis-adduct are irrelevant for the subsequent sol-gel process, the crude mixture of fullerene adducts was used for all experiments.

In order to determine the reactivity of the siloxane substituent, **5** was exposed to moisture for 2 days. As expected, the hydrolysis of **5**, followed by cross-linking, led to insoluble condensation products which were characterized by CP-MAS ^{29}Si and ^{13}C NMR spectroscopy. The formation of Si–O–Si bonds was shown by the solid phase CP-MAS ^{29}Si NMR spectrum (Fig. 1). Next to the signals (T^0_3 and T^0_2) of the monomer **5**, it also showed weaker signals (T^1_2, T^1_1 and T^1_0)



Scheme 1

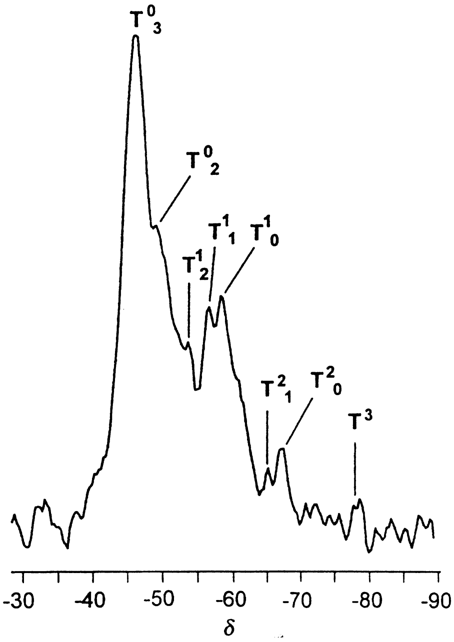
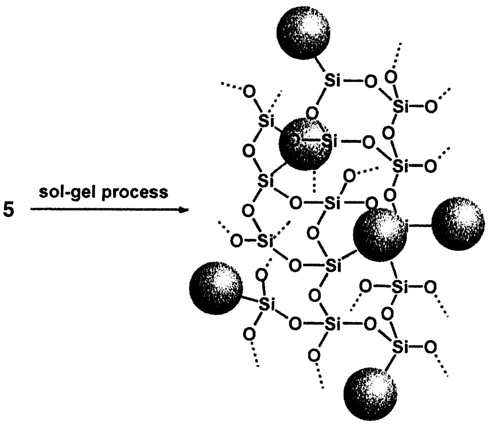


Fig. 1 CP-MAS ^{29}Si NMR spectrum of **5** after 2 days exposure to moisture



Scheme 2

of the dimerisation products of **5**. Furthermore, traces of chains (T^2_1 and T^2_0) and networks (T^3) were detectable.†

The observed self-condensation of **5** and the high solubility of **5** in THF (10 mg ml^{-1}) demonstrate that it is especially well-suited for the sol-gel process.

The silica sols were prepared by adding a mixture of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) (molar ratio 1:1) to a solution of varying amounts of **5** in THF (Scheme 2). Hydrochloric acid (0.1 M) was added in catalytic quantities and the hydrolysis was carried out at 55–60 °C. This procedure provided brown sols with a content of **5** of up to 5 wt%; the sols were homogeneous and transparent up to a content of 2 wt%.

The sols could be either processed to give films on glass substrates (thickness: 150–200 nm) by spin coating or to give monolithic silica gel glasses. In order to form monoliths, highly viscous sols were prepared by evaporating most of the solvent. A further annealing process, starting at 45 °C and ending at 120 °C after a time period of 24 h, led to transparent brown monoliths. In the UV spectrum of the monoliths, the absorption band at 432 nm, typical for all [60] fullerene monoadducts, was detectable.

To demonstrate the advantage of our concept of covalent bonding to the silica gel, we also prepared monoliths containing an acetoxy-substituted fullerene derivative **6** ($n=1$)[11] (Scheme 1), which was then physically admixed into the sol mixture. Although the solubility of **6** ($n=1$) in THF is sufficient to prepare sols with a fullerene content of up to 2 wt%, **6** ($n=1$) showed a high tendency to precipitate out of the sol after a few days and failed to afford homogeneous monoliths. In contrast, sols containing **5** proved to be stable for a period of weeks.

It appears that triethoxysilyl-substituted [60]fullerene adducts are well-suited for the sol-gel process. By the covalent attachment of the fullerene adduct *via* the triethoxysilyl substituent, the content of fullerenes in the silica matrix has been increased to 2 wt% (with respect to SiO_2). The resulting glasses are transparent and homogeneous in contrast to those which have been prepared only by physical addition of an unreactive fullerene derivative. Besides the use in the sol-gel process, reactive siloxane-substituted fullerene derivatives are also promising compounds for all kinds of coating processes and the formation of fullerene-containing polymers. The synthesis of polymers, based on diethoxysilyl-substituted fullerenes, is the subject of current investigations.

Experimental

N-(3-Triethoxysilylpropyl)cyclobutabenzene-1-carboxamide 3

Dry cyclobutabenzene-1-carboxylic acid **1** (200 mg, 1.35 mmol) and (3-isocyanatopropyl)triethoxysilane **2** (334 mg, 1.35 mmol) were refluxed under an inert atmosphere for 12 h. After evaporation of the solvent, the *N*-(3-triethoxysilylpropyl)cyclobutabenzene-1-carboxamide **3** was formed as a highly viscous, colourless oil in nearly quantitative yield which could be used for further reactions without purification; m/z(FD) 351 (M^+, 100%); δ_H (300 MHz; $CDCl_3$; 28 °C) 0.63 (2 H, m, CH_2), 1.22 (9 H, t, J 7.3 Hz, CH_3), 1.63 (2 H, m, CH_2), 3.2 (2 H, m, CH_2), 3.49 (2 H, d, J 6.6 Hz, CH_2), 3.82 (6 H, t, J 7.3 Hz, CH_2), 4.34 (1 H, t, J 6.6 Hz, CH), 7.1–7.28 (4 H, m, CH); δ_C (75 MHz; $CDCl_3$; 28 °C) 8.09 (CH_2), 18.72 (CH_3), 23.8 (CH_2), 34.46 (CH_2), 36.12 (CH_2), 46.11 (CH), 58.92 (CH_2), 123.03 (CH), 123.37 (CH), 128.08 (CH), 128.77 (CH), 171.96 (C=O).

Fullerene adducts 5

[60]Fullerene (1 g, 1.38 mmol) and amide **3** (470 mg, 1.35 mmol) were dissolved in 70 ml of dry *o*-dichlorobenzene and refluxed under inert conditions. The colour changed from violet to brown, and after 30 min the reaction was finished. After removing the solvent by distillation, the mixture of adducts **5** (1.2 g) was separated from unreacted [60]fullerene by extraction with dry THF; m/z(FD) 1071 (M^+ of **5** ($n=1$), 100%), higher adducts were not detected; λ_{max}($CHCl_3$)/nm [**5** ($n=1$)] 257, 310, 432; ν_{max}(KBr)/cm^{-1} [**5** ($n=1$)] 2922(s), 1704(s), 1660(s), 1617(m), 1519(m), 1455(s), 1430(s), 1183(m), 1074(s), 747(s), 575(w), 526(s); δ_H (500 MHz; $C_2D_2Cl_4$; 28 °C) 0.06 (1 H, br s, $SiCH_2$), 0.85 (9 H, t, J 7 Hz, CH_3), 1.22 (2 H, m, CH_2), 3.68 (6 H, q, J 7 Hz, OCH_2), 4.00 (2 H, m, NCH_2), 4.32 (1 H, m, NH), 4.37 (1 H, d, J 14 Hz, CH), 5.47 (1 H, d, J 14 Hz, CH), 5.53 (1 H, s, CH), 7.62 (2 H, m, CH), 7.66 (2 H, m, CH); δ_C (125 MHz; $C_2D_2Cl_4$; 28 °C) 14.29 (CH_2), 18.89 (CH_3), 23.42 (CH_2), 30.16 (CH_2), 45.10 (CH_2), 46.90 (CH), 58.81 (CH_2), 60.98 ([60]fullerene, sp^3), 125.77 (CH), 129.25 (CH), 131.07 (CH), 132.29 (CH), 134.97, 136.76, 138.22, 138.46, 138.87, 140.35, 142.19*, 142.26, 142.74, 142.76, 142.93, 143.02, 143.14, 143.33*, 143.83, 145.42, 145.58, 145.66, 145.84, 146.13, 146.14, 146.26, 146.39, 146.54, 146.72, 146.88*, 146.97, 147.21*, 147.95, 148.51, 148.58, 151.58 ([60]fullerene, * = several signals overlapped), 173.21 (C=O).

After exposure to atmospheric humidity for 2 days; δ_{Si} (CP-MAS; 25 °C) 46 (T^0_3), 49 (T^0_2), 53.5 (T^1_2), 56.5 (T^1_1), 58.3 (T^1_0), 65.4 (T^2_1), 67.6 (T^2_0), 78 (T^3, very weak); δ_C (CP-MAS; 25 °C) 11.0 ($SiCH_2$), 20.0 (CH_3), 23.5 (CH_2), 31.5 ($NHCH_2$), 44.2 (CH_2), 46.3 (CH), 59.0 ($SiOCH_2$), 66.3 ([60]fullerene, sp^3), 129.4 (CH), 137.2, 143.3, 146.3, 158.0 ([60]fullerene), 172.0 (C=O).

Sol-gel process

The silica sols were prepared by adding a mixture of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) to a solution of **5** in THF. The initial molar ratio of TEOS, MTEOS and water was 1:1:3.5. The hydrolysis was carried out at 55–60 °C under acidic conditions (0.1 M HCl). In this way, transparent brownish sols with C_{60}–SiO_2 ratios of up to 5 wt% were obtained. The sols could be then used for film formation (on glass substrates) by spin coating, or monolithic silica gel glasses as well. In order to prepare monoliths, a highly viscous sol was obtained by evaporating most of the solvent. A Teflon vessel was filled with the sol and a further annealing process starting at 45 °C and ending at 120 °C over 24 h period led to transparent brown monoliths.

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† Three Si–O bonds are marked by the T, the number of Si–O–Si bonds and the number of hydroxy groups are indicated by the superscript or the subscript, respectively.

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