A One-Pot Synthesis of Chromophoric Silicate-Based Xerogels**

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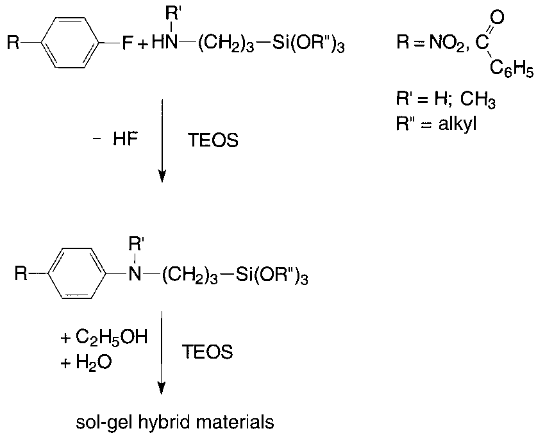
The development of the sol–gel process has had a significant impact on materials science and catalysis research during the last 15 years, and has opened up completely new perspectives in the planning of the synthesis and structure of complex hybrid materials.[1–5] One area of this field, the synthesis of hydro- and xero-hybrid gels, has a wide variety of applications, such as nonlinear-optical (NLO) materials, semiconductors, or for use in sensors.[6–13]

The first step of the synthesis involves the covalent modification of a trialkoxysilane with an organic (e.g. chromophoric) group. This functionalized trialkoxysilane (ormosile) is converted into an organically modified silica gel (hydrogel or xerogel) by addition of tetraalkoxysilane in a sol–gel process. Class 2 xerogels are obtained in this way.[9, 14] The direct encapsulation of, for example, dissolved dyes during the sol–gel process leads to class 1 xerogels.[9, 14] This procedure is often not effective, because in most cases the dye is only physically bound. The encapsulated components are thus frequently extracted by organic solvents, and phase separation between the organic components and the inorganic matrix can also occur.

We now present a new procedure for the synthesis of organofunctionalized class 2 silicate-based xerogels, in which the sol–gel process is carried out immediately after the one-pot synthesis of the chromophoric trialkoxysilane components in tetraethoxysilane (TEOS). The key step of the procedure is the nucleophilic substitution of a fluorine atom in an electron-deficient activated aromatic system (such as -NO_2 or -COR substituted aromatic groups) by a primary or secondary amine that is bonded by an alkyl chain to a trialkoxysilane group (Scheme 1). One of these aminoalkylalkoxysilanes, which are widely commercially available, is 3-aminopropyltrimethoxysilane (APS).[15] Although the nucleophilic substitution of fluorine in activated aromatics by amino groups is an often used synthetic method,[16, 17] it has only recently been used in the preparation of ormosiles and organofunctionalized silicates.[18, 19] One particular advantage of the reaction is that it can be carried out in TEOS (or another tetraalkoxysilane) as solvent (see Experimental Section).



Scheme 1. One-pot synthesis of chromophoric sol–gel hybrid materials.

The combined procedure was tested on a series of structurally different aromatic fluorine compounds (Table 1, 4,4′-difluorobenzophenone (**6**), 4-fluoronitrobenzene, 4,4′-difluorobenzil (**7**), and 1,5-difluoro-2,4-dinitrobenzene (**8**) are not shown). Surprisingly, in the case of fluorine compounds with additional C=C bonds, such as **5**, no Michael addition was observed but only nucleophilic substitution, which lead to the formation of the chromophoric xerogel. However, the yields of the nucleophilic substitution were low, we are currently working on an optimized synthesis which involves, in particular, enhancement of the nucleophilicity of the amino nitrogen atom by the introduction of an activating group (e.g. $Si(CH_3)_3$), or by the addition of base (e.g. NaH). Activation with sodium hydride has given promising results in preliminary experiments.

In the UV/Vis spectrum of the xerogel, the corresponding absorption band (or bands) of the chromophoric group can be detected easily (Table 1). Because of the high polarity of the silicate matrix, bathochromic shifts of the UV/Vis absorption bands are sometimes observed, as the chromophoric groups used are all positively solvatochromic.[23, 24] The intense colors of the new xerogels can be seen in Figure 1. The materials contain up to 20% of the organofunctionalized silane components and thus are also suitable for use as pigments.

When 4-nitroaniline derivatives (starting from **2**) are incorporated into the silicate matrix, uniformly spherical particles with a narrow size-distribution in the µm region are formed in the sol–gel process, as the scanning electron micrograph of a $4\text{-}O_2NC_6H_4NH(CH_2)_3SiO_{1.5}(SiO_2)_x$ material (Figure 2) demonstrates.

Light-scattering experiments[25] indicate that the polar nitroaniline derivative forms micellelike aggregates in TEOS, which also has a structure-determining effect during the sol–gel process. The polar push–pull-substituted aromatic ring in $4\text{-}O_2NC_6H_4NH(CH_2)_3Si(OC_2H_5)_3$ seems to be responsible for the structure formation. Through this simultaneous formation of the catalyst (HF) and the structure-forming agent, there is synergy between the two reactions (nucleophilic aromatic substitution and the sol–gel process). The ratio of ormosile to

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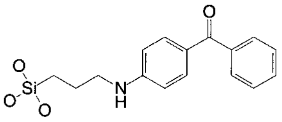
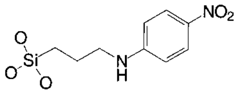
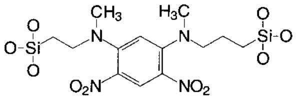
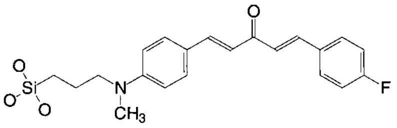
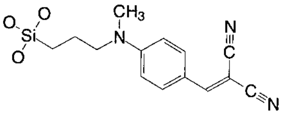
Table 1. Chromophore groups of the xerogels prepared from fluoroaromatics **1**–**5** and aminosilanes, and their UV/Vis absorption bands.

Components[a]	Molar ratio [b]	Chromophore group	λ_{max} [nm]
4-fluorobenzophenone **1**:APS[c]	1:1:10		355 nm
4-fluoronitrobenzene **2**:APS[c]	1:2.5:4.6		350 nm, 443 nm
1,5-difluoro-2,4-dinitrobenzene **3**:MAPS[d]	1:4:10		350 nm, 398 nm
7,7′-difluorodibenzylidenacetone **4**:MAPS[d]	1:2:10		445 nm
1,1-dicyano-2-(4-fluorophenyl)ethene **5**:MAPS[d]	1:1:10		358 nm, 425 nm

[a] Solvent:TEOS. [b] Fluoroarene:aminosilane:solvent. [c] 3-Aminopropyltrimethoxysilane = APS. [d] *N*-methylaminopropyltrimethoxysilane = MAPS.

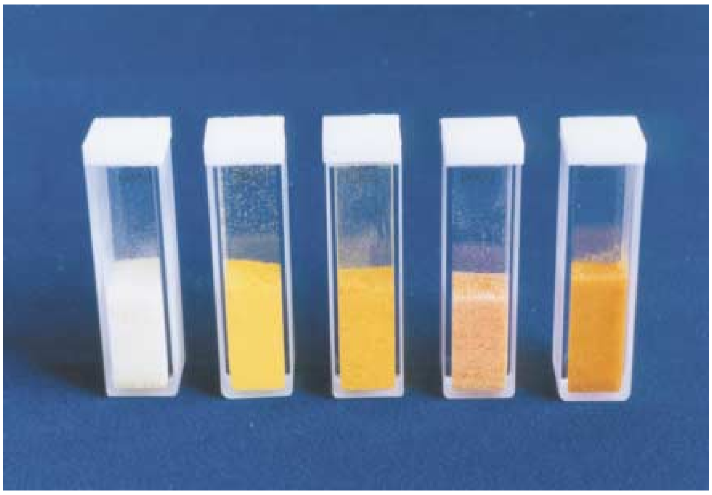


Figure 1. Photograph of the xerogels prepared from fluoroaromatics **1**–**5** (from left to right) and APS or MAPS in TEOS (see Table 1).

TEOS seems to be the morphology-controlling factor that determines the particle size of the 4-nitroaniline-functionalized xerogels.[26a]

A solid-state cross-polarization magic-angle spinning (CPMAS) {^{1}H}-^{29}Si NMR spectrum of the ormosile prepared from **2** and APS in TEOS shows only three signals. The signal at $\delta = -68.9$ ppm (T^3-signal) arises from the trialkoxysilane components which are completely incorporated into the silicate matrix, and the signals at $\delta = -101.6$ (Q^3) and $\delta = -111.9$ ppm (Q^4) are assigned to the silanol groups and the siloxane bridges of the silicate matrix.[20, 21]

The use of bifunctional fluoroaromatic molecules, for example **3** or **6**, could give rise to disubstituted products. In the case of **3**, which because of the two nitro groups is highly activated towards nucleophilic aromatic substitution, after two hours stirring at 130 °C, complete disubstitution was observed; half an hour of stirring at 50 °C lead to the monosubstituted product (see Figure 3). In the case of the less activated **6**, even at a reaction temperature of 210 °C complete disubstitution does not occur, and a mixture of mono- and disubstituted products was obtained. The xerogels were synthesized in TEOS with molar ratios of **3** to *N*-methylaminopropyltrimethoxysilane (MAPS) of 1:1 for monosubstitution and 1:4 for disubstitution (**3**:TEOS 1:10). The assignment of the ^{13}C NMR spectrum signals is shown in Figure 3. The disubstituted product is characterized by a higher symmetry than that of the monosubstituted one and gives rise to fewer signals in the NMR spectrum.

At room temperature and a 1:1 molar ratio of **3**:MAPS, only one fluorine atom is replaced (Figure 3). This monofunctionalized xerogel can be further functionalized with primary or secondary amino compounds. This offers an elegant possibility for the covalent immobilization of water-soluble polymers containing amino groups (such as proteins or polyvinylamines) on chromophoric xerogels.[22]

Several degradation steps are seen in the thermogravimetric analysis of the xerogels. For example, the xerogel synthesized by disubstitution of **3** with MAPS shows two degradation steps. The first arises from the physically bound water and is as expected at 100 °C. The second appears between 300 and 350 °C and arises from degradation of the organic component. Preliminary Brunauer–Emmett–Teller (BET) measurements on the compounds described here show the possibility of formation of both relatively compact and also porous materials, depending on the reaction conditions.[26a,b]

Experimental Section

Reaction of **1** with APS in TEOS: **1** (2.14 g, 10.5 mmol) was dissolved in TEOS (23.5 mL, 105 mmol) with stirring. APS (1.9 mL, 1.88 g, 10.5 mmol)

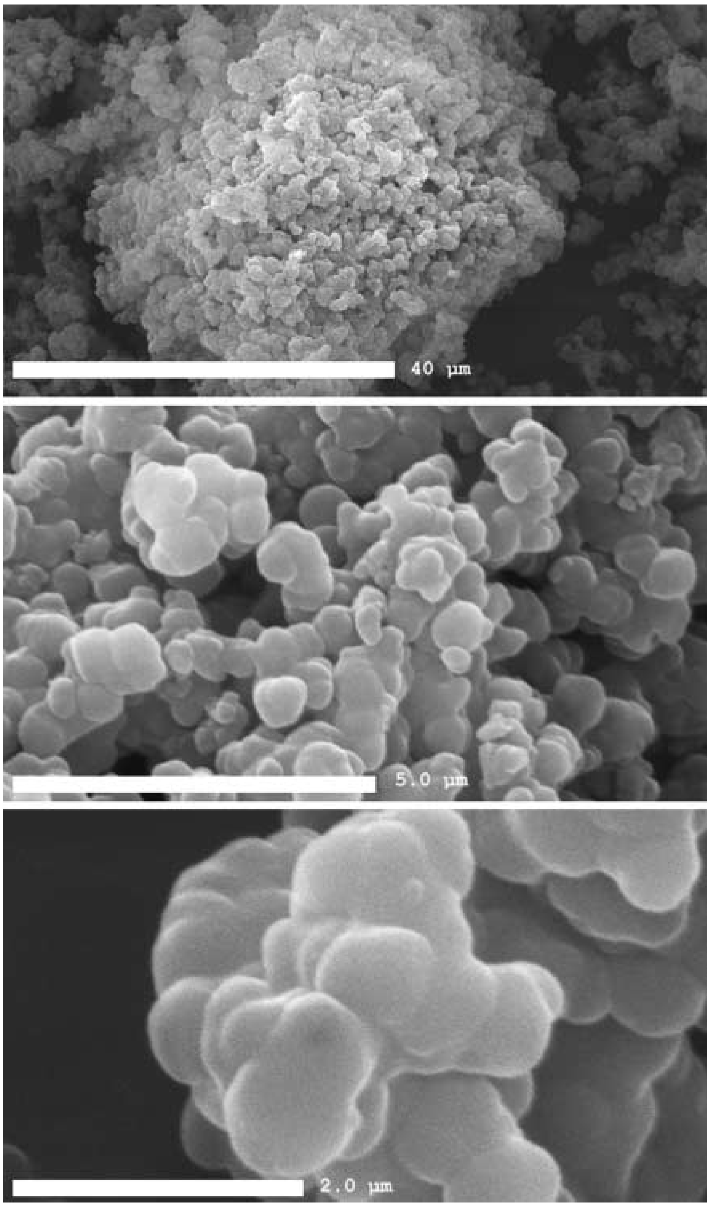


Figure 2. Scanning electron micrograph of the xerogel which was prepared from **2** and APS in TEOS (also see Figure 1 and Table 1).

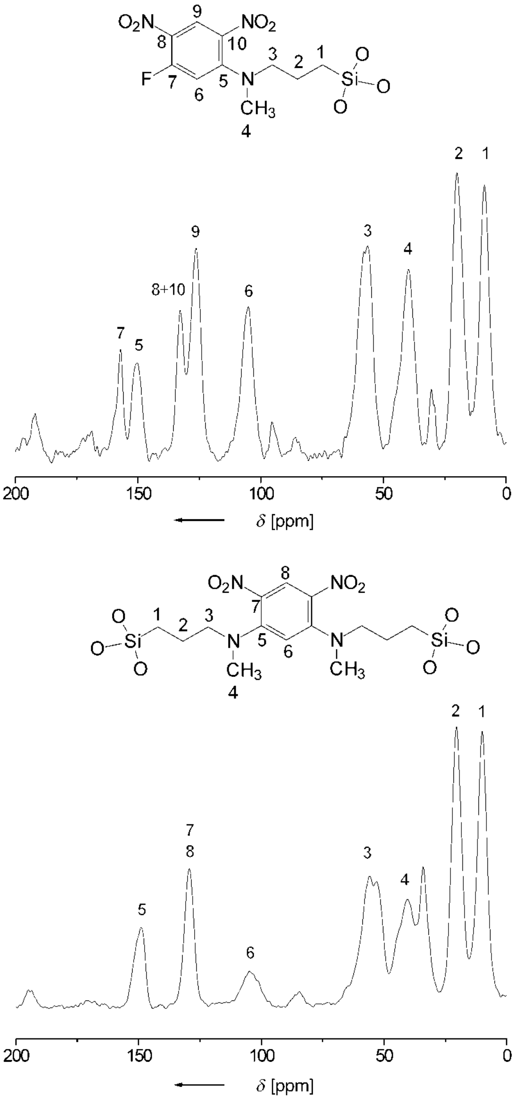


Figure 3. Solid-state $^{13}C\{^1H\}$-CPMAS-NMR spectrum of xerogels prepared from **3** and MAPS in TEOS. A molar ratio of 1:1:10 (**3**:MAPS:TEOS) and a reaction temperature of 50 °C (30 min) leads to monosubstitution (top spectrum). Disubstitution (bottom spectrum) can be achieved by a molar ratio of 1:4:10 at 130 °C (2 h). The ^{13}C resonance signals between $\delta = 8-60$ ppm are assigned to the CH_2 groups of the MAPS. Unlabelled signals arise from unreacted MAPS, or are rotational side-bands.

and *N*,*N*-dimethyloctylamine (2.2 mL, 1.65 g, 10.5 mmol) were then added. The mixture was heated to reflux 14 h (b.p. TEOS: 166–169 °C). An intense yellow coloration developed and a nonviscous yellow solution formed. After cooling to room temperature (25 °C), the dark yellow solution was treated first with ethanol (30 mL) and then with distilled water (8.2 mL, 0.45 mol). After a few seconds or minutes, gel formation began. When the gel was solid, it was dried at 25 °C in vacuo and then unreacted **1** was removed by Soxhlet extraction with acetone. The xerogel was then redried in vacuo. $HOSi^{Q3}O_{1.5}(Si^{Q4}O_{1.5})_xO_{1.5}Si^{T3}C^aH_2C^bH_2C^cH_2NHC_6H_4\text{-}COC_6H_5$: $^{13}C\{^1H\}$-CPMAS-NMR: $\delta = 10$ (C^a), 23 (C^b), 43 (C^c), 115, 128–133 (br. s), 158 (br. s). ^{29}Si NMR: $\delta = 68.9$ (T^3), 101.6 (Q^3), 111.9 ppm(Q^4).

The reaction of **2** with APS in TEOS was carried out analogously but at 140 °C. No gel formation occurred after the addition of water, but a homogeneous yellow powder precipitated (Figure 2). $HOSi^{Q3}O_2(Si^{Q4}O_2)_x\text{-}O_2Si^{T3}C^aH_2C^bH_2C^cH_2NHC_6H_4NO_2$: $^{13}C\{^1H\}$-CPMAS-NMR: $\delta = 10.1$ (C^a), 22.1 (C^b), 42.9 (C^c), 111.2 (C1 aromatic), 127.0 (C2 aromatic), 136.4 (C3 aromatic), 155.4 (C4 aromatic).

The $^{13}C\{^1H\}$-CPMAS-NMR spectra were measured on a Bruker AMX 400 and the $^{29}Si\{^1H\}$-CPMAS-NMR spectra with a Tecmag spectrometer. Chemical shifts were measured relative to adamantane for the ^{13}C NMR spectra, and hexamethyldisiloxane (HMDS) for the ^{29}Si NMR signals, respectively. The UV/Vis spectra were measured using a MCS 400 (Carl Zeiss Jena) UV/Vis spectrometer with a special reflection instrument. The scanning electron micrographs were recorded in the electron-microscope laboratory of the Institute of Physics at the Technical University of Chemnitz, on a Philips SEM 515. Before the photographs were taken, gold was evaporated onto the samples to render them electrically conductive.

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Silicon – Enamine Complexes: Pentacoordinate Silicon Compounds**

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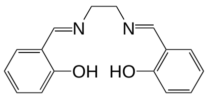
Organosilicon compounds with hypercoordinate Si atoms are interesting both because of their structural features as well as their use in syntheses and as catalytically active intermediates.[1] Their chemical reactivity is controllable by ligand variation. In addition polysilanes which contain hypercoordinate Si atoms in their skeleton display unique electronic and optical properties.[2] Although there are a large number of compounds with penta- or hexacoordinate Si atoms, to date, the principles for a deliberate "switch" between the penta- and hexacoordination are not known. Nevertheless, recently some examples have been described in which the coordination number of a silicon atom can be controlled by the variation of temperature, solvent, and stoichiometry, or by UV irradiation.[3]

The dianions of the compounds **1** and **2** of the type (sal^{2-}) are well established in transition-metal-complex chemistry. We have shown that their tetradentate donor-atom system $^{-}O\frown N\frown N\frown O^{-}$ enables the synthesis of highly coordinated Si complexes, such as **4**, **5**, and **7**.[4] The remaining Si-bound chlorine atoms in **5** can be exchanged for fluorine atoms, for example, by reaction with ZnF_2, (→**6**; Scheme 1). The hexacoordination in **6** is demonstrated by X-ray crystal-structure analysis.[4]



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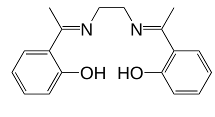

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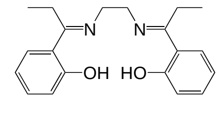

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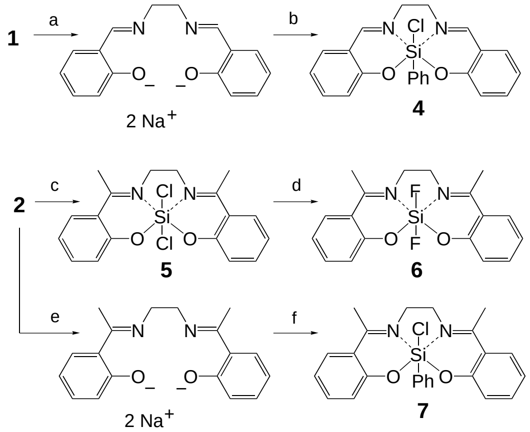

Scheme 1. Syntheses of hexacoordinate silicon – salene complexes. a) NaO*i*Pr/*i*PrOH; b) $PhSiCl_3$/*i*PrOH/88 °C; c) $SiCl_4$/THF/65 °C/2 h; d) ZnF_2/THF/65 °C/1 h; e) 1) NaOMe/THF/MeOH 2) hexane; f) $PhSiCl_3$/THF/30 min.

In contrast to H_2salene (**1**; ethylene-*N*,*N*-bissalicylidenimine), in the methyl- and ethyl-substituted compounds **2** and **3** there is the possibility of imine – enamine tautomerism. However, in complexes with transition-metal ions the enamine structures of **2** and **3** have not yet been observed. To our surprise we found this type of arrangement in the pentacoordinate silicon complexes **8** – **10** (Scheme 2). The synthesis of this new class of enamine complexes can be easily performed by the addition of diethylamine as a base in the reaction of the chlorosilanes $PhSiCl_3$, $MeSiCl_3$, or vinyl$SiCl_3$ with the ligands **2** and **3**. The driving force for this unusual HCl elimination, which is clearly promoted by the hypercoordinate silicon atom, arises from both the high basicity of amine used as well

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