DOI: 10.1002/ejoc.200900332

Carbamate-Linked (Oligo)phenothiazines in Mesoporous Silica by Post-Synthetic Grafting: Fluorescent Redox-Active Hybrid Materials

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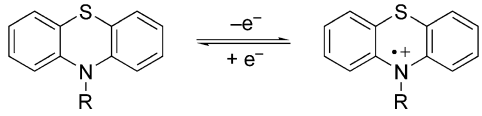
Keywords: Cyclic voltammetry / Fluorescence / Heterocycles / Mesoporous materials / Radical ions

Mesoporous hybrid materials of (oligo)phenothiazines covalently grafted onto MCM-41 or SBA-15 silica have been readily prepared from (oligo)phenothiazinyl carbamates. The phenothiazine precursors show interesting electronic properties according to electronic spectroscopy and cyclic voltammetry. The resulting electronically active hybrid materials display fluorescence and can be oxidized to give stable radical-cationic species upon mild oxidation.

Introduction

Mesoporous silica materials[1] contain regular and well-ordered pores with very high specific surfaces (1000 m^2/g) that can be chemically modified through the reaction of the Si–OH bonds present in the cavities.[2] As intriguing host structures for functional molecules their applications include nanoscale chemistry and physics,[3] optical and magnetic materials,[4] catalysis,[5] and even functional materials and molecular machines.[6] Particularly important for the development of functional materials are electronically active entities as mesoporous hosts are not only transparent to visible light, but they can also stabilize reactive redox or photoexcited intermediates. Of the redox-active heterocycles, phenothiazines,[7] tricyclic nitrogen- and sulfur-containing heterocycles that are well-established due to a broad spectrum of pharmacological activity,[8] possess particularly interesting properties. Owing to their low oxidation potentials, they readily form stable radical cations by reversible one-electron oxidations (Scheme 1) and some of their physiological activity can be attributed to this type of reactivity.[9]



Scheme 1.

Furthermore, the radical cations give rise to a fingerprint of characteristic, deep-colored absorptions.[7,10] As spectroscopic probes, phenothiazine derivatives have found entry into molecular and supramolecular arrangements for photoinduced electron transfer (PET) studies[11] and as motifs in organic materials.[12] The inherent adsorption of phenothiazines on silica surfaces is quite small[13] and does not lead to irreversible anchorage. EPR studies of photo-oxidized phenothiazines adsorbed on porous silica have shown that radical cations are formed and presumably the silica framework acts as an electron acceptor. This property has been applied in a sensor system for the analysis of redox enzymes in which phenothiazines serve as electron shuttles. Interestingly, phenothiazines covalently bound to silica or mesoporous silica have not been reported prior to our studies. Just recently, we disclosed a proof of principle for the incorporation of functionalized phenothiazines in mesoporous MCM-41 by post-synthetic grafting.[14]

As part of our program to synthesize and investigate (oligo)phenothiazinyl-based molecular wires,[15] we have communicated the syntheses, structures, and first cyclic voltammetry measurements of directly linked phenothiazinyl dyads, triads,[16] and oligomers,[17] which can be regarded as models for polymer-based coupled electrophores. Herein, we report on the syntheses and properties of various carbamate-based phenothiazines and (oligo)phenothiazines, that is higher oligomers of phenothiazines, and the synthe-

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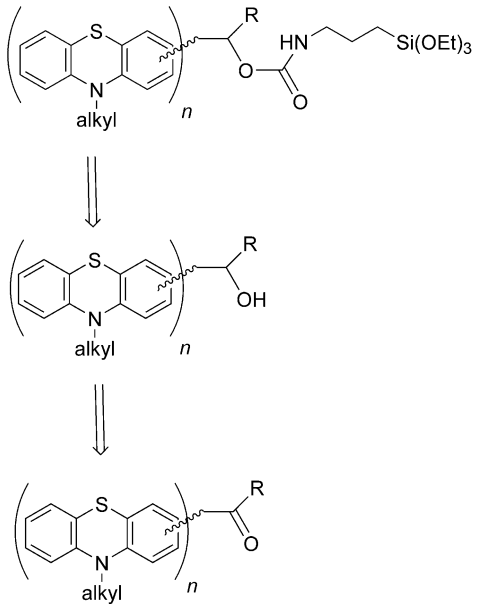
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900332.

ses and properties of novel redox-active structured hybrid materials by covalently grafting these electrochromophores onto mesoporous silica.

Results and Discussion

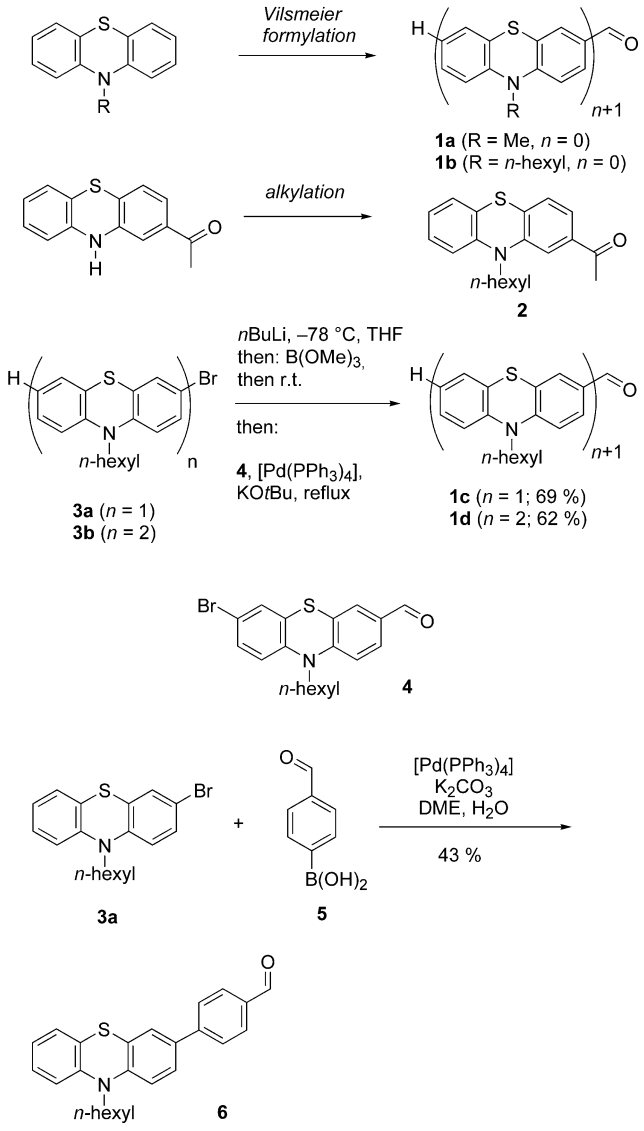
Synthesis of Phenothiazinyl Building Blocks

Carbamates are synthetically accessible by straightforward addition of an alcohol to an isocyanate. The major advantage of this approach lies in its highly atom-economic use of both starting materials. The reaction proceeds without the formation of any byproducts. Therefore, the retrosynthetic analysis for carbamate-based phenothiazinyl and (oligo)phenothiazinyl building blocks for incorporation into mesoporous silica suggests carbamate formation from a phenothiazinyl-substituted alcohol with a commercially available triethoxysilyl-functionalized isocyanate (Scheme 2). The alcohol in turn can be prepared by reduction of the corresponding carbonyl compound.

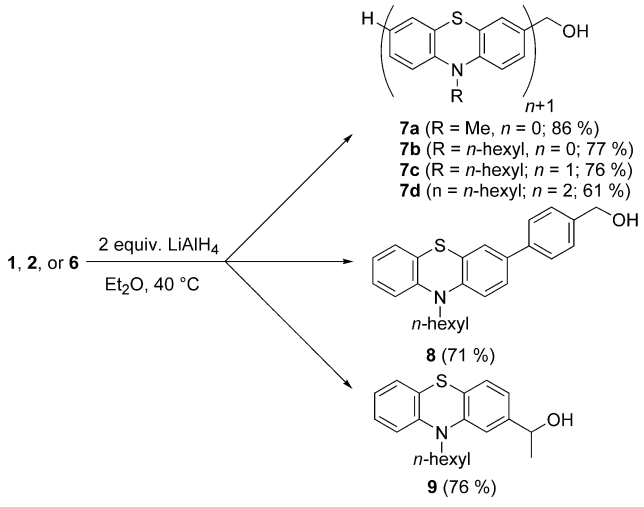


Scheme 2. Retrosynthetic analysis of carbamate-based (oligo)-phenothiazinyl building blocks.

Phenothiazinyl aldehydes **1a** and **1b** (n = 0) are easily prepared by Vilsmeier formylation of 10-methyl- or 10-*n*-hexylphenothiazine and ketone **2** is obtained by alkylation of the commercially available 2-acetylphenothiazine (Scheme 3). For aldehydes with extended π conjugation, Suzuki cross-coupling is the most favorable, mild, and straightforward access to functionalized phenothiazines. Therefore, one-pot borylation–coupling of bromophenothiazines **3**[18] with 7-bromo-10-*n*-hexylphenothiazine-3-carbaldehyde (**4**) or the coupling of **3a** with *p*-formylphenylboronic acid (**5**) leads to the aldehydes **1c**, **1d**, and **6** in moderate-to-good yields.



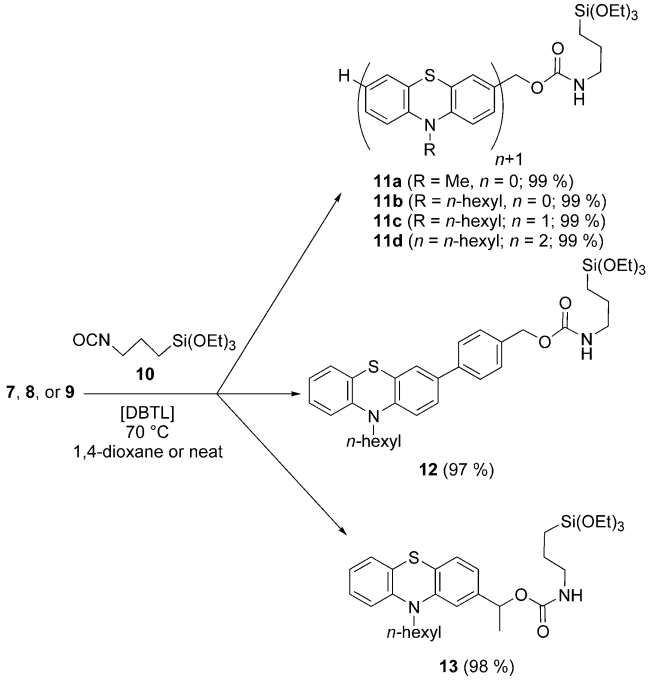
Scheme 3. Synthesis of phenothiazinylcarbonyl compounds.



Scheme 4. Reduction of (oligo)phenothiazinylcarbonyl compounds **1**, **2**, and **6** with $LiAlH_4$ to the corresponding alcohols **7**, **8**, and **9**.

By standard reduction with lithium aluminium hydride[19] in diethyl ether at reflux the carbonyl compounds **1**, **2**, and **6** provide the corresponding alcohols **7**, **8**, and **9** in good yields (Scheme 4). With these alcohols in hand the stage is set for the introduction of the triethoxysilane linker by isocyanate addition.

Reaction of the alcohols **7**, **8**, and **9** with 3-(triethoxysilyl)propyl isocyanate (**10**)[20] in dry 1,4-dioxane or neat at 70 °C under argon and in the presence of dibutyltin dilaurate (DBTL) as catalyst gave the desired carbamates **11**–**13** in quantitative yields (Scheme 5). The structures of the carbamates were unambiguously confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and combustion analyses or high-resolution mass spectrometry.



Scheme 5. Synthesis of (oligo)phenothiazinecarbamates **11**–**13**.

Electronic Properties of the Carbamates 11–13

The electronic properties of the (oligo)phenothiazinecarbamates **11**–**13** were investigated by absorption and emission spectroscopy and by cyclic voltammetry (Table 1). Most characteristically, for all the carbamates, the absorption in the UV region is accompanied by an intense blue-to-greenish blue fluorescence. The emission maxima lie between 441 and 474 nm. The Stokes shifts are quite remarkable and lie in the range $\Delta\tilde{\nu}$ = 5600–10500 cm^{-1}. Substantial Stokes shifts have also been observed for many other phenothiazine derivatives[15,16] and can be attributed to significant geometrical changes upon excitation from a highly nonplanar ground state to a largely planar excited state.[21] The electrochemical data for the phenothiazines prepared in this work were obtained by cyclic voltammetry in the anodic region (up to 1.2 V). For all the compounds reversible oxidation steps are found, which reflects the number of phenothiazine cores in the individual molecules. The first oxidation potentials stemming from the most electron-rich phenothiazine core are found to range from $E_0^{0/+1}$ = 542 mV (terphenothiazine **11d**) to $E_0^{0/+1}$ = 768 mV (monophenothiazine **11a**).

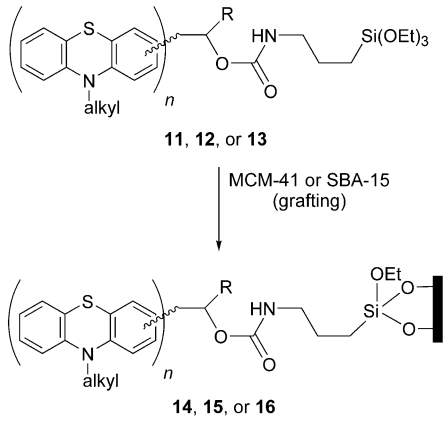
Table 1. Selected absorption and emission spectral[a] and cyclovoltammetric data for compounds **11**–**13**.

Compound	Absorption $\lambda_{max,abs}$ [nm]	Emission $\lambda_{max,em}$ [nm]	Stokes shift $\Delta\tilde{\nu}$[c] [cm^{-1}]	$E_0^{0/+1}$ [mV]	$E_0^{+1/+2}$ [mV]	$E_0^{+2/+3}$ [mV]
11a	312, 290, 258	465	10500	768	–	–
11b	314, 260	441	9500	735	–	–
11c	366, 322, 268	461	5600	729	893	–
11d	373, 324, 270	474, 514 (sh)	5700	542	710	827
12	322, 268, 240	467	9600	669	–	–
13	312, 260	453	10000	734	–	–

[a] Recorded in CH_2Cl_2, T = 20 °C. [b] Recorded in CH_2Cl_2, T = 20 °C, v = 100 mV/s, electrolyte: nBu$_4$N$^+$ PF$_6^-$, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode. [c] $\Delta\tilde{\nu}$ = $\lambda_{max,abs} - \lambda_{max,em}$ [cm^{-1}].

Synthesis of Mesoporous Hybrid Materials

The carbamate linker is sufficiently stable to allow post-synthetic grafting of the electrophore units in toluene onto MCM-41 or SBA-15 under reflux conditions. Unreacted precursors were removed by Soxhlet extraction with dichloromethane and the organic/inorganic hybrid materials obtained [(oligo)phenothiazine@MCM-41 or (oligo)phenothiazine@SBA-15] are denoted as **14**–**16** (Scheme 6, Table 2). To probe the size effect of different (oligo)phenothiazine units in detail, the functionalized MCM-41 materials were prepared under the same conditions. Elemental analyses showed that the loading of MCM-41 with phenothiazines varies (**14a** > **14b** > **16** > **15** > **14c**). We attribute these differences to variations in the molecular size of the organic unit. In particular, in the case of the biphenothiazine **11c**, only traces of nitrogen (ca. 0.1%) could be detected by elemental analysis. In addition, TG-DTA analysis exhibited only 1.8% mass loss in the temperature range of 300–600 °C, which corresponds to a grafting of 0.03 mmol/g of



Scheme 6. Mesoporous hybrid materials obtained by post-synthetic grafting onto MCM-41 or SBA-15.

Table 2. The textural parameters of parent MCM-41, SBA-15, **14**, **15**, and **16** derived from nitrogen adsorption/desorption analysis and the content of loaded phenothiazines in the hybrid materials.

Sample	Substrate	BET surface area [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$]	Pore diameter [Å]	Content of phenothiazine[a] [mmol g^{-1}]	[wt.-%]
	Neat MCM-41	1092	0.95	28	–	–
	Neat SBA-15	1101	1.58	65	–	–
14a	MCM-41	814	0.62	23	0.41	15.5
14b	MCM-41	846	0.68	23	0.34	15.3
14c	MCM-41	996	0.90	28	0.03[b]	1.8[b]
14c*	SBA-15	806	1.19	60	0.32	23.4
14d	SBA-15	716	0.96	56	0.17	17.2
15	MCM-41	935	0.80	26	0.24	12.6
16	MCM-41	903	0.72	23	0.30	13.9

[a] Calculated according to the content of nitrogen (CHN elemental analysis). [b] Calculated from the data of a TG-DTG analysis (weight loss from 300–600 °C).

11c onto MCM-41. The molecular size of **11c** was estimated by molecular modeling to be about 2.9 nm, which is larger than the mean pore size of the substrate MCM-41 (2.8 nm). This size effect may hinder the diffusion of **11c** into the pore channels during the post-synthetic grafting process. Therefore, only the "outer" surface of the support is decorated with the redox-active organic substrate. We thus used SBA-15 as the support for the grafting of the phenothiazine dyad **11c** and the even larger triad **11d**. SBA-15 possesses the same mesostructure as MCM-41, but provides a relatively large medium pore diameter (6.5 nm in our case). This led in the case of **14c*** (SBA-15) to a significant increase in the loading with respect to **14c** (MCM-41).

Structural Properties of the Mesoporous Hybrid Materials

The powder XRD patterns of extracted neat MCM-41 and **14a**–**c**, **15**, and **16** are shown in Figure 1A; those of samples **14c*** and **14d** together with neat SBA-15 are presented in Figure 1B. Neat MCM-41 shows four Bragg reflections from the (100), (110), (200), and (210) planes, which can be indexed to a two-dimensional (2D) hexagonal *p6mm* symmetry and indicate a highly ordered hexagonal structure. Neat SBA-15 is characterized by three reflections from the (100), (110), and (200) planes in the 2θ range of 0.8–2°, which can also be indexed to a hexagonal cell. After modification, all the samples still exhibit the first- [(100)] and second-order reflections [(110) and (200)], which indicates the structural preservation of the materials. The lower intensities of the modified samples in comparison with the neat materials can be attributed to a diminished mesostructural order and/or to a reduced scattering contrast between the silica wall and the porous system.[22]

Nitrogen sorption was used to follow the changes in the pore structure that result from modification of the surface by the grafting of the organic compounds. The specific surface areas and the textural properties of neat MCM-41, SBA-15, and all hybrid samples are summarized in Table 2. Both parent mesoporous substrates exhibit type IV isotherms, which is typical of periodic mesoporous materials (Figure 2, A and B).[23] The isotherm of MCM-41 shows no hysteresis, which indicates a uniform pore size and ordered

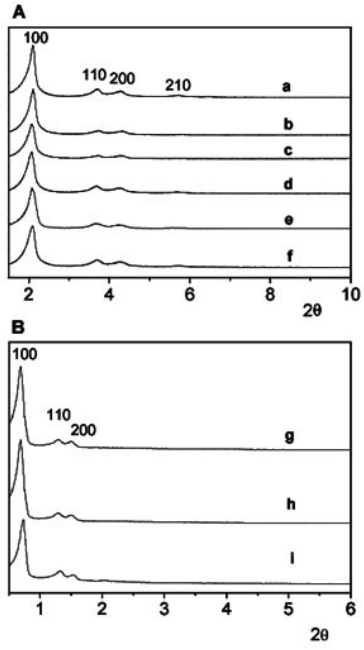


Figure 1. A: Powder XRD patterns of (a) parent MCM-41, (b) **14a**, (c) **14b**, (d) **14c**, (e) **15**, and (f) **16**; B: powder XRD patterns of (g) parent SBA-15, (h) **14c*,** and (i) **14d**.

cylindrical channels.[24] SBA-15 displays a distinct hysteresis loop (type H1) and a sharp increase in the adsorption at higher P/P_0 values (0.65), which indicates a uniform mesostructure with large pores.[25] The pore size distribution curves of the neat supports and the hybrid samples are illustrated in Figure S1 of the Supporting Information). The volumes and pore sizes were calculated by using the Barrett–Joyner–Halenda (BJH) method and the specific surface areas were obtained by Brunauer–Emmett–Teller (BET) treatment of the isotherm. The phenothiazine contents of the materials are given in Table 2. Clearly the specific surface areas, the pore sizes, and the pore volumes of all the hybrid materials are smaller than those of neat MCM-41 and SBA-15 due to the presence of the organic fragments in the pore channels.[26] However, the type IV isotherms and the narrow pore size distributions are maintained in all the modified samples proving the ordering of the mesoporous structures of these materials.

IR and NMR Investigations

FTIR spectroscopy was used to provide information on the organic modifications of the silica systems. The IR spectra of all the hybrid materials are shown in Figure 3, except sample **14c**. In this case the characteristic absorptions of the organic group could not be observed due to the small amount of organic species in the material. For comparison, the spectra of neat MCM-41 and SBA-15 are presented in Figure S2 of the Supporting Information. The broad band in the range of 3600–3200 cm^{-1} can be assigned to the O–H stretching absorption of bonded internal Si–OH groups. The band at around 1100 cm^{-1} is attributed to the asymmetric Si–O–Si vibration, and the peak at 800 cm^{-1} to the symmetric Si–O–Si vibration. Absorptions at 950 and 460 cm^{-1} can be assigned to the bending vibrations of the surface silanols and Si–O, respectively.[27] In addition to these bands, which characterize the bulk SiO_2 material, the anchoring of the organic groups can be proved by the presence of aliphatic CH stretching (3000–2700 cm^{-1}) and deformation vibrations (1470 cm^{-1}).[28] Furthermore, typical peaks of C=O carbamate stretching vibrations are observed at about 1700 cm^{-1} These findings confirm the introduction of carbamate-linked phenothiazine molecules in the mesoporous supports.

The successful introduction and covalent ligation of the phenothiazine components were additionally verified by solid-state ^{13}C CP-MAS NMR spectroscopy. All the hybrid materials show solid-state ^{13}C NMR spectra similar to those of the corresponding free phenothiazines. Figure 4, as an example, shows the spectrum of **14c***; the red lines provide information on the resonances in the solution $^{13}C\{^1H\}$ NMR spectrum of **11c**. The strong peak at δ = 8 ppm can be assigned to the C–Si unit, which demonstrates that this bond is not cleaved during the grafting process. The overlapping resonances between δ = 20 and 40 ppm are due to the presence of alkyl groups. The peaks in the aromatic region can be assigned to the electron-rich phenothiazine core. Compared with the spectrum in solution, a small downfield shift of the carbon resonance of the C=O group is observed, which can be assigned to an interaction between the carbonyl group and Brønsted/Lewis acidic surface sites.[14]

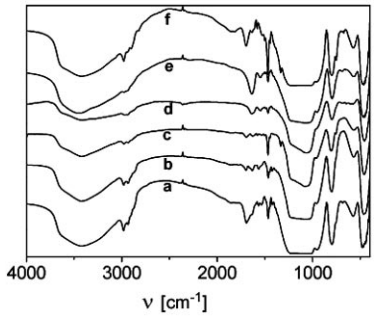


Figure 3. FTIR spectra of (a) **14a**, (b) **14b**, (c) **14c***, (d) **14d**, (e) **15**, and (f) **16**.

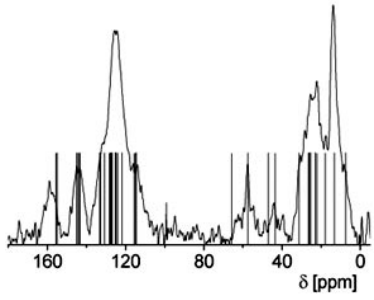


Figure 4. ^{13}C CP-MAS NMR spectra of **14c***; the lines give information on the resonances in the solution NMR spectra of **11c**.

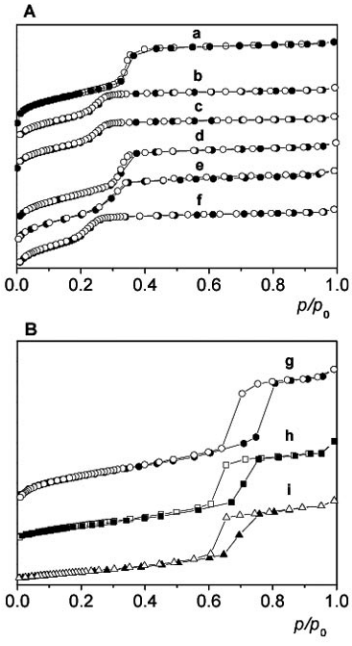


Figure 2. A: N_2 adsorption/desorption isotherms of (a) neat MCM-41, (b) **14a**, (c) **14b**, (d) **14c**, (e) **15**, and (f) **16**; B: N_2 adsorption/desorption isotherms of (g) neat SBA-15, (h) **14c***, and (i) **14d** (adsorption points are marked by solid symbols and desorption points by empty symbols).

Optical Properties of the Hybrid Materials

All the phenothiazine-containing hybrid materials show several strong absorptions in the ultraviolet region (Figure 5, solid lines, and Table S4 of the Supporting Information). These are similar to the absorptions of the pure organic compounds (see Table 1). A slight redshift of the peak maxima can be observed by increasing the number of phenothiazine cores or by linking a phenyl group to the phenothiazine site. On the basis of the absorption spectra of the hybrid materials it can be postulated that the interaction between the phenothiazine moieties and the silica framework is only weak. The slight band-broadening in the spectra of incorporated phenothiazine molecules compared with the pure organic compounds in solution may be attributed to weak π-electron interactions with surface hydroxy groups. This phenomenon is often observed for aromatic chromophores adsorbed on silica materials.[29]

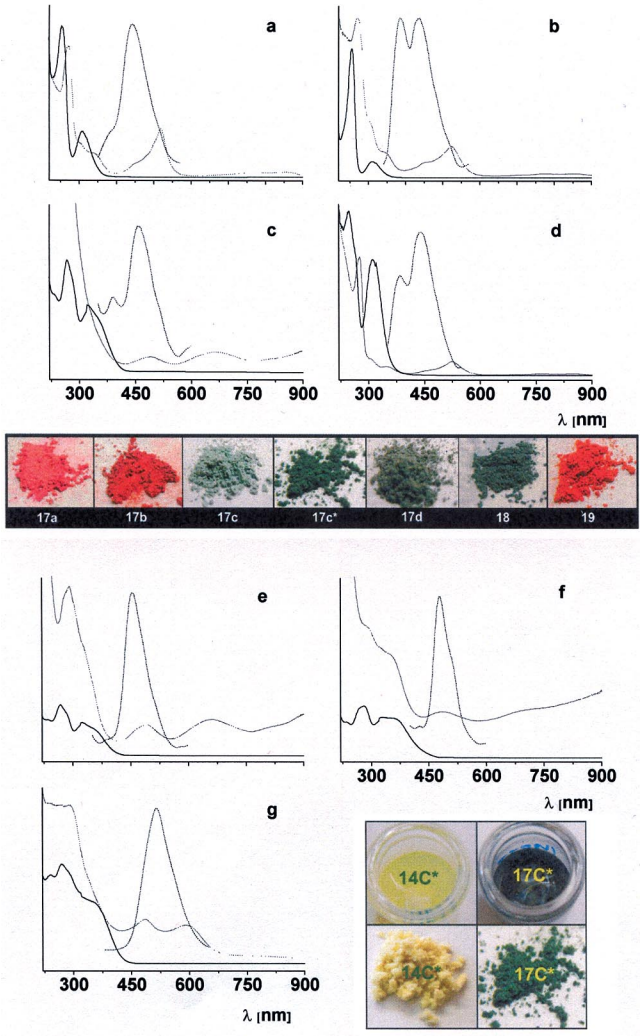
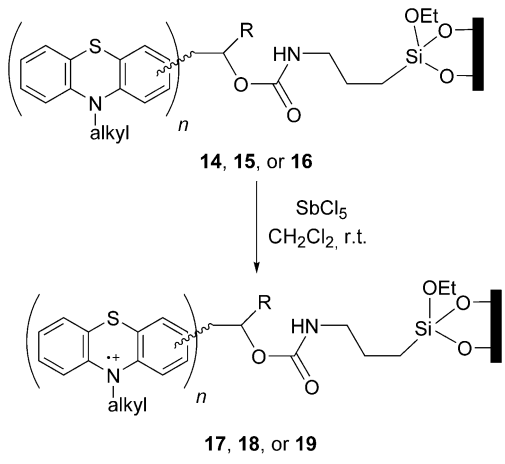


Figure 5. UV/Vis absorption spectra of modified samples of (a) **14a**, (b) **14b**, (c) **14c**, (d) **16**, (e) **14c***, (f) **14d**, and (g) **15** (solid lines), the absorptions of the corresponding radical-cation samples **17a**, **17b**, **17c**, **19**, **17c***, **17d**, and **18** (dotted lines), and the emission spectra of modified samples (dashed lines). The inset in the middle exhibits the different colors of the solid products after oxidation. The inset in the bottom panel shows the color change caused by the oxidation of **14c*** in suspension and in the solid state.

The photoluminescence spectra of the hybrid materials are also shown in Figure 5 (dashed lines). Similar to the corresponding purely organic precursors, the hybrid materials show emission at about 440–470 nm. Only sample **15** reveals a pronounced bathochromic shift of the emission maximum relative to its precursor **12**; a similar effect was observed in the absorption spectra of **15**. At the moment there is only speculation on this finding: **12** is the largest phenothiazine that could be introduced into the narrow pores of MCM-41. Interaction of the π system with the walls of the support may cause an increase in the parallel orientation of the phenyl ring and the phenothiazine moiety and thus lead to a redshift of the absorption and emission. In addition, for **14b**, **14c**, and **16**, besides the expected maxima at around 430 nm, additional maxima at 390 nm can be observed, which are absent in the solution spectra of the precursor carbamates **11**–**13**. This dual emission is either caused by conformational biases as a consequence of restricted molecular rotation and relaxation inside the pores or by population of TICT (twisted intramolecular charge transfer) states.[30]

Detection of Stable Phenothiazine Radical Cations in the Materials

Phenothiazines in MCM-41 or SBA-15 form stable radical cations upon treatment with oxidizing agents (Scheme 7). The oxidation of phenothiazine was carried out with the one-electron acceptor antimony pentachloride in a dichloromethane suspension, leaving $SbCl_6^-$ as the counterion.[31] For the materials **14a**, **14b**, and **16**, functionalized with monophenothiazine, a color change to red was observed during the oxidation reaction (Figure 5, middle inset). This color change is manifested by an absorption band at around 515 nm, which is typical of a phenothiazine radical cation (see parts a,b,d in Figure 5).[32] In contrast, oxidation of the (oligo)phenothiazine functionalized materials **14c**, **14c***, and **14d** furnished greenish products with absorption spectra that are different to those of the monophenothiazine radical cations. This result indicates besides phenothiazine radical cations the presence of di- and even tricationic species as a consequence of the oxidation of (oligo)phenothiazines.[33,34] Therefore, we assigned the broad absorption band in the Vis/NIR region to intramolecular charge-transfer (CT) bands. Furthermore, because the oxidation of phenothiazine moieties results in a considerable structural change, from the butterfly conformation of the native neutral form to the planar radical cation,[21] intermolecular interactions between the native and oxidized phenothiazine moieties within the pores can also be expected. Hence, the observed solid-state UV/Vis spectra of the oxidized materials **17**–**19** represent a superposition of intra- and intermolecular electronic interactions, which accounts for the formation of intensely colored materials. Note that the resulting deeply colored materials **17**–**19** preserve their color and thus the radical-cation nature of the oxidized hy-



Scheme 7. Oxidation of mesoporous phenothiazinyl hybrids.

brid materials for weeks at ambient temperature when stored under nitrogen.

The existence of stable phenothiazine radical cations in the hybrid materials was additionally confirmed by EPR spectroscopy. The EPR spectrum of **15** is shown as an example in Figure 6 (the spectra of **14c*** and **14d** are shown in the Supporting Information) and reveals a *g* value of 2.0051. Because the EPR signal is not resolved, hyperfine coupling constants and anisotropic *g* tensors could not be determined. However, the high symmetry of the EPR spectrum indicates that the phenothiazine radicals are in an isotropic environment in the hybrid materials.

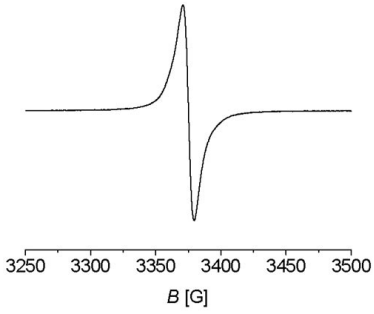


Figure 6. Q-band EPR spectrum of **15** at 297 K.

Conclusions

A series of novel hybrid organic/inorganic mesoporous silica materials have been synthesized by covalently grafting carbamate-linked (oligo)phenothiazines onto MCM-41 or SBA-15. The molecular precursors display fluorescence and low oxidation potentials, that is, they possess favorable electronic properties for electronically active materials. Highly ordered hexagonal mesoporous structures were confirmed by XRD and N_2 adsorption measurements. ^{13}C CP-MAS NMR and FTIR data show the successful incorporation of the organic species into the solid materials. The existence of stable phenothiazine radical cations in the materials is clearly observed by UV/Vis and EPR spectroscopy. Further studies towards increasing the phenothiazine content in the pores and elucidating the properties of the novel hybrid systems are underway in our laboratories.

Experimental Section

General: Reagents, catalysts, and solvents were purchased reagent grade and used without further purification. THF, diethyl ether, and 1,4-dioxane were dried and distilled according to standard procedures.[35] Phenothiazinecarbaldehyde **1** was prepared according to procedures published in the literature.[36,37] Column chromatography: silica gel 60, mesh 70–230. TLC: silica gel plates. ^1H and ^{13}C NMR spectra: CD_2Cl_2, $CDCl_3$, and [D_6]acetone (referenced to Me_4Si).[38] The assignments of quaternary C, CH, CH_2, and CH_3 were made by using DEPT spectroscopy. Elemental analyses were carried out in the Microanalytical Laboratories of the Organisch-Chemisches Institut, Ruprecht-Karls-Universität, Heidelberg, Germany, the Institut für Pharmazeutische Chemie, Heinrich-Heine-Universität, Düsseldorf, Germany, and the Fachbereich Chemie, Technische Universität Kaiserslautern.

Electrochemistry: Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed CH_2Cl_2 at room temperature and at scan rates of 100, 250, 500, and 1000 mV/s. The electrolyte was Bu_4NPF_6 (0.025 M). The working electrode was a 1 mm platinum disk, the counter-electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. The potentials were corrected to the internal standard of ferrocene/ferrocenium in CH_2Cl_2 ($E_0^{0/+1}$ = 450 mV).[39]

Characterization of the Hybrid Materials: The loading of the silica samples with organic groups was calculated from the nitrogen content of the elemental analysis obtained with a Carlo–Erba (model EA 1108) Elemental Analyzer. Thermogravimetric and differential thermogravimetric analyses (TG-DTG) were carried out with a Rheometric Scientific STA 1500 analyzer using an alumina pan in air and by heating from ambient temperature to 800 °C at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) patterns of the solid samples were obtained with a Siemens D5005 diffractometer with Cu-K_α radiation (λ = 1.5404 Å, 30 kV, 30 mA). N_2 adsorption/desorption isotherms were measured at 77 K with a Quantachrome Autosorb 1 sorption analyzer after evacuating the samples at a temperature of 120 °C for 12 h. The specific surface areas were calculated from the BET equation by using the adsorption data obtained in the low relative pressure range of 0.04–0.2 and the pore size distribution curves were obtained from the desorption branch by the BJH method. The infrared spectra (KBr) were recorded using a Jasco FT/IR-6100 spectrometer. Proton-decoupled solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra were obtained with a Bruker DSX Avance spectrometer at resonance frequencies of 100.6 and 79.5 MHz, respectively. UV/Vis diffuse reflectance spectra were recorded with a Perkin–Elmer Lambda-18 spectrophotometer with neat MCM-41 or SBA-15 as the background standard. Q-band CW EPR experiments were performed at 297 K with a Bruker EMX 10–40 spectrometer.

2-Acetyl-10-hexyl-10*H*-phenothiazine (2): 2-Acetyl-10*H*-phenothiazine (9.61 g, 40 mmol) was dissolved in dry THF (100 mL), potassium *tert*-butoxide (4.71 g, 42 mmol) was added, and the solution was stirred at room temp. for 1 h. Then 1-bromohexane (10.2 mL, 72 mmol) was slowly added dropwise to the reaction mixture and the stirring was continued at 70 °C for 16 h. The dark solution was cooled to room temp and diluted with dichloromethane. The solution was washed with water and sodium sulfite solution, the organic layer was dried with magnesium sulfate, and the solvents were removed in vacuo. The residue was purified by chromatography on silica gel (hexane/acetone, 15:1) to give 8.01 g (62%) of **2** as an orange oil. R_f (hexane/acetone, 5:1) = 0.45. ^1H NMR ([D_6]-acetone, 300 MHz): δ = 0.77 (t, J = 7.1 Hz, 3 H), 1.21 (m, 4 H), 1.34 (m, 2 H), 1.68 (m, 2 H), 2.43 (s, 3 H), 3.78 (t, J = 7.1 Hz, 2 H), 6.80 (m, 2 H), 6.99 (dd, J = 7.5, 1.5 Hz, 1 H), 7.07 (m, 2 H), 7.34 (m, 2 H) ppm. ^{13}C NMR ([D_6]acetone, 75 MHz): δ = 14.2 (CH_3), 23.0 (CH_2), 26.8 (CH_3), 26.9 (CH_2), 27.0 (CH_2), 31.8 (CH_2), 47.9 (CH_2), 114.3 (CH), 116.2 (CH), 123.0 (CH), 123.2 (CH), 123.9 (C_{quat}), 125.0 (C_{quat}), 127.3 (CH), 127.6 (CH), 128.0 (CH), 136.8 (C_{quat}), 145.0 (C_{quat}), 145.9 (C_{quat}), 197.4 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 2955, 2929, 2856, 1680, 1592, 1559, 1463, 1444, 1378, 1357, 1324, 1275, 1226, 1132, 1108, 921, 810, 750, 636 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (22600), 282 (22600), 374 (1500 L/mol cm) nm. MS (FAB$^+$): *m*/*z* (%) = 325.3 (100) [M]$^+$, 254.2 (19) [M – C_5H_{11}]$^+$, 240.2 (15) [M – C_6H_{13}]$^+$. $C_{20}H_{23}NOS$ (325.3): calcd. C 73.53, H 7.24, N 4.39, S 9.49; found C 73.81, H 7.12, N 4.30, S 9.85.

4-(10-Hexyl-10*H*-phenothiazin-3-yl)benzaldehyde (6): A solution of 3-bromo-10-hexyl-10*H*-phenothiazine (**3a**; 1.83 g, 5.06 mmol), 4-formylphenylboronic acid (**5**; 630 mg, 4.21 mmol), potassium carbonate (1.74 g, 12.6 mmol), and tetrakis(triphenylphosphane)palladium (190 mg, 0.16 mmol) in a degassed mixture of dimethoxyethane (28 mL) and distilled water (14 mL) was stirred at reflux for 14 h under argon. After cooling to room temperature, a solution of sodium sulfite and water was added to the reaction mixture. The aqueous layer was washed several times with small portions of dichloromethane, the combined organic layers were dried with magnesium sulfate, and the solvents were removed in vacuo. The residue was purified by chromatography on silica gel (hexane/diethyl ether, 10:1) to give 860 mg (43%) of **6** as an orange resin. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.83 (t, J = 6.9 Hz, 3 H), 1.28 (m, 4 H), 1.45 (m, 2 H), 1.79 (m, 2 H), 3.95 (t, J = 7.0 Hz, 2 H), 6.97–7.22 (m, 4 H), 7.40–7.66 (m, 3 H), 7.81 (d, J = 8.3 Hz, 2 H), 7.94 (d, J = 8.3 Hz, 2 H), 10.03 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]-acetone, 75 MHz): δ = 14.2 (CH$_3$), 23.2 (CH$_2$), 27.1 (CH$_2$), 27.5 (CH$_2$), 32.1 (CH$_2$), 47.9 (CH$_2$), 116.7 (CH), 116.9 (CH), 123.5 (CH), 124.8 (C$_{quat}$), 126.4 (CH), 127.2 (CH), 127.5 (CH), 128.1 (CH), 128.4 (CH), 129.1 (CH), 129.8 (CH), 129.9 (CH), 130.4 (CH), 130.9 (CH), 134.3 (C$_{quat}$), 136.2 (C$_{quat}$), 145.6 (C$_{quat}$), 146.2 (C$_{quat}$), 146.6 (C$_{quat}$), 192.3 (CH) ppm. IR (film): $\tilde{\nu}$ = 2954, 2930, 1696, 1602, 1574, 1465, 1444, 1362, 1334, 1251, 1214, 1171, 810, 749 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 (28800), 282 (2900), 302 (1900), 376 (1100 L/mol cm) nm. MS (FAB$^+$): m/z (%) = 387.3 (100) [M]$^+$, 358.3 (3) [M – CHO]$^+$, 302.2 (22) [M – C$_6$H$_{13}$]$^+$. $C_{25}H_{25}NOS$ (387.5): calcd. C 77.48, H 6.50, N 3.61; found C 77.05, H 6.61, N 3.50.

General Procedure for the Reduction of Phenothiazinyl-Substituted Carbonyl Compounds 1, 2, and 6 with Lithium Aluminium Hydride (GP1): A solution of the phenothiazinyl-substituted carbonyl compound **1**, **2**, or **6** (1 equiv.) in dry diethyl ether (30 mL per equiv. of carbonyl compound) was slowly added through a dropping funnel to a well-stirred mixture of lithium aluminium hydride (2.0 equiv.) in dry diethyl ether (20 mL per equiv. of $LiAlH_4$) heated to 40 °C over 20–30 min. The reaction mixture was stirred at 40 °C for 16 h and was then cooled to 0 °C. Then water (50 mL) and diluted hydrochloric acid (10 mL) were added. The aqueous phase was washed with small portions of diethyl ether, the combined organic phases were dried with magnesium sulfate, and the solvents were removed in vacuo. The residue was purified by chromatography on silica gel to furnish the pure phenothiazinyl-substituted alcohols **7**, **8**, or **9** as solids or oils.

(10-Methyl-10*H*-phenothiazin-3-yl)methanol (7a): According to GP1 and after chromatography on silica gel (hexane/diethyl ether, 5:1) the alcohol **7a** (604 mg, 84%) was isolated as light-yellow needles, m.p. 132–133 °C. R_f (hexane/acetone, 5:1) = 0.08. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 3.27 (s, 3 H), 4.46 (s, 2 H), 6.74 (m, 2 H), 6.85 (dt, J = 1.0, J = 7.5 Hz, 1 H), 7.05 (m, 3 H), 7.13 (m, 1 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 35.6 (CH$_3$), 64.7 (CH$_2$), 114.4 (CH), 114.5 (CH), 122.8 (CH), 123.4 (C$_{quat}$), 123.8 (C$_{quat}$), 126.2 (CH), 126.7 (CH), 127.3 (CH), 127.9 (CH), 135.9 (C$_{quat}$), 145.6 (C$_{quat}$), 146.2 (C$_{quat}$) ppm. MS (FAB$^+$): m/z (%) = 243.2 (100) [M]$^+$, 228.2 (14) [M – CH$_3$]$^+$, 226.2 (22), 213.2 (11) [M – CH$_2$OH]$^+$. $C_{14}H_{13}NOS$ (243.3): calcd. C 69.11, H 5.39, N 5.76, S 13.18; found C 68.88, H 5.31, N 5.46, S 12.94.

(10-Hexyl-10*H*-phenothiazin-3-yl)methanol (7b): According to GP1 and after chromatography on silica gel (hexane/diethyl ether, 4:1) the alcohol **7b** (770 mg, 77%) was isolated as a yellow oil. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 0.76 (t, J = 7.0 Hz, 3 H), 1.15–1.35 (m, 6 H), 1.60–1.70 (m, 2 H), 3.70 (t, J = 7.3 Hz, 2 H), 4.37 (br., 2 H), 6.69–6.80 (m, 3 H), 6.97–7.06 (m, 4 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 14.6 (CH$_3$), 23.4 (CH$_2$), 27.3 (CH$_2$), 27.6 (CH$_2$), 32.2 (CH$_2$), 48.1 (CH$_2$), 65.0 (CH$_2$), 116.1 (CH), 116.2 (CH), 123.0 (CH), 125.0 (C$_{quat}$), 125.6 (C$_{quat}$), 126.8 (CH), 126.9 (CH), 128.0 (CH), 136.1 (C$_{quat}$), 145.4 (C$_{quat}$), 146.0 (C$_{quat}$) ppm. IR (film): $\tilde{\nu}$ = 3346, 2954, 2827, 2855, 1577, 1496, 1467, 1444, 1362, 1333, 1287, 1244, 1040, 1011, 814, 747 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (3700), 314 (7100 L/mol cm) nm. MS (EI$^+$): m/z (%) = 313.1 (92) [M]$^+$, 242.1 (78) [M – C$_5$H$_{11}$]$^+$, 228.1 (100) [M – C$_6$H$_{11}$]$^+$, 210.1 (35). $C_{19}H_{23}NOS$ (313.5): calcd. C 72.80, H 7.40, N 4.47; found C 72.53, H 7.45, N 4.44.

(10,10′-Dihexyl-10*H*,10′*H*-3,3′-biphenothiazin-7-yl)methanol (7c): According to GP1 and after chromatography on silica gel (hexane/diethyl ether, 3:1) the alcohol **7c** (415 mg, 76%) was isolated as a yellow oil. R_f (hexane/acetone, 5:1) = 0.13. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 0.88 (t, J = 7.0 Hz, 6 H), 1.32 (m, 8 H), 1.44 (m, 4 H), 1.79 (m, 4 H), 3.85 (t, J = 7.0 Hz, 4 H), 4.54 (s, 2 H), 6.85 (d, J = 8.0 Hz, 1 H), 6.90 (m, 4 H), 7.14 (m, 4 H), 7.30 (m, 2 H), 7.32 (dd, J = 2.0, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 13.4 (2 C, CH$_3$), 22.3 (2 C, CH$_2$), 26.3 (2 C, CH$_2$), 26.5 (2 C, CH$_2$), 31.1 (2 C, CH$_2$), 47.1 (2 C, CH$_2$), 64.0 (CH$_2$), 114.9 (CH), 115.0 (CH), 115.1 (CH), 115.2 (CH), 121.9 (CH), 123.9 (C$_{quat}$), 124.0 (C$_{quat}$), 124.5 (2 C, CH), 124.7 (C$_{quat}$), 124.8 (2 C, CH), 125.7 (CH), 125.8 (CH), 126.9 (2 C, CH), 133.7 (2 C, C$_{quat}$), 135.1 (2 C, C$_{quat}$), 143.8 (C$_{quat}$), 143.9 (C$_{quat}$), 144.0 (C$_{quat}$), 144.8 (C$_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2928, 1630, 1460, 1414, 1384, 1333, 1251, 1106, 873, 808, 747 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 (52400), 324 (19200), 364 (12200 L/mol cm) nm. MS (FAB$^+$): m/z (%) = 594.4 (100) [M]$^+$, 577.4 (37) [M – OH]$^+$, 523.3 (16) [M – C$_5$H$_{11}$]$^+$, 509.3 (32) [M – C$_6$H$_{13}$]$^+$, 424.2 (30) [M – 2C$_6$H$_{13}$]$^+$, 407.2 (32) [M – 2C$_6$H$_{13}$ – OH]$^+$, 394.2 (14) [M – 2C$_6$H$_{13}$ – CH$_2$OH]$^+$. $C_{37}H_{42}N_2OS_2 \cdot 0.3CH_2Cl_2$ (594.3 + 25.2): calcd. C 72.33, H 6.93, N 4.52; found C 72.30, H 6.74, N 4.52.

[10,10′-Dihexyl-7′-(10-hexyl-10*H*-phenothiazin-3-yl)-10*H*,10′*H*-3,3′-biphenothiazin-7-yl]methanol (7d): According to GP1 and after chromatography on silica gel (hexane/diethyl ether, 3:1) the alcohol **7d** (152 mg, 61%) was isolated as a yellow oil. R_f (hexane/acetone, 5:1) = 0.13. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 0.88 (m, 9 H), 1.32 (m, 12 H), 1.44 (m, 6 H), 1.80 (m, 6 H), 3.85 (t, J = 7.0 Hz, 6 H), 4.54 (s, 2 H), 6.89 (m, 7 H), 7.14 (m, 4 H), 7.32 (m, 8 H) ppm. ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 13.4 (3 C, CH$_3$), 22.3 (3 C, CH$_2$), 26.2 (3 C, CH$_2$), 26.5 (3 C, CH$_2$), 31.1 (3 C, CH$_2$), 47.1 (3 C, CH$_2$), 64.0 (CH$_2$), 114.9 (CH), 115.0 (CH), 115.1 (CH), 115.2 (CH), 121.9 (CH), 123.8 (C$_{quat}$), 124.0 (C$_{quat}$), 124.2 (C$_{quat}$), 124.5 (2 C, CH), 124.7 (CH), 124.8 (2 C, CH), 125.7 (CH), 125.8 (2 C, CH), 126.9 (3 C, CH), 133.6 (3 C, C$_{quat}$), 135.1 (3 C, C$_{quat}$), 143.9 (3 C, C$_{quat}$), 144.8 (C$_{quat}$) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2853, 1701, 1604, 1458, 1376, 1330, 1239, 1104, 1039, 872, 805, 745 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 (24600), 324 (10600), 368 (8500 L/mol cm) nm. HRMS (MALDI-TOF): calcd. for 875.398; found 875.300. $C_{37}H_{42}N_2OS_2 \cdot 0.3\ CH_2Cl_2$ (594.3 + 25.2): calcd. C 72.33, H 6.93, N 4.52; found C 72.30, H 6.74, N 4.52.

[4-(10-Hexyl-10*H*-phenothiazin-3-yl)phenyl]methanol (8): According to GP1 and after chromatography on silica gel (hexane/diethyl ether, 4:1) the alcohol **8** (620 mg, 71%) was isolated as a yellow oil. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 0.86 (t, J = 7.1 Hz, 3 H), 1.27–1.42 (m, 4 H), 1.44 (m, 2 H), 1.80 (m, 2 H), 3.95 (t, J = 7.0 Hz, 2 H), 4.31 (t, J = 5.8 Hz, 1 H), 4.67 (d, J = 5.6 Hz, 2 H), 6.92–7.00 (m, 3 H), 7.14–7.23 (m, 2 H), 7.42 (dd, J = 2.6, J = 3.6 Hz, 3 H), 7.47 (dd, J = 2.2, J = 2.2 Hz, 1 H), 7.58 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 14.2 (CH$_3$), 23.2 (CH$_2$), 27.1 (CH$_2$), 27.5 (CH$_2$), 32.1 (CH$_2$), 47.9 (CH$_2$), 116.7 (CH), 116.9

(CH), 123.5 (CH), 124.8 (C_{quat}), 126.4 (CH), 127.2 (CH), 127.5 (CH), 128.1 (CH), 128.4 (CH), 129.1 (CH), 129.8 (CH), 129.9 (CH), 130.4 (CH), 130.9 (CH), 134.3 (C_{quat}), 136.2 (C_{quat}), 145.6 (C_{quat}), 146.2 (C_{quat}), 146.6 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 3332, 2953, 2928, 2856, 1601, 1576, 1491, 1459, 1364, 1250, 1193, 1039, 1011, 810, 787, 748 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 240 (18100), 270 (33300), 324 (8300 L/mol cm) nm. MS (EI^+): *m/z* (%) = 389.2 (56) $[M]^+$, 318.2 (40) $[M - C_5H_{11}]^+$, 304.1 (100) $[M - C_6H_{13}]^+$, 286.1 (28), 274.1 (20). $C_{25}H_{27}NOS$ (389.5): calcd. C 77.08, H 6.99, N 3.60; found C 77.21, H 7.21, N 3.59.

1-(10-Hexyl-10*H*-phenothiazin-2-yl)ethanol (9): According to GP1 and after chromatography on silica gel (hexane/diethyl ether, 1:1, then 2-propanol/hexane, 1:1) the alcohol **9** (3.84 g, 76%) was isolated as a yellow oil. R_f (hexane/acetone, 5:1) = 0.37. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 0.87 (m, 3 H), 1.30 (m, 3 H), 1.45 (m, 6 H), 1.78 (m, 2 H), 3.86 (t, *J* = 7.2 Hz, 2 H), 4.81 (q, *J* = 6.4 Hz, 1 H), 6.87 (m, 1 H), 6.91 (m, 3 H), 7.06 (m, 1 H), 7.10 (m, 1 H), 7.16 (m, 1 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 14.1 (CH_3), 22.9 (CH_2), 25.5 (CH_3), 26.9 (CH_2), 27.2 (CH_2), 31.8 (CH_2), 47.6 (CH_2), 70.3 (CH), 113.0 (CH), 115.8 (CH), 119.6 (CH), 122.6 (CH), 123.9 (C_{quat}), 125.2 (C_{quat}), 127.4 (CH), 127.5 (2 C, CH), 145.7 (C_{quat}), 145.9 (C_{quat}), 146.1 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 3430, 3063, 2959, 2928, 2856, 1706, 1596, 1586, 1572, 1464, 1444, 1421, 1366, 1321, 1288, 1252, 1239, 749 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (33700), 312 (5600 L/mol cm) nm. MS (EI^+): *m/z* (%) = 327.1 (100) $[M]^+$, 256.1 (68) $[M - C_5H_{11}]^+$, 242.0 (76) $[M - C_6H_{13}]^+$. $C_{20}H_{25}NOS$ (327.3): calcd. C 73.35, H 7.69, N 4.28, S 9.79; found C 73.04, H 7.78, N 4.15, S 9.44.

General Procedure for the Synthesis of the Phenothiazinyl-Substituted Carbamates 11–13 from the Phenothiazinyl-Substituted Alcohols 7–9 with 3-(Triethoxysilyl)propyl Isocyanate (GP2): The phenothiazinyl-substituted alcohol **7**, **8**, or **9** (1.0 equiv.), 3-(triethoxysilyl)propyl isocyanate (**10**; 1.0 equiv.), and dibutyltin dilaurate (DBTL; 0.002 equiv.) were placed under argon in a screw-capped pressure vessel. In some cases dry 1,4-dioxane was added as a solvent. The mixture was stirred at 70 °C for 16 h. After drying in vacuo the phenothiazinyl-substituted carbamates **11**–**13** were isolated as viscous oils.

(10-Methyl-10*H*-phenothiazin-3-yl)methyl 3-(Triethoxysilyl)propylcarbamate (11a): According to GP2 (without solvent) and after drying at 10^{-3} mbar for 1 d the carbamate **11a** (970 mg, 99%) was isolated as a dark-yellow oil. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 0.58 (t, *J* = 8.1 Hz, 2 H), 1.18 (t, *J* = 7.2 Hz, 9 H), 1.57 (m, 2 H), 3.12 (m, 2 H), 3.34 (s, 3 H), 3.77 (q, *J* = 7.1 Hz, 6 H), 4.94 (s, 2 H), 6.78 (m, 1 H), 6.82 (dd, *J* = 0.9, *J* = 7.8 Hz, 1 H), 6.92 (dt, *J* = 1.2, *J* = 7.5 Hz, 1 H), 7.09–7.20 (m, 4 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 7.8 (CH_2), 18.4 (CH_3), 23.6 (CH_2), 35.5 (CH_3), 43.8 (CH_2), 58.6 (CH_2), 65.9 (CH_2), 114.2 (CH), 114.4 (CH), 122.7 (CH), 123.3 (C_{quat}), 123.7 (C_{quat}), 127.2 (CH), 127.3 (CH), 127.8 (2 C, CH), 131.5 (C_{quat}), 145.9 (2 C, C_{quat}), 156.5 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 3341, 2973, 2927, 2886, 1720, 1528, 1467, 1444, 1333, 1250, 1165, 1104, 1080, 958, 812, 776, 752 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (42000), 290 (6300), 312 (7000 L/mol cm) nm. MS (EI^+): *m/z* (%) = 490.2 (100) $[M]^+$, 226.1 (46). HRMS (EI^+): calcd. for $C_{24}H_{34}N_2O_5SSi$ 490.1958; found 490.1956. $C_{24}H_{34}N_2O_5SSi \cdot 0.2C_{10}H_{21}NO_4Si$ (490.3 + 49.5): calcd. C 57.81, H 7.13, N 5.70; found C 57.74, H 7.09, N 5.62.

(10-Hexyl-10*H*-phenothiazin-3-yl)methyl 3-(Triethoxysilyl)propylcarbamate (11b): According to GP2 (without solvent) and after drying at 10^{-3} mbar for 1 d the carbamate **11b** (1.09 g, 99%) was isolated as a yellow oil. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 0.60 (t, *J* = 7.8 Hz, 2 H), 0.88 (t, *J* = 7.1 Hz, 3 H), 1.21 (t, *J* = 7.0 Hz, 9 H), 1.29–1.45 (m, 6 H), 1.60 (m, 2 H), 1.77 (m, 2 H), 3.13 (m, 2 H), 3.80 (m, 6 H), 4.95 (br., 2 H), 5.17 (br., 1 H), 6.81–6.92 (m, 3 H), 7.09–7.17 (m, 4 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 7.8 (CH_2), 14.0 (CH_3), 18.4 (CH_3), 22.9 (CH_2), 23.6 (CH_2), 26.8 (CH_2), 27.0 (CH_2), 31.7 (CH_2), 43.8 (CH_2), 47.7 (CH_2), 58.6 (CH_2), 65.9 (CH_2), 115.4 (CH), 115.7 (CH), 122.6 (CH), 124.7 (C_{quat}), 125.1 (C_{quat}), 127.4 (CH), 127.5 (CH), 127.6 (CH), 127.6 (CH), 131.4 (C_{quat}), 145.4 (C_{quat}), 145.5 (C_{quat}), 156.5 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 2972, 2928, 2886, 1722, 1529, 1466, 1333, 1243, 1166, 1104, 1080, 958, 777, 749 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (31100), 314 (5100 L/mol cm) nm. MS (EI^+): *m/z* (%) = 560.3 (82) $[M]^+$, 296.1 (38), 247.1 (100), 202.0 (46). HRMS (EI): calcd. for $C_{29}H_{44}N_2O_5SSi$ 560.2740; found 560.2759.

(10,10′-Dihexyl-10*H*,10′*H*-3,3′-biphenothiazin-7-yl)methyl 3-(Triethoxysilyl)propylcarbamate (11c): According to GP2 (with dioxane as solvent) and after drying at 10^{-3} mbar for 1 d the carbamate **11c** (2.40 g, 99%) was isolated as a brown oil. ^1H NMR (CD_2Cl_2, 500 MHz): δ = 0.59 (t, *J* = 8.0 Hz, 2 H), 0.88 (t, *J* = 7.0 Hz, 6 H), 1.19 (t, *J* = 7.0 Hz, 9 H), 1.32 (m, 8 H), 1.44 (m, 4 H), 1.60 (m, 2 H), 1.80 (m, 4 H), 3.14 (q, *J* = 6.5 Hz, 2 H), 3.79 (q, *J* = 7.0 Hz, 6 H), 4.94 (s, 2 H), 5.17 (br., 1 H), 6.84 (d, *J* = 6.5 Hz, 1 H), 6.90 (m, 4 H), 7.14 (m, 4 H), 7.29 (m, 2 H), 7.33 (dd, *J* = 2.0, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 7.2 (CH_2), 13.4 (CH_3), 17.8 (CH_3), 22.3 (CH_2), 23.0 (CH_2), 26.3 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 31.1 (CH_2), 43.1 (CH_2), 47.1 (CH_2), 58.0 (CH_2), 66.7 (CH_2), 114.7 (CH), 115.0 (CH), 115.2 (CH), 121.9 (CH), 123.9 (C_{quat}), 124.5 (CH), 124.7 (CH), 124.8 (CH), 126.8 (CH), 126.9 (CH), 127.0 (CH), 127.1 (CH), 130.8 (C_{quat}), 133.6 (C_{quat}), 133.8 (C_{quat}), 143.6 (C_{quat}), 143.9 (C_{quat}), 144.5 (C_{quat}), 144.8 (C_{quat}), 155.3 (C_{quat}), 155.8 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 3423, 2926, 1719, 1638, 1509, 1459, 1332, 1212, 1077, 747 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (qual.) = 268, 322, 366. HRMS (MALDI): calcd. for $C_{47}H_{63}N_3O_5S_2Si$ 841.398; found 841.427. $C_{47}H_{63}N_3O_5S_2Si \cdot 2C_4H_8O_2$ (841.3 + 176.1): calcd. C 64.86, H 7.82, N 4.13; found C 64.45, H 8.02, N 4.25.

[10,10′-Dihexyl-7′-(10-hexyl-10*H*-phenothiazin-3-yl)-10*H*,10′*H*-3,3′-biphenothiazin-7-yl]methyl 3-(Triethoxysilyl)propylcarbamate (11d): According to GP2 (with dioxane as solvent) and after drying at 10^{-3} mbar for 1 d the carbamate **11d** (2.40 g, 99%) was isolated as a brown oil. ^1H NMR (CD_2Cl_2, 500 MHz): δ = 0.60 (m, 2 H), 0.88 (m, 9 H), 1.20 (t, *J* = 7.0 Hz, 9 H), 1.31 (m, 12 H), 1.42 (m, 6 H), 1.58 (m, 2 H), 1.80 (m, 6 H), 3.11 (m, 2 H), 3.82 (q, *J* = 7.0 Hz, 6 H), 3.86 (m, 6 H), 4.95 (s, 2 H), 6.84 (m, 1 H), 6.89 (m, 6 H), 7.13 (m, 4 H), 7.32 (m, 8 H) ppm. ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 7.2 (CH_2), 13.4 (CH_3), 14.1 (CH_3), 17.8 (CH_3), 22.3 (CH_2), 23.0 (CH_2), 23.4 (CH_2), 26.3 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 31.1 (CH_2), 42.6 (CH_2), 47.1 (CH_2), 47.2 (CH_2), 58.0 (CH_2), 66.7 (CH_2), 114.7 (CH), 115.0 (CH), 115.1 (CH), 115.2 (CH), 121.9 (CH), 123.9 (C_{quat}), 124.0 (C_{quat}), 124.2 (C_{quat}), 124.5 (CH), 124.7 (C_{quat}), 124.8 (CH), 126.8 (CH), 126.9 (CH), 127.1 (CH), 130.8 (C_{quat}), 133.6 (C_{quat}), 133.7 (C_{quat}), 143.6 (C_{quat}), 143.7 (C_{quat}), 143.9 (C_{quat}), 144.5 (C_{quat}), 144.8 (C_{quat}), 157.7 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 3367, 2928, 1719, 1561, 1459, 1414, 1388, 1333, 1213, 1195, 1079, 957, 874, 805 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 (9600), 324 (3900), 373 (3100 L/mol cm) nm. HRMS (MALDI): calcd. for $C_{65}H_{82}N_4O_5S_3Si$ 1122.522; found 1122.533.

4-(10-Hexyl-10*H*-phenothiazin-3-yl)benzyl 3-(Triethoxysilyl)propylcarbamate (12): According to GP2 (without solvent) and after drying at 10^{-3} mbar for 1 d the carbamate **12** (724 mg, 99%) was isolated as a yellow resin. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 0.60 (t, *J* = 6.9 Hz, 2 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 1.19 (t, *J* = 7.0 Hz, 9 H), 1.30–1.47 (m, 6 H), 1.60 (m, 2 H), 1.80 (m, 2 H), 3.16 (m, 2

H), 3.79 (m, 8 H), 5.08 (br., 2 H), 5.31 (s, 1 H), 6.91 (t, J = 9.2 Hz, 3 H), 7.11–7.19 (m, 2 H), 7.38 (m, 4 H), 7.53 (d, J = 8.2 Hz) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 7.84 (CH_2), 14.0 (CH_3), 18.4 (CH_3), 22.9 (CH_2), 23.6 (CH_2), 26.9 (CH_2), 27.1 (CH_2), 31.7 (CH_2), 43.8 (CH_2), 47.7 (CH_2), 58.6 (CH_2), 66.2 (CH_2), 115.7 (CH), 115.8 (CH), 122.6 (CH), 124.5 (C_{quat}), 125.4 (C_{quat}), 125.7 (CH), 126.1 (CH), 126.6 (CH), 127.5 (CH), 127.6 (CH), 128.7 (CH), 135.0 (C_{quat}), 136.1 (C_{quat}), 139.8 (C_{quat}), 144.9 (C_{quat}), 145.3 (C_{quat}), 156.5 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 3400, 2954, 2928, 2871, 1700, 1535, 1492, 1464, 1279, 1251, 1195, 1105, 1017, 810, 793, 748 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 240 (144900), 268 (23900), 322 (6400 L/mol cm) nm. MS (FAB$^+$): m/z (%) = 636.3 (100) [M]$^+$, 565.2 (8) [M – C_5H_{11}]$^+$, 551.2 (12) [M – C_6H_{13}]$^+$. HRMS (FAB$^+$): calcd. for $C_{35}H_{48}O_5N_2SiS$ 636.3053; found 636.3029.

1-(10-Hexyl-10*H*-phenothiazin-2-yl)ethyl 3-(Triethoxysilyl)propylcarbamate (13): According to GP2 (without solvent) and after drying at 10^{-3} mbar for 1 d the carbamate **13** (1.52 g, 98%) was isolated as a dark-yellow oil. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 0.59 (t, J = 8.8 Hz, 2 H), 0.87 (t, J = 7.0 Hz, 3 H), 1.20 (t, J = 7.0 Hz, 9 H), 1.31 (m, 4 H), 1.44 (m, 2 H), 1.47 (m, 4 H), 1.57 (m, 3 H), 1.78 (m, 2 H), 3.80 (q, J = 7.0 Hz, 6 H), 3.85 (t, J = 7.0 Hz, 2 H), 5.02 (br., 1 H), 5.68 (m, 1 H), 6.85 (m, 1 H), 6.91 (m, 3 H), 7.07 (d, J = 7.5 Hz, 1 H), 7.10 (d, J = 7.0 Hz, 1 H), 7.15 (t, J = 7.7 Hz, 1 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 7.9 (CH_2), 14.1 (CH_3), 18.5 (CH_3), 22.7 (CH_2), 23.0 (CH_2), 23.7 (CH_2), 26.9 (CH_2), 27.2 (CH_2), 31.9 (CH_2), 43.8 (CH_2), 47.7 (CH_2), 58.7 (CH_2), 113.7 (CH), 115.9 (CH), 120.1 (CH), 122.7 (CH), 124.4 (C_{quat}), 125.2 (C_{quat}), 127.4 (CH), 127.5 (CH), 127.6 (CH), 142.6 (C_{quat}), 145.7 (C_{quat}), 145.8 (C_{quat}), 156.0 (C_{quat}) ppm. IR (film): $\tilde{\nu}$ = 3343, 2974, 2928, 2855, 1720, 1526, 1463, 1445, 1423, 1278, 1241, 1195, 1166, 1104, 1078, 957, 776, 751 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (28500), 312 (4400) nm. MS (FAB$^+$): m/z (%) = 574.1 (100) [M]$^+$, 310.1 (90). HRMS (FAB): calcd. for $C_{30}H_{46}N_2O_5SSi$ 574.2897; found 574.2859. $C_{30}H_{46}N_2O_5SSi{\cdot}0.3C_{10}H_{21}NO_4Si$ (574.33 + 74.3): calcd. C 61.07, H 8.12, N 4.96; found C 61.09, H 8.21, N 5.03.

Synthesis of the MCM-41 and SBA-15 Supports: Siliceous MCM-41 was synthesized as described in the literature.[40] A typical procedure was as follows: a 70% aqueous solution of ethylamine (15.46 g, 240 mmol ethylamine) was added to a stirred solution of distilled water (175 mL) and cetyltrimethylammonium bromide (CTAB; 5.10 g, 14 mmol). Tetraethyl orthosilicate (TEOS; 20.80 g, 100 mmol) was added dropwise. The reaction mixture was stirred for further 4 h at room temperature before being heated to 100 °C for 1 d. The product was recovered by filtration and washed thoroughly with distilled water and dried at 80 °C for 12 h. The template was eliminated by Soxhlet extraction with HCl/EtOH to obtain a high content of Si–OH groups on the silica surface. SBA-15 was synthesized according to the procedure reported by Stucky and co-workers.[41] In a typical preparation Pluronic 123 (4 g) was dissolved whilst stirring in 1.9 M HCl (125 g) at room temperature. The solution was heated to 40 °C before tetraethyl orthosilicate was added. The resultant mixture was stirred for 20 h at 40 °C, followed by aging at 100 °C for 24 h under static conditions. The solid product was recovered by filtration and dried at 80 °C overnight. The template was removed from the raw material by extraction with ethanol under reflux conditions.

General Procedure for the Synthesis of the Phenothiazine-Functionalized Hybrid Materials 14–16: Just before the grafting process, the silica support was dehydrated carefully at 200 °C for 4 h. The aim of this prior process was to avoid self-condensation of precursors in the presence of surface H_2O and to achieve more exposed single silanol groups on the surface of the materials. In a typical process, for the synthesis of the samples **14a**, **14b**, **14c**, **14c***, **15**, and **16**, the silica precursor (1.0 g) was heated for 24 h at reflux under nitrogen with the appropriate phenothiazine (ca. 1.0 mmol) in dry toluene (50 mL). The resulting solid was filtered and washed with toluene and dichloromethane. Subsequently it was subjected to Soxhlet extraction for 24 h under nitrogen with dichloromethane as the solvent. After being dried under a vacuum at room temperature, the products **14a**, **14b**, **14c**, and **16** were obtained as white powders and the products **14c*** and **15** as yellow powders. Sample **14d** was prepared by a similar procedure except that the amount of **11d** was 0.135 mmol per 300 mg of SBA-15.

General Procedure for the Oxidation of the Hybrid Materials 14–16 with $SbCl_5$: In a typical process, the hybrid material (0.10 g) was suspended in dry dichloromethane (5 mL). The solution was stirred at room temperature and a molar excess of $SbCl_5$ was added. The color of the samples immediately changed. The solids were filtered off, extracted with dichloromethane, and dried under vacuum.

Supporting Information (see also the footnote on the first page of this article): Six figures; pore size distribution curves of hybrid materials, FT-IR spectra of MCM-41 and SBA-15, ^{13}C CP-MAS NMR spectra of **14d** and solution ^{13}C NMR spectra of **11d**, Selected adsorption and emission spectra of solid hybrid materials, Q-band EPR spectra of **14c*** and **14d**.

Acknowledgments

The support of this work by the Deutsche Forschungsgemeinschaft (DFG) (Priority Program SPP 1181 NANOMAT) and by the Fonds der Chemischen Industrie is gratefully acknowledged. R.T. is an Erasmus Socrates student and a recipient of a Consiliul National al Cercetarii Stiintifice din Invatamantul Superior (CNCSIS) grant (1315) and heartily wishes to thank Prof. I. Grosu (Babes-Bolyai University, Cluj-Napoca) for his generous support.

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Received: March 27, 2009
Published Online: July 1, 2009

