

# Novel Organic/Inorganic Hybrid Materials by Covalent Anchoring of Phenothiazines on MCM-41

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Triethoxysilyl functionalized phenothiazinyl carbamates were synthesized and covalently grafted onto mesoporous MCM-41. XRD and N<sub>2</sub> adsorption measurements indicated the presence of a highly ordered two-dimensional hexagonal structure of functional materials, while the incorporation of organic compounds in the solid materials was proven by means of <sup>13</sup>C and <sup>29</sup>Si solid-state NMR spectroscopy as well as by FT-IR spectroscopy. Upon oxidation with (NO)BF<sub>4</sub>, stable phenothiazine radical cations were generated in the pores of the materials, which can be detected by means of UV–vis and EPR spectroscopy.

## Introduction

Since the discovery of mesoporous silicas in 1992,<sup>1,2</sup> research on these materials has rapidly developed. They can be readily obtained by micellar condensation of silicic acid derivatives. The pores of such solids can be used for different applications.<sup>2,3</sup> Chemical and physical manipulation of the outer and inner surface as well as in the bulk material have been reported.<sup>4</sup> One of the main areas of research in this field is related to applications in catalysis.<sup>5</sup> However, due to pore sizes in the range of 2–30 nm, these solids also have been used for the stabilization of nanoparticles (quantum dots),<sup>6</sup> for the synthesis of nano wires,<sup>7</sup> or for magnetic and optic materials.<sup>8</sup>

Adsorption of reactive species at the walls of those materials was used for stabilization, almost similar to isolation in the cavities of zeolites. This idea was taken to stabilize photochromic dyes in mesoporous materials,<sup>9</sup> to stabilize and organize chlorophyll *a* to mimic energy transfer and charge separation of photosynthesis,<sup>10</sup> to heterogenize VO<sup>2+</sup> and cytochrome *c* for oxygen activation,<sup>11</sup> to investigate the photoinduced charge separation of pyrene,<sup>12</sup> and

to stabilize benzene radicals in the mesopores of phenyl-substituted MCM-41.<sup>13</sup>

Phenothiazines represent nitrogen and sulfur containing heterocycles<sup>14</sup> that have gained different applications such as pharmaceuticals.<sup>15</sup> An important feature of the phenothi-

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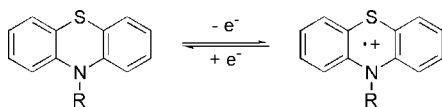
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azine motif is a reversible one-electron oxidation process with a low potential that leads to stable and deeply colored radical cations (Chart 1).<sup>16</sup>

Chart 1



This redox behavior is not only responsible for the physiological properties of phenothiazines<sup>17</sup> but also for their capability to cleave DNA when irradiated with UV light.<sup>18</sup> Consequently, phenothiazine derivatives have found application in materials sciences as electrophoric sensors in supramolecular systems for photoinduced electron transfer (PET)<sup>19</sup> and as electron donors in electronically conducting charge-transfer composites.<sup>20</sup> Furthermore, phenothiazine polymers obtained by polycondensation play an important role, for example, as electrochromic materials for displays.<sup>21</sup> On the other hand, the low oxidation potential of polyphenothiazines is responsible for the capability of acting as an electron donor in fluorescent donor–acceptor chromophores, which are of special benefit as emitters in organic light-emitting diodes (OLED)<sup>22,23</sup> as well as for nonlinear optical and electrooptical effects.<sup>24</sup>

To date, there are only a few reports on the physisorption of phenothiazines on silica, presumably due to weak forces between the aromatic molecules and the silica surface,<sup>25</sup> which hampers the formation of stable materials. It was shown by means of EPR spectroscopy that phenothiazine

physisorbed on porous silicas can form stable radical cations by photooxidation, where the silica network might act as an electron acceptor.<sup>26</sup> Doping the support with transition metal ions or using transition metal oxides as the support facilitates the electron-transfer process.<sup>27</sup> Furthermore, chlorinated hydrocarbons can be used as electron acceptors,<sup>28</sup> which is most favorable for the photochemical degradation of persistent and ecotoxic compounds.

The generation of efficient devices not only requires the control of the electronic but also of the spatial properties of a given system. It has been shown, that the electronic properties of  $\pi$ -conjugated materials strongly depend on the interaction of the molecules and, thus, on their intermolecular orientation.<sup>29</sup> From this point of view, it appears to be beneficial to combine the properties of inorganic mesoporous materials (strong orientation of the pore system) and phenothiazines (electrooptic features) for a rational design of one-dimensionally stacked redox active molecules. In the present paper, we report the first examples for phenothiazines covalently grafted on mesoporous MCM-41.

## Experimental Procedures

**General Remarks.** All manipulations were carried out under an inert atmosphere of nitrogen, and the solvents were dried by standard methods. Reagents were purchased and used without further purification, unless otherwise noted.

**Characterization Techniques.** The infrared spectra (KBr) were recorded using a Jasco FT/IR-6100 spectrometer. X-ray powder

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diffraction (XRD) patterns were obtained on a Siemens D5005 diffractometer with Cu K $\alpha$  radiation (30 kV, 30 mA). Nitrogen absorption and desorption isotherms were measured at 77 K on a Quantachrome Autosorb 1 sorption analyzer after evacuation of the samples at 120 °C overnight. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) equation in the low relative pressure interval (<0.3), and the pore size distribution curves were analyzed with the adsorption branch by the BJH method.  $^{13}\text{C}$  CP-MAS and  $^{29}\text{Si}$  CP-MAS NMR were carried out on a Bruker DSX Avance spectrometer at resonance frequencies of 100.6 and 79.5 MHz, respectively. UV–vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda-18 with neat-MCM-41 as the background standard. Q-band CW ESR experiments were performed at 297 K on a Bruker EMX 10-40 spectrometer.

**Synthesis of 2-Acetyl-10-hexyl-10H-phenothiazine (1b).** A total of 9.61 g (40 mmol) of 2-acetyl-10H-phenothiazine was dissolved in 100 mL of dry THF. A total of 4.71 g (42 mmol) of potassium *t*-butylate was added, and the solution was stirred at room temperature for 1 h. Then, 10.2 mL (72 mmol) of 1-bromohexane 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 temperature and diluted with dichloromethane. The solution was washed with water and Na $_2$ SO $_3$  solution, the organic layer was dried with MgSO $_4$ , 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 **1b** as an orange oil.  $R_f$  (hexane/acetone 5:1): 0.45.  $^1\text{H}$  NMR (acetone- $d_6$ , 300 MHz):  $\delta$  = 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,  $^4J$  = 1.5, 7.5 Hz, 1 H), 7.07 (m, 2 H), 7.34 (m, 2 H).  $^{13}\text{C}$  NMR (acetone- $d_6$ , 75 MHz):  $\delta$  = 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 $_{\text{quat}}$ ), 125.0 (C $_{\text{quat}}$ ), 127.3 (CH), 127.6 (CH), 128.0 (CH), 136.8 (C $_{\text{quat}}$ ), 145.0 (C $_{\text{quat}}$ ), 145.9 (C $_{\text{quat}}$ ), 197.4 (C $_{\text{quat}}$ ). 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 $_2$ Cl $_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 246 (22 600), 282 (22 600), 374 (1500) nm. MS (FAB $^+$ )  $m/z$  (%): 325.3 (100, M $^+$ ), 254.2 (19, M $^+$  – C $_5$ H $_{11}$ ), 240.2 (15, M $^+$  – C $_6$ H $_{13}$ ). Anal. calcd for C $_{20}$ H $_{23}$ NOS (325.3): 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.

**Synthesis of 10-Methyl-10H-phenothiazin-3-yl-methanol (2a).** A solution of 700 mg (2.9 mmol) of 10-methyl-10H-phenothiazin-3-yl carbaldehyde (**1a**) $^{30}$  in dry diethyl ether was added over 20–30 min via a dropping funnel to a well-stirred mixture of 220 mg (5.8 mmol) of LiAlH $_4$  in dry diethyl ether heated to 40 °C. The reaction mixture was stirred at 40 °C for 16 h and was then cooled to 0 °C. Then, 50 mL of water and 10 mL of diluted HCl were added. The aqueous phase was washed with small portions of diethyl ether, the combined organic phases were dried with MgSO $_4$ , and the solvents were removed in vacuo. The residue was purified by chromatography on silica gel (hexane/diethyl ether 5:1) to furnish 604 mg (84%) of **2a** as light yellow needles. mp.: 132–133 °C.  $R_f$  (hexane/acetone 5:1): 0.08.  $^1\text{H}$  NMR (CD $_2$ Cl $_2$ , 300 MHz):  $\delta$  = 3.27 (s, 3 H), 4.46 (s, 2 H), 6.74 (m, 2 H), 6.85 (dt,  $^4J$  = 1.0 Hz,  $^1J$  = 7.5 Hz, 1 H), 7.05 (m, 3 H), 7.13 (m, 1 H).  $^{13}\text{C}$  NMR (CD $_2$ Cl $_2$ , 75 MHz):  $\delta$  = 35.6 (CH $_3$ ), 64.7 (CH $_2$ ), 114.4 (CH), 114.5 (CH), 122.8 (CH), 123.4 (C $_{\text{quat}}$ ), 123.8 (C $_{\text{quat}}$ ), 126.2 (CH), 126.7 (CH), 127.3 (CH), 127.9 (CH), 135.9 (C $_{\text{quat}}$ ), 145.6 (C $_{\text{quat}}$ ), 146.2 (C $_{\text{quat}}$ ). MS (FAB $^+$ )  $m/z$  (%): 243.2 (100, M $^+$ ), 228.2 (14, M $^+$  – CH $_3$ ), 226.2 (22), 213.2 (11, M $^+$  – CH $_2$ OH). Anal. calcd for C $_{14}$ H $_{13}$ NOS (243.3): 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.

**Synthesis of rac-1-(10-Hexyl-10H-phenothiazin-2-yl)ethanol (2b).** Compound **2b** was synthesized according to the procedure given for **2a** starting from 4.96 g (15.2 mmol) of **1b** and 1.15 g (30.4 mmol) of LiAlH $_4$ . After chromatography on silica gel (hexane/diethyl ether 1:1, then isopropyl alcohol/hexane 1:1) 3.84 g (76%) of **2b** was obtained as a yellow oil.  $R_f$  (hexane/acetone 5:1): 0.37.  $^1\text{H}$  NMR (CD $_2$ Cl $_2$ , 300 MHz):  $\delta$  = 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).  $^{13}\text{C}$  NMR (CD $_2$ Cl $_2$ , 75 MHz):  $\delta$  = 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 $_{\text{quat}}$ ), 125.2 (C $_{\text{quat}}$ ), 127.4 (CH), 127.5 (CH, 2 C), 145.7 (C $_{\text{quat}}$ ), 145.9 (C $_{\text{quat}}$ ), 146.1 (C $_{\text{quat}}$ ). 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 $_2$ Cl $_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 258 (33 700), 312 (5600) nm. MS (EI $^+$ )  $m/z$  (%): 327.1 (100, M $^+$ ), 256.1 (68, M $^+$  – C $_5$ H $_{11}$ ), 242.0 (76, M $^+$  – C $_6$ H $_{13}$ ). Anal. calcd for C $_{20}$ H $_{25}$ NOS (327.3): 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.

**Synthesis of (10-Methyl-10H-phenothiazin-3-yl)methyl-3-(triethoxysilyl)propylcarbamate (3a).** A total of 487 mg (2.00 mmol) of **2a**, 0.5 mL (2.00 mmol) of 3-(triethoxysilyl)propylisocyanate, and 2  $\mu\text{L}$  (3.4  $\mu\text{mol}$ ) of dibutyl tin dilaurate (DBTL) were placed under argon atmosphere in a screw-capped pressure vessel. The mixture was stirred at 70 °C for 16 h. After drying at 10 $^{-3}$  mbar for 24 h, 970 mg (99%) of the phenothiazinyl substituted carbamate **3a** was isolated as a dark yellow oil.  $^1\text{H}$  NMR (CD $_2$ Cl $_2$ , 300 MHz):  $\delta$  = 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 Hz,  $J$  = 7.8 Hz, 1 H), 6.92 (dt,  $J$  = 1.2 Hz,  $J$  = 7.5 Hz, 1 H), 7.09–7.20 (m, 4 H).  $^{13}\text{C}$  NMR (CD $_2$ Cl $_2$ , 75 MHz):  $\delta$  = 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 $_{\text{quat}}$ ), 123.7 (C $_{\text{quat}}$ ), 127.2 (CH), 127.3 (CH), 127.8 (CH, 2 C), 131.5 (C $_{\text{quat}}$ ), 145.9 (C $_{\text{quat}}$ , 2 C), 156.5 (C $_{\text{quat}}$ ). 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 $_2$ Cl $_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 258 (42 000), 290 (6300), 312 (7000) nm. MS (EI $^+$ )  $m/z$  (%): 490.2 (100, M $^+$ ), 226.1 (46). HRMS (EI $^+$ ) calcd. for C $_{24}$ H $_{34}$ N $_2$ O $_5$ SSi: 490.1958; found: 490.1956. Anal. calcd for C $_{24}$ H $_{34}$ N $_2$ O $_5$ SSi  $\times$  (C $_{10}$ H $_{21}$ NO $_4$ Si) $_{0.02}$  (490.3 + 5.0): C 57.81, H 7.13, N 5.70; found: C 57.74, H 7.09, N 5.62.

**Synthesis of 1-(10-Hexyl-10H-phenothiazin-2-yl)ethyl-3-(triethoxysilyl)propylcarbamate (3b).** Compound **3b** was synthesized according to the procedure given for **3a** starting from 887 mg (2.71 mmol) of **2b**, 0.77 mL (2.71 mmol) of 3-(triethoxysilyl)propylisocyanate, and 3  $\mu\text{L}$  (5.2  $\mu\text{mol}$ ) of DBTL. Yield: 1.52 g (98%) of **3b**, dark yellow oil.  $^1\text{H}$  NMR (CD $_2$ Cl $_2$ , 300 MHz):  $\delta$  = 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).  $^{13}\text{C}$  NMR (CD $_2$ Cl $_2$ , 75 MHz):  $\delta$  = 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 $_{\text{quat}}$ ), 125.2 (C $_{\text{quat}}$ ), 127.4 (CH), 127.5 (CH), 127.6 (CH), 142.6 (C $_{\text{quat}}$ ), 145.7 (C $_{\text{quat}}$ ), 145.8 (C $_{\text{quat}}$ ), 156.0 (C $_{\text{quat}}$ ). 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 $_2$ Cl $_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 260 (28 500), 312 (4400) nm. MS (FAB $^+$ )  $m/z$  (%): 574.1 (100, M $^+$ ), 310.1 (90). HRMS (FAB) calcd. for C $_{30}$ H $_{46}$ N $_2$ O $_5$ SSi: 574.2897; found: 574.2859.

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Anal. calcd for  $C_{30}H_{46}N_2O_5SSi \times (C_{10}H_{21}NO_4Si)_{0.03}$  (574.33 + 7.4): C 61.07, H 8.12, N 4.96; found: C 61.09, H 8.21, N 5.03.

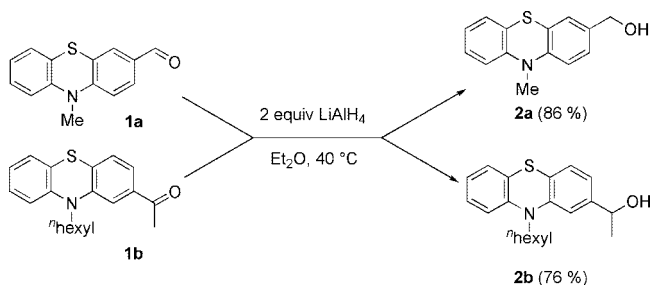
**Synthesis of Organic/Inorganic Hybrid Materials 4a,b.** A total of 1.50 g of pure siliceous MCM-41,<sup>31</sup> which was previously degassed at 200 °C, was suspended in 80 mL of dry toluene. A total of 0.71 g (1.43 mmol) of **3a** or 0.83 g (1.44 mmol) of **3b**, dissolved in 10 mL of dry toluene, was added, and the mixture was heated to reflux for 24 h under a  $N_2$  atmosphere. The solids were filtered off, washed with dichloromethane, and subsequently transferred to Soxhlet extraction equipment to be extracted with dichloromethane for 24 h under  $N_2$  protection. After being dried under vacuum at room temperature, products **4a,b** were obtained as colorless powders. Elemental analysis for **4a**: found C, 12.10; H, 2.17; N, 1.14, which corresponds to a loading of 0.41 mmol/g. Elemental analysis for **4b**: found C, 13.10; H, 2.66; N, 0.85, which corresponds to a loading of 0.30 mmol/g.

**Generation of Radical Cations 5a,b.** A total of 0.30 g of hybrid materials **4a,b** was suspended in 5 mL of dry dichloromethane. The solution was stirred at room temperature, and a molar excess of  $(NO)BF_4$  was added. The color of the samples immediately changed to deep red. The solids were filtered off, extracted with dichloromethane, and dried under a vacuum.

## Results and Discussion

The covalent grafting of an organic compound on a silica surface requires the introduction of a reactive silyl function such as  $-SiCl_3$  or  $-Si(OR)_3$ . Attempts to directly connect  $-Si(OR)_3$  to the phenothiazine core by reacting a phenothiazine lithiated in the 3-position with an excess of  $Si(OMe)_4$  and use of the resulting 3-trimethoxysilylphenothiazine for postsynthetic grafting on MCM-41 failed, probably due to protodisilylation during the grafting process. Thus, we decided to use the hydroxy functionalized phenothiazines **2a,b**, which can be readily obtained by reduction of the corresponding carbonyl compounds **1a,b** with  $LiAlH_4$  (Scheme 1).

Scheme 1. Synthesis of Phenothiazinyl Alcohols 2a,b



The alcohols **2a,b** can be quantitatively transformed by the addition of 1-isocyanato-3-trimethoxysilylpropane at 70 °C under an argon atmosphere in the presence of DBTL as a catalyst to give the desired triethoxysilyl functionalized carbamates **3a,b** (Scheme 2).

The electronic properties of the (oligo)phenothiazine carbamates **3a,b** were investigated by absorption and emission spectroscopy and CV in the anodic region (up to 1.2 V) (Table 1). Most characteristically for the carbamates, absorption in the UV is accompanied by an

intense blue fluorescence. The emission maxima lie at 453 and 456 nm, and the Stokes shifts are quite remarkable ( $\Delta\tilde{\nu} = 10\,000\text{--}10\,500\text{ cm}^{-1}$ ). Substantial Stokes shifts also were observed for many phenothiazine derivatives<sup>32</sup> and can be attributed to significant geometrical changes upon excitation from a highly nonplanar ground state to a largely planarized excited state.<sup>33</sup>

The carbamate linker is sufficiently stable to allow postsynthetic grafting of the electrophore units on MCM-41, resulting in organic/inorganic hybrid materials **4a,b** (Scheme 3). These materials undergo the formation of surface bound radical cations when treated with oxidizing agents (Scheme 4). For this purpose, we used the one-electron acceptor  $(NO)BF_4$ , which is excellently soluble in polar organic solvents and provides the weak nucleophile  $BF_4^-$  as the counterion for the phenothiazine radical cation and gaseous NO as the only side product. The resulting deep red materials **5a,b** are stable under ambient temperature for weeks when stored in the dark under an atmosphere of nitrogen.

The organic/inorganic hybrid materials **4a,b** and **5a,b** were characterized by a series of different methods. Powder XRD patterns of extracted neat MCM-41 and **4a,b** are presented in Figure 1. MCM-41 can clearly be characterized by four reflections in the  $2\theta$  range of  $2\text{--}10^\circ$ , which can be indexed to a hexagonal cell as (100), (110), (200), and (210), respectively. After functionalization of the host material with phenothiazines **3a,b**, both samples retain their (110) and (200) reflections, indicating that the structural integrity was well-preserved. The intensity of all reflections decreased as compared to the parent material, suggesting a less diminished mesostructural order and the reduction of X-ray scattering contrast between the silica wall and the pore-filling system.<sup>34</sup> Sample **4a** with the higher content of organic molecules shows less intense reflections than **4b**, which further proves the decrease of the peak intensity due to the influence of the scattering contrast.

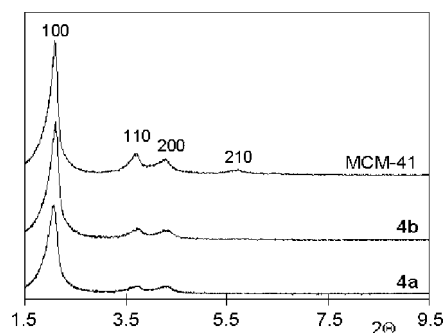
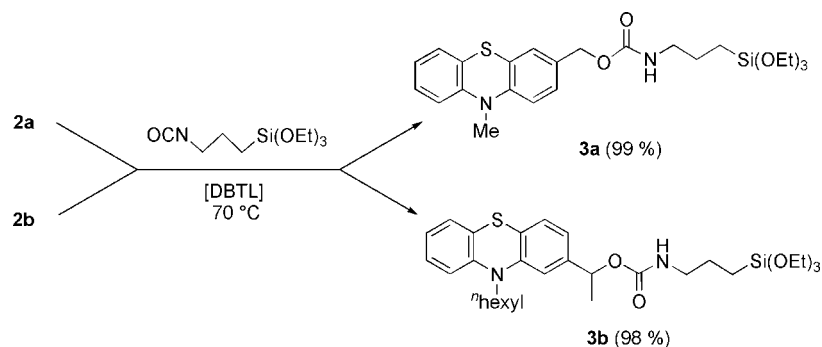


Figure 1. Powder XRD patterns of parent MCM-41 and **4a,b**.

Analysis of nitrogen adsorption and desorption data exhibited a reversible typical type-IV isotherm for neat MCM-41 and all organically modified materials (Figure 2), which is characteristic for a mesoporous structure.<sup>35</sup> The sharpness of the capillary condensation/evaporation steps of all the samples reflects the uniform pore size distributions. The relative pressure at which pore filling occurs in the modified samples **4a,b** is shifted to lower values in comparison to the parent materials MCM-41 because of the

(31) The template was extracted by HCl/EtOH to obtain a higher content of Si-OH groups on the surface of the material.

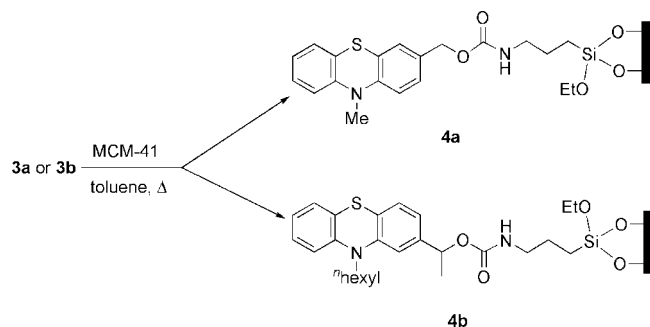
## Scheme 2. Synthesis of Triethoxysilyl Functionalized Phenothiazinyl Carbamates 3a,b

Table 1. Selected Absorption and Emission Spectra<sup>a</sup> and CV Data<sup>b</sup> of 3a,b

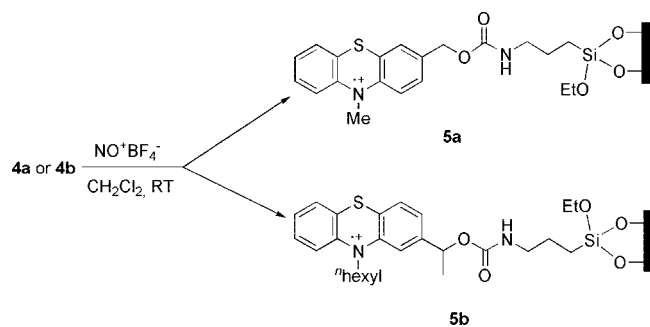
| compound | absorption $\lambda_{\text{max,abs}}$<br>(nm) ( $\epsilon$ ) | emission $\lambda_{\text{max,em}}$<br>(nm) | Stokes shift $\Delta\tilde{\nu}$<br>(cm <sup>-1</sup> ) | $E_0^{0/+1}$<br>(mV) |
|----------|--|--|---|----------------------|
| 3a       | 258 (42000), 290 (6300), 312 (7000)                          | 465  | 10 500  | 768                  |
| 3b       | 260 (28500), 312 (4400)                                      | 453  | 10 000  | 734                  |

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub>,  $T = 20$  °C. <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub>,  $T = 20$  °C,  $\nu = 100$  mV/s. Electrolyte: (nBu<sub>4</sub>N)PF<sub>6</sub>, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode.

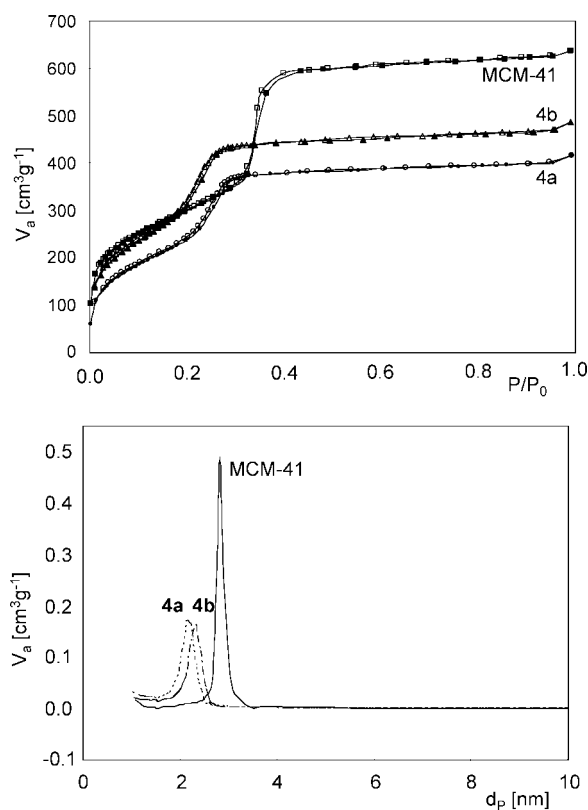
## Scheme 3. Synthesis of Mesoporous Hybrid Materials 4a,b



## Scheme 4. Oxidation of Mesoporous Phenothiazinyl Hybrids



reduction of the pore diameter due to organic modification. Otherwise, the isotherms of hybrid materials show a lower N<sub>2</sub> uptake, accounting for the decrease of surface area. These results confirm that the immobilization of the ligands occurred on the internal silica surface of the channels.<sup>36</sup> The calculation of volume and pore size was estimated with the



**Figure 2.** Top: N<sub>2</sub> adsorption/desorption isotherms of parent MCM-41, 4a,b; adsorption points are marked by solid circles and desorption points by empty circles. Bottom: pore size distribution.

BJH method, the specific surface area was obtained from the BET treatment of the isotherm,<sup>37</sup> and the content of

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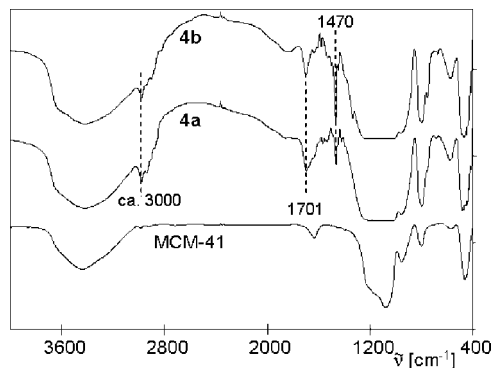


Figure 3. FT-IR spectra of MCM-41 and 4a,b.

organic compounds in the materials is given in Table 2. The loading of phenothiazine in sample 4a is ~25% higher than in 4b, although the two materials are synthesized under similar conditions with equal amounts of 3a and 3b in the precursor solution. We explain this by the different sizes of 3a,b: the bulky hexyl chain of 3b may hinder diffusion of this compound inside the pore channels during the post-synthetic grafting process.

Table 2. Textural Parameters of Parent MCM-41 and 4a,b Derived from Nitrogen Sorption Analysis and Loading of Materials with Phenothiazines

| sample | BET surface area (m <sup>2</sup> g <sup>-1</sup> ) | pore volume (cm <sup>3</sup> g <sup>-1</sup> ) | pore diameter (Å) | content of phenothiazine <sup>a</sup> |        |
|--------|--|--|-------------------|---------------------------------------|--------|
|        |  |  |                   | (mmol g <sup>-1</sup> )               | (wt %) |
| MCM-41 | 1092   | 0.95   | 28.3              |                                       |        |
| 4a     | 814  | 0.62   | 23.1              | 0.41                                  | 15.5   |
| 4b     | 903  | 0.72   | 22.6              | 0.30                                  | 13.9   |

<sup>a</sup> Calculated according to the content of nitrogen (CHN elemental analysis).

FT-IR spectroscopy was used to confirm the modification of the materials (Figure 3). For parent MCM-41 as well as for 4a,b, the asymmetric Si—O—Si vibration appears at 1070 cm<sup>-1</sup>, while the symmetric Si—O—Si vibration can be assigned to a band at 790 cm<sup>-1</sup>. The OH stretching vibration of the Si-OH groups is observed as a broad band at ~3430 cm<sup>-1</sup>.<sup>38</sup> Additionally, to those signals that can be assigned to the silica matrix, the functionalized materials show a strong absorption at 1701 cm<sup>-1</sup> due to the C=O stretching vibration of the carbamate unit. Further absorptions in the range of 2700–3000 and 1470 cm<sup>-1</sup> can be assigned to aliphatic CH stretching and deformation vibrations, respectively.<sup>39</sup> These results confirm the introduction of phenothiazine molecules in the mesoporous materials.

A further direct confirmation for the incorporation of phenothiazines into the MCM-41 support is given by <sup>13</sup>C CP-MAS NMR spectroscopy. Both 4a and 4b present solid-state NMR spectra that show resonances with chemical shifts similar to those of the free compounds 3a,b. This is exemplarily shown for 4a in Figure 4. The two especially sharp signals at ca. δ 60 and 16 can be assigned to free ethanol formed as a side product of the grafting reaction or

the remnant ethanol from the template extracting process. These signals overlap with the resonances of residual Si-OCH<sub>2</sub>CH<sub>3</sub> groups (see discussion of the <sup>29</sup>Si NMR spectrum). A characteristic resonance at δ 35 proves the preservation of the phenothiazine N-CH<sub>3</sub> group. The presence of some of the carbon resonances of the phenothiazine moiety in the high field region (δ 114) is typical for an electron-rich aromatic system. A small shift of carbon resonance of the C=O group (δ 158) in the hybrid material as compared to the solution data is due to an interaction of the carbonyl group with surface Si—OH units.

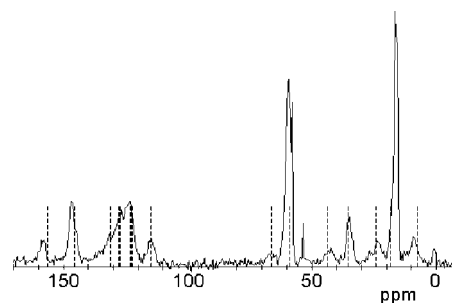


Figure 4. <sup>13</sup>C CP-MAS NMR spectra of 4a; dashed lines give information on position and relative intensities in solution NMR spectra of 3a.

The covalent linkage of phenothiazines on the mesostructured materials also can be monitored by means of <sup>29</sup>Si CP-MAS NMR spectroscopy (shown exemplarily for 4a in Figure 5). The spectrum of parent MCM-41 shows three signals at δ -110, -101, and -92 corresponding to Si(OSi)<sub>4</sub> (Q<sup>4</sup>), HOSi(OSi)<sub>3</sub> (Q<sup>3</sup>), and (HO)<sub>2</sub>Si(OSi)<sub>2</sub> (Q<sup>2</sup>) sites of the silica framework.<sup>40</sup> Covalently grafting phenothiazines 3a,b onto the surface makes the Q<sup>2</sup> signal disappear, decreases Q<sup>3</sup>, and concomitantly increases the Q<sup>4</sup> intensity, which is due to the consumption of isolated Si-OH groups and geminal silandriols during the reaction.<sup>41</sup> For modified materials 4a,b, three additional broad and overlapping signals appear at δ -49, -58, and -67, which can be assigned to R-Si(HO)<sub>2</sub>(OSi) (T<sup>1</sup>), R-Si(HO)(OSi)<sub>2</sub> (T<sup>2</sup>), and R-Si(OSi)<sub>3</sub> (T<sup>3</sup>) organosiloxane species.<sup>42</sup>

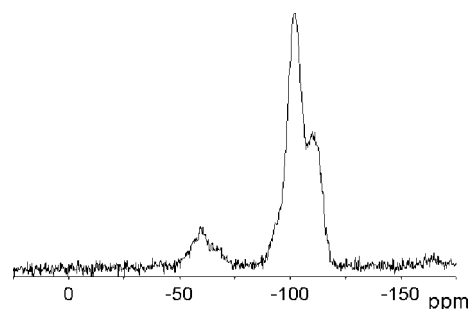
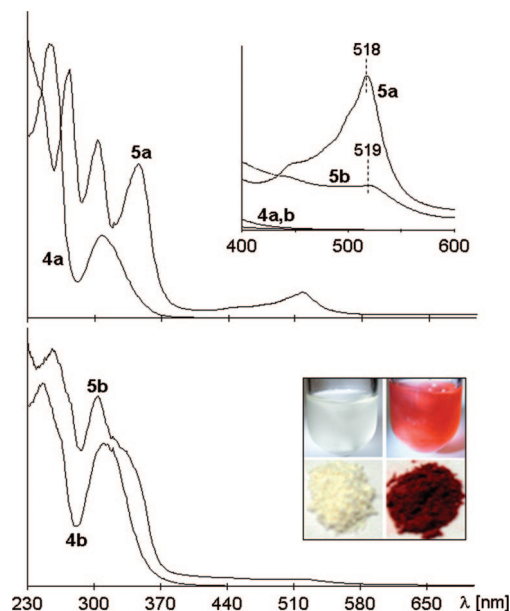


Figure 5. <sup>29</sup>Si CP-MAS NMR spectra of 4a.

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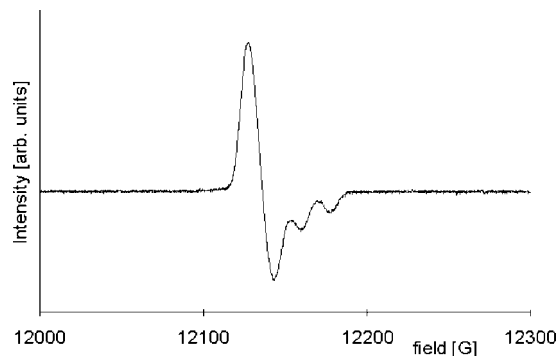
The formation of radical cations from phenothiazines in the presence of (NO)BF<sub>4</sub> through a one-electron transfer process is a well-known reaction.<sup>43</sup> When **4a,b** are treated with (NO)BF<sub>4</sub>, the color of the solid hybrid materials changes immediately from colorless to deep red, which is typical for phenothiazine radical cations.<sup>44</sup> The novel hybrid materials **5a,b** were characterized by UV-vis spectroscopy under diffuse reflectance conditions (Figure 6).



**Figure 6.** UV-vis spectra of **4a** and **5a** (top) and **4b** and **5b** (bottom). Inset in the top panel shows an enlargement of the absorption of phenothiazine radical cations, and inset in the bottom panel demonstrates the color change caused by oxidation of **4a** in suspension and in solid material.

The precursor materials **4a,b** only show UV-vis absorptions in the UV region (**4a**: 254 and 308 nm and **4b**: 245 and 310 nm), while the hybrid materials **5a,b** containing the phenothiazine radical cations show three absorptions in this region. An additional absorption band at ~518 nm appears (Figure 6b, top inset), which is typical for phenothiazine radical cations.<sup>45</sup> The existence and distinguished stability of these species in solids was further confirmed by means of EPR spectroscopy. The EPR spectrum of **5b** shown

exemplarily in Figure 7 was recorded ~10 days after the synthesis of the material, which still showed no color change after this time. The derived parameters ( $g_{\perp} = 2.007$ ,  $g_{\parallel} = 2.001$ , and  $A_{\parallel} = 18$  G) are typical for phenothiazine radical cations.<sup>46</sup> However, the EPR spectrum is less symmetric than expected for such a species, most likely due to the anisotropic influence of the chemical environment (interaction with pore surface and/or anion BF<sub>4</sub><sup>-</sup>).



**Figure 7.** Q-band EPR spectrum of **5b** at 297 K.

## Conclusion

Novel hybrid organic/inorganic mesoporous silica materials were synthesized by covalently anchoring phenothiazines on MCM-41. The highly ordered hexagonal mesoporous structure was confirmed by XRD and N<sub>2</sub> adsorption measurements. <sup>13</sup>C CP-MAS, <sup>29</sup>Si CP-MAS NMR, and FT-IR data exhibited the successful incorporation of organic species into the solid materials. The existence of stable phenothiazine radical cations in the materials can be clearly detected by UV-vis and EPR spectroscopy methods. In our ongoing project, we are working to increase the phenothiazine content in the pores. This should lead to systems showing charge-transfer properties or even electronic conductivities.

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**Note Added after ASAP Publication.** The upper graph of Figure 2 was missing in the version published ASAP July 3, 2008; the corrected version was published ASAP July 10, 2008.

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