Synthesis and Crystal Structures of Axially Substituted Titaniumphthalocyanines and Preparation of PcTi@SBA-15 and PcTi&TiO_x@SBA-15 Materials

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Dedicated to Professor Bernt Krebs on the Occasion of His 70th Birthday

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Abstract. Four axially substituted titanium(IV)phthalocyanines of formula *trans*-[PcTi(OSiPh₃)₂], [PcTi{(NH)₂C₆H₄}], [PcTi(η^2 -S₂)], and [PcTi=S] were prepared starting from the reactive species N,N'-di-4-tolylureato(phthalocyaninato)titanium(IV). The prepared compounds were characterized by using UV/Vis-spectroscopy, FT-IR and raman spectroscopy, TGA, elemental analysis and MALDI-TOF measurements. The compound *trans*-[PcTi(OSiPh₃)₂] crystallizes from chlorobenzene in the triclinic space group PI with *a* = 10.4160(8) Å, *b* = 11.2160(8) Å, *c* =

Introduction

Titanium phthalocyanines (Pc) have a wide range of interesting properties and found a lot of applications in many industrially fields such as the manufacture of electrophotographic and electrochromic materials [1] or NLO materials and molecular sieves pigments [2]. Synthesis of new axially substituted TiPcs by reaction of [PcTiCl₂] with oxalic acid, Ph₃SiOH, H₂O₂, etc [3] or reaction of [PcTiO] with strongly chelating oxygen or sulfur donor ligands [4] is established in the literature. Also, chalcogenido-TiPcs of formula [R₄PcTi = X], where X = O, S, Se were mentioned in a patent as useful materials in charge-generating layers,

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13.1495(9) Å, $\alpha = 114.124(5)^\circ$, $\beta = 99.452(6)^\circ$, $\gamma = 96.174(6)^\circ$, and Z = 1. [PcTiS₂] crystallizes from chlorobenzene in the monoclinic space group $P2_1/n$ with a = 13.114(3) Å, b = 9.752(2) Å, c = 20.975(5) Å, $\beta = 100.46(2)$, and Z = 4. The crystal structures of both compounds are discussed. The reactive ureato complex could also successfully be anchored onto SBA-15 and TiO_x@SBA-15 materials using the apical ureato ligand as a good leaving group for the reaction with the silanol groups of the host material.

however no complete characterization of the sulfido and selenido complex was presented [5]. Titanium porphyrins such as [(TTP)Ti=S] or [(TTP)Ti=Se] (TTP = tetratolyl-porphyrine) have been prepared by atom transfer reaction of $[(TTP)Ti(\eta^2-PhC=CPh)]$ with Ph₃P=S or Ph₃P=Se [6]. The dichalcogenido species $[(TTP)Ti(\eta^2-S_2)]$ and $[(TTP)Ti(\eta^2-Se_2)]$ are reported in the literature as well [7].

Segura et al. [8] prepared Ti-SBA-15 by heating solutions of [TiO(acac)₂] with SBA-15 and the titanyl function was found to covalently bind to most of the OH groups on SBA-15 surface. Landau et al. [9] achieved TiO₂ loading of (30-80%) inside the pores of SBA-15 silica by chemical solution decomposition (CSD) or internal hydrolysis (IH) of $[Ti(OnBu)_4]$ as titanium precursor. Both methods yielded composites with high TiO₂ crystalinity (anatase). Perathoner et al. [10] reported that in case of titanium loadings up to 12-13 wt%, the XRD patterns are in agreement with the model of a guest phase layer uniformly covering the inner part of SBA-15 walls, while higher titanium loading leads to patterns like that of separate TiO₂ nanoparticles. Calleja et al. [11] studied the grafting of titanium (1-3 wt%) in SBA-15 using titanocene dichloride [Cp₂TiCl₂]. The UV/Vis spectrum of the prepared Ti-SBA-15 showed the presence of titanium isolated species tetrahedrally coordinated and the absence of bulk TiO₂ phase. *Peng Wu* et al. [12 a] studied the preparation of Ti-SBA-15 by titanation of pure SBA-15 with $[Ti(OnBu)_4]$ in glycerol containing quaternary ammonium hydroxide. Srivastava et



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al. [13] functionalized Ti-SBA-15 to Ti-SBA-15-pr-Cl and Ti-SBA-15-pr-NH₂ using the corresponding isopropyl titanate. Afterwards adenine was grafted in these active sites and an active catalyst for the synthesis of cyclic carbonates was obtained.

In many applications, the phthalocyanine compounds display improved properties when they are included in mesoporous materials such as the semiconductor clusters anchored in molecular sieves [14]. [PcZn] was impregnated onto Si-MCM-41 by heating it in a solutions of [PcZn] in dry DMF [15]. *Palomares* et al. [16] described TiPc species anchored in nanocrystalline TiO₂ films via the axial carboxylate ligand without the use of co-adsorbents, and the state selective electron injection into the TiO₂ was demonstrated to result in an efficient photocurrent generation in a dye sensitized photoelectrochemical solar cell. The choice of titanium(IV) as a central metal ion allows axial ligation to the metal atom.

Previously, we reported the synthesis and crystal structure of a N,N-diphenylureato-TiPc species [17]. In this work we utilize the reactive dianionic ureato functionality as convenient and stable leaving group (as urea), to establish a straight forward synthetic protocol for the preparation of other axially substituted [TiPc(L)] complexes via protolysis with OH-, NH- and SH-acidic substrates. Furthermore we investigated this strategy to covalently anchor the titanium phthalocyanine dye on SBA-15 and TiO_x@SBA-15.

Results and Discussion

The ureato leaving group in 1 can be utilized for preparation of other axially substituted titanium phthalocyanines (Scheme 1). The axial ligand exchange reactions of the ureato moiety with the incoming ligands proceed smoothly yielding pure products. The use of [PcTi(ureato)] (1) rather than [PcTiO] as starting material provides many advantages because of the better solubility and higher reactivity of 1.



Scheme 1. Axial ligand exchange reactions of 1.

$[PcTi(OSiPh_3)_2]$ (2)

Compound 1 reacts with two equivalents of Ph_3SiOH forming *trans*-bis (triphenylsiloxy)phthalocyaninatotitanium(IV) (2) (Scheme 1). The blue green compound is air sensitive; it turns readily into [PcTiO] in air as indicated by

mass and IR spectroscopic measurements. The UV/Vis spectrum of 2 in chloronaphthalene (Figure 1) shows a split (Q_{0.0}) absorption band at $\lambda_{max} = 741$ nm and 698 nm. Another allowed $\pi - \pi^*$ transition at $\lambda_{max} = 356.5 \text{ nm}$ (B-band) is observed. The shoulders at $\lambda_{max} = 663.5 \text{ nm}$ and 630.0 nm are observed and attributed to the $(Q_{1,0})$ and $(Q_{2,0})$ vibronic transitions. The broadening and splitting of the Q band into two maxima at $\lambda_{max} = 741 \text{ nm}$ and 698.0 nm, which is not observed in spectra of PcTiO or ureato-TiPcs, may be attributed to the exciton interaction between the Pc ligand and the two triphenylsiloxy groups in the axial positions [18]. The IR spectrum of 2 is very similar to that shown by the same product obtained from [PcTiCl₂] as a starting material [3]. The small absorption band at 821 cm⁻¹ in the IR spectrum of **2** is attributed to the antisymmetric stretching of the (O-Si-O) group.



Figure 1. UV/Vis spectrum of (1) $(10^{-5}M, \text{ chloronaphthalene})$.

The ¹H-NMR spectrum of **2** (Figure 2) shows the typical expected resonance patterns and integration values for the pure compound **2**. In the aromatic region, the phthalocyanine unit shows a characteristic resonance pattern for an unsubstituted Pc with two multiplets: the first multiplet in the region 9.62-9.70 ppm for eight protons in the 1,4-positions and the second multiplet in the region 8.25-8.32 ppm for eight protons in the 2,3-positions. The protons of the axial ligand show upfield-shifted signals due to the well known ring current effect of the phthalocyanine macrocycle [4]. The aromatic protons of the axial ligand are found in the region 5.23-6.87 ppm.

Crystal Structure of 2

The crystal structure of trans-[Ti(OSiPh₃)₂Pc] (2) is shown in Figure 3. The compound crystallizes in the centrosymmetric space group PI with one molecule per unit cell. The structure is very similar to that of [(TTP)Ti(OP(Oct)₃)₂] [19]. The titanium atom resides in an octahedral environment with the four nitrogen atoms of the four isoindoline rings in the equatorial plane and the two (OSiPh₃) groups occupying the axial positions. Owing to a center of symmetry at titanium, the [TiN₄] unit is planar and the (OSiPh₃) groups adopt a staggered *trans* conformation. A



Figure 2. ¹H-NMR spectrum of 2, 500 MHz, in C_6D_5Br , 373 K.

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cis configuration is not possible because of the high steric demand of the triphenylsilanolate groups. Some selected bond lengths and bond angles are given in Table 1.



Figure 3. The molecular structure of 2. Displacement ellipsoids at the 40% probability level. (H atoms are omitted for clarity).

Table 1. Selected bond lengths /Å and angles /° of 2.

Ti-N1	2.023(13)	Ti-O1	1.852(11)
Ti-N12	2.002(14)	Sil-O1	1.627(11)
Sil-Ol-Ti	162.97(8)	O1-Ti-N1	89.67(5)
Ola-Ti-Nl	90.33(5)	01-Ti-N12	90.17(5)
N1-Ti-N12	90.64(6)	N1-Ti-N12a	89.36(6)

The molecular packing of 2 is shown in Figure 4. All molecules are oriented parallel and approach a primitive hexagonal sphere packing along the a axis.

$[PcTi\{(NH)_2C_6H_4)\}]$ (3)

Compound (1) reacts with 1,2-phenylenediamine to form compound 3 in quantitative yield (Scheme 1). The corre-



Figure 4. View of the molecular packing of *trans*-[PcTi(OSiPh₃)₂] (2) in the crystal lattice.

sponding urea derivative is formed as a perfect leaving group. The IR spectrum of **3** shows the expected absorption of the N–H group ($v_{N-H} = 3450 \text{ cm}^{-1}$). Thermogravimetric analysis (TGA) of compound **3** shows two weight losses. The first occurs in the temperature range 350-450 °C and is attributed to the loss of the axial moiety (C₆H₄(NH)₂), weight loss calcd./found 14/14 % (Scheme 2). The second one starts at about 600 °C and is attributed to the thermal destruction of the basic skeleton of the phthalocyanine macrocycle. Such TGA data have been documented in the literature for other axially substituted Pcs [20].

$$\begin{array}{c|c} & & \\ & & \\ HN & NH \\ & & \\ & & \\ Pc \ Ti \end{array} \end{array} \xrightarrow{350 - 450^{\circ}C} - \{C_{6}H_{4}(NH)_{2}\} \\ \hline & Pc \ Ti \end{array} \qquad Pc \ Ti \end{array}$$

Scheme 2. Thermal decomposition of the axial moiety of 3.

[PcTiS] (4) and $[PcTiS_2]$ (5)

The reaction of a solution of 1 in chloronaphthalene with H_2S gas in the absence of air yields [PcTi=S] (4). The molecular ion of [PcTi=S] (4) (M⁺ = 592) is detected in EI-MS and MALDI-TOF. IR spectrum of 4 shows ($v_{Ti=S}$) at 563 cm⁻¹ and in Raman spectrum at 560 cm⁻¹, which is in agreement with values reported for the analogue porphyrins [6]. A ¹H-NMR spectrum of 4 shows resonance patterns of a single phthalocyanine product with two multiplets at $\delta = 8.03-8.11$ and 9.45–9.59.

The presence of small amounts of air leads to formation of perchalcogenido species $[PcTiS_2]$ (5). The disulfur compound $[PcTiS_2]$ may be formed as a result of an oxidation of the intermediate $[PcTi(SH)_2]$ by oxygen (Scheme 3).

The Raman spectrum of **5** shows (v_{Ti-S}) at 424.6 cm⁻¹ and (v_{S-S}) at 548.4 cm⁻¹ and this in accord with the values reported for the analogue porphyrins at (426.0) and (549–553 cm⁻¹) respectively [7]. Comparison of the S–S vibration in **5** with the ones in free S₂ (725 cm⁻¹), ionic



Scheme 3. Suggested mechanism for the formation of 5. The molecular ion of [PcTiS₂] ($M^+ = 624$) is detected in EI-MS and MALDI-TOF. The values of elemental analysis are in agreement with the calculated values for 5.

 S_2^- (589 cm⁻¹), and S_2^{2-} (446 cm⁻¹) indicates that the S–S bond strength of **5** lies between that of S_2^- and S_2^{2-} [7].

The ¹H-NMR spectrum of **5** shows two multiplets at 8.38-8.32 ppm and 9.82-9.72 ppm. The electronic absorption spectrum of **5** is similar to that of **4** with a small blue shift of Q_{1.0} and Q_{2.0}. A TGA diagram of **5** shows two weight losses (Figure 5), the first at 220 °C and is attributed to the loss of the TiS₂ moiety as shown in Scheme 4. The second weight loss is starts about 600 °C and is attributed to the destruction of the skeletal Pc macrocycle.



Figure 5. TGA diagram of 5.

$$\begin{array}{c} S \longrightarrow S \\ \swarrow & (220^{\circ}\text{C}) \ (-\text{TiS}_2) \end{array} \\ \hline Pc \stackrel{}{\longrightarrow} & \text{Wt loss calc. /found} \ (18\%/22\%) \end{array}$$

Scheme 4. Thermal decomposition of the axial moiety of 5.

The reaction of [PcTiO] with P_4S_{10} was found to result in the formation of a mixture of [PcTiS] (M⁺ = 592) and [PcTi(η^2 -S₂)] (M⁺ = 624) (Scheme 5). Reduction of the [PcTi(η^2 -S₂)] portion was achieved successfully by reaction of the mixture with melted Ph₃P at 160 °C yielding a homogeneous product of [PcTiS] (4). The byproduct Ph₃P=S had to be removed by extraction with different organic solvents.

PcTiO + P₄S₁₀
$$\xrightarrow{CIN}$$
 PcTi=S + PcTiS₂
 $\xrightarrow{Ph_3P}$ PcTi=S + Ph_3P=S
 $160^{\circ}C / 4 \text{ hrs}$ 4

Scheme 5. Synthesis of [PcTiS] (4) starting from [PcTiO].

Crystal Structure of 5

Compound 5 crystallizes monoclinic in the centrosymmetric space group $P2_1/n$ with four molecules per unit cell (Figure 6). The molecule consists of a six-coordinate titanium(IV) atom surrounded by four equatorial isoindoline rings of the Pc molecule. The S₂ group is side-on bonded to the titanium atom with an average Ti-S distance of 2.320(9) Å (Figure 4 and Table 2). The S-S distance is 2.020(10) Å. This is close to the distance found in $[(TPP)Ti(\eta^2-S_2)]$ [7] and is between that expected for ionic S_2^{-} (2.00 Å) and S_2^{2-} (2.13 Å) [21]. The coordination at the Ti atom is square-pyramidal with the four isoindoline nitrogen atoms forming the basal plane and the dichalcogen group at the apical site. The titanium atom is not situated in the cavity of the Pc macrocycle, but is located 0.708(5) A above the plane of the four nitrogen atoms. This distance is comparable to the corresponding distance of 0.658(1) Å observed for $[(TPP)Ti(n^2-S_2)]$ [7]. Such "atop" situation is well known for analogue complexes and called extra-coordination. This out-of-plane displacement of the titanium(IV) atom from the N₄ core of the Pc ligand, drives the macrocycle to adapt to this special situation by deformation [22]. Here, the maximum deviation from the best plane through all phthalocyanin atoms is 0.28(2) A. Similar coordination schemes are documented in the literature for peroxo-, disulfur-, and diselenium analogues [7]. The Ti-N distances parallel to the S-S bond [Ti-N(1) = 2.13(2)], Ti-N(3) = 2.09(2) Å are somewhat larger than the ones perpendicular to this group [Ti-N(2) = 2.05(2)], Ti-N(4) = 2.05(2) Å]. Some further selected bond lengths (Å) and bond angles (deg.) of 5 are given in Table 2. A comparison between some structural parameters of 5 and $[(TPP)Ti(\eta^2-S_2)]$ is shown in Table 3.

Table 2. Selected structural parameters (in Å and degrees) of **5**. Low precision because of very small crystal. Data for the TiS_2 unit see Table 3.

Ti-N1	2.13(2)	N1-Ti-N2	84.8(8)	N1-Ti-N3	138.4(8)
Ti-N2	2.05(2)	N1-Ti-N4	81.5(7)	N2-Ti-N4	141.7(7)
Ti-N3	2.09(2)	N2-Ti-N3	83.6(8)	N1-Ti-S1	87.5(5)
Ti-N4	2.13(2)	N3-Ti-N4	83.4(8)	N3-Ti-S2	82.5(6)

Table 3. Comparison between some structural parameters (in Å, degrees) of **5** and $[(TPP)Ti(\eta^2-S_2)]$ [7].

Structural parameter	$PcTi(\eta^2-S_2)$ (5)	$(TpTP)Ti(\eta^2-S_2)$
Ti-S1	2.313(9)	2.283(2)
Ti-S2	2.327(9)	2.311(2)
S1-S2	2.020(10)	2.042(2)
S1-Ti-S2	51.6(3)	52.78(6)
S2-S1-Ti	64.6(3)	64.30(7)
S1-S2-Ti	63.8(3)	62.92(8)

The molecular packing of **5** (Figure 7) can be characterized by "face-to-face dimers" generated by an inversion center and shifted against each other by about 3.5 Å. The distance between the best planes calculated by all C, N atoms of the Pc units is 3.31 Å only, indicating $\pi - \pi$ interaction similar to that in the imido and ureato-TiPcs [17]. In





Figure 6. Top view of 5 with atom labeling Scheme. Displacement ellipsoids (isotropic for C and N atoms) at the 50 % probability level.

the latter compound, the distance between the Pc planes is 3.50 Å and the shift about 2.5 Å. In **5** the molecule pairs are stacked along the *a* axis to columns. Equivalent columns with mutual perpendicular orientations of the Pc planes are packed in the way of a hexagonal rod packing. No close S···S contacts are observed.



Figure 7. The molecular packing of $[PcTi(\eta^2-S_2)]$ (5).

Anchoring of 1 onto SBA-15 and (TiO_x@SBA-15)

The methods we applied to prepare SBA-15 were reported previously in the literature [23]. For the preparation of $(TiO_x@SBA-15)$, we used a method similar to that previously used for impregnation of titanium species [12, 15]. Thus titanium species were impregnated in a previously synthesized calcined siliceous SBA-15 using tetrabutylor-thotitanate (TBOT) as a precursor of titanium species. It is known, that TBOT interacts with the surface silanol groups of SBA-15 [12]. In our experiments, unreacted TBOT was removed by extraction with dried solvents under inert conditions. During the following calcination in air at 600 °C, the remaining butoxy ligands are assumed to be burned off

while the TiO_x species remained fixed via a Si-O-Ti linkage at the surface of SBA-15. According to AAS we obtained a titanium loading of about 2.66 wt.-% and this value is comparable to that achieved applying this method for MCM-41 materials where loadings of 1.7-8.6 % were reported [12 b]. The lower titanium loading in the pores compared with that achieved for MCM-41 using TiO(acac)₂ may be attributed to the weaker interaction of TBOT with the OH groups because of its hydrophobic hydrocarbon chain [12 b]. While high loadings (30-80%) of TiO₂ in SBA-15 led to the presence of anatase [9], the material TiO_x@SBA-15 prepared in this work having relatively low titanium loading displays monodispersed isolated Ti^{IV} sites. This is in agreement with other reports of SBA-15 materials of low titanium loading [8, 10, 11]. Raman spectrum of the prepared TiO_x@SBA-15 shows absorption bands at 789, 832 cm^{-1} assigned to the Si-O-Si linkage, and at 488 and 601 cm^{-1} assigned to four and three membered siloxane rings [24]. The absence of the typical Raman absorption bands of anatase TiO₂ (638, 519, 399, 147 cm⁻¹) ensures the absence of the anatase [8]. It is suggested that due to the strong extraction of the unreacted TBOT under inert atmosphere and low titanium content Ti^{IV} is only covalently bonded to the surface of SBA-15 via 1-3 Ti-O-Si links forming thin layer of TiO_x. The good ureato leaving group in 1 results in smooth reaction with the silanol groups of Ph₃SiOH. In the following part, compound 1 was used to anchor and fix the TiPc dye in the pores of SBA-15 and $TiO_x(a)SBA-15$ where the titanium atom in 1 can smoothly link to the silanol groups in SBA-15 molecular sieves (Figure 8).

Several samples were included in this study (Scheme 6). In Sample A the conventional silica (SiO_2) was heated with a dilute solution of the phthalocyanine dye. In Sample B the SBA-15 material was heated with a dilute solution of the phthalocyanine dye. Consequently, the TiPc species are expected to be immobilized predominantly inside the channels to give the modified material shown in Figure 8. In Sample C the prepared TiO_x@SBA-15 (Ti 2.66 wt.-%) was heated with a diluted solution of 1 and since some surface silanol groups are still unreacted, the hypothetical monolayer coverage of SBA-15 with TiOx is about 35 wt.-% [10], the dye molecules are presumably covalently bound via the remaining silanol groups or via the Ti–OH groups which may be present at the TiO_x(OH)_v sites (Figure 8).



Scheme 6. Preparation of PcTi@silica, PcTi@SBA-15, and PcTi&TiO_x@SBA-15 materials.

In all samples the physically adsorbed phthalocyanine dye was supposed to be removed by intensive extraction of all samples with different organic solvents such as toluene,



[Sample B]

[Sample C]

Figure 8. Covalent anchoring of [PcTi] onto different SBA-15 materials.

MeCN and chlorobenzene. Finally, the samples were dried at high vacuum.

Mass Spectrometry

In mass spectrometric measurements (MALDI-TOF) of all prepared samples the ion peak of $[PcTi^+] m/z = 560$ instead of the molecular ion peak of N,N'-di-4-tolylureato(phthalocyaninato)titanium(IV) (1). This is giving rise to the assumption that the ureato complex reacted with the silanol groups on the surface of the SBA-15 material. The formed urea derivative (TolNHCONHTol) was extracted from the produced materials by successive washing by several organic solvent such as boiling acetonitrile.

Ti Analysis

The amounts of the loaded titanium in $TiO_x@SBA-15$ and PcTi&TiO_x@SBA-15 were determined by using Atom Absorption Spectra (AAS) and the following results were obtained:

- %Ti in TiO_x@SBA-15 = 2.66
- %Ti in PcTi&TiO_x@SBA-15 (Sample C) = 3.44
- %Ti because of PcTi dye = 0.78 (consequently content of PcTi-dye = 9.13 %).

Absorption Spectra of the Prepared Materials

The absorption spectra (200-2000 nm) of pure mesoporous and conventional silica, pure Pc dye, dye/silica materials and mechanical mixture of dye and silica are shown in Figure 9. The measurements involved also a mechanically ground mixture of the respective silica and ureato-TiPc for comparison. It is apparent that the spectral patterns are different and this is attributed to different interactions of the dye with the silica when the components are mechanically grounded in a mortar and when the dye is covalently anchored onto the pores by heating the SBA-15 with the dye solution. In another work [17], we reported the crystal structures of two PcTi(diarylureato) compounds and discussed the molecular packing of the molecules in the unit cell. We identified that the PcTi(ureato) complex (1) exists in the solid state as dimeric species in a face to face configu-



Figure 9. Absorption spectra of several materials (powder measurements).



ration. The absorption band of **1** at about 800 nm in the UV/Vis spectrum of the solid is attributed to this dimeric stacking in solid phthalocyanines. [17] This absorption band is not observed in the solution spectrum because of the absence of the dimeric stacking of the molecules in solutions (Table 4). The presence of this band in the mechanical mixtures of the PcTi(ureato) compound (1) with SiO₂ or SBA-15 indicates that the dimeric stacking of the phthalocyanine molecules is present in these mixtures. However, the absence of this band in (PcTi(ureato)@SiO₂) and (PcTi[ureato]@SBA-15), as previously observed in Pc solutions, gives strong support for the assumption that the Pc molecules are anchored as monomers on the template and not stacked in dimeric configuration any more.

Table 4. UV/Vis Spectroscopic Data of 1 and Pc-modified SBA-15 Materials.

Material	λ max /nm				
PcTi(ureato) (1) solid	306	575	716	828	932
PcTi(ureato)/SiO ₂ (mechanical mixing)	310	602	713	818	930
PcTi(ureato)/SBA-15 (mechanical mixing)	329	586	702 (w)	793	
PcTi(ureato)@SiO ₂ (Sample A)	324	612	700		
PcTi@SBA-15 (Sample B)	340	640	698		
PcTi(ureato) (1) Solution in ClN	347	629	697		



Figure 10. Raman spectra of [PcTiO], [PcTi(ureato)] (1), (PcTi@SBA-15), and (PcTi/TiO_x@SBA-15). The dotted lines are hand made for an ease comparison.

Raman Spectra

Raman spectra (RS) of N,N'-di-4-tolylureato-(phthalocyaninato)titanium(IV) (1), PcTi@SBA-15, and PcTi&TiO_x@SBA-15 at $\lambda(exc) = 632$ nm are shown in Figure 10 and the band positions are reported in Table 5. (Line 1 and 2) in Figure 10 are made for comparison of the most important band positions in the spectra of the prepared materials. There are remarkable differences in the spectra of 1 and the two prepared materials due to the different compositions of each material. The appearance of the basic absorptions of the titaniumphthalocyanine dye emphasizes the inclusion of the dye in the impregnated materials. The absence of ($v_{Ti=O}$ at 965 cm⁻¹) [25] rules out the assumption that [PcTiO] may be formed and hydrogen bonded to the OH groups at the pores surface.

Table 5. Raman bands of the prepared materials.

Material	Wavenumber /cm ⁻¹
PcTi(ureato) (1)	1506, 1491, 1449, 1433, 1338, 1303,
	1212, 1192, 1142, 1104, 1009, 971 , 938, 835,
	751, 677, 591, 484, 308, 254, 235, 216, 188.
PcTi@SBA-15,	1611 , 1529 , 1511, 1451, 1432, 1338, 1304,
(Sample B)	1210, 1190, 1142, 1104, 952 , 937, 835, 778,
	749, 677, 589, 483, 215.
PcTi&TiO _x @SBA-15,	1528, 1514, 1453, 1433, 1338, 1307, 1210,
(Sample C)	1190, 1143, 1105, 953 , 938, 837, 825, 780,
	751, 679, 599, 485, 236, 217.

Transmission Electron Microscopy (TEM) on (TiPc@SBA-15) Material

The material (PcTi@SBA-15) (Sample A) obtained from anchoring of (ureato)TiPc on SBA-15 was investigated by electron microscopy. Transmission electron microscopy (TEM) images were taken for the on-top view and a crosssection of the pore system (Figure 11). The TEM micrographs show small and very distributed dark contrasts from the metal-containing dye anchored on the wall surface. No extended areas of accumulated dye molecules are found on the micrographs, which is in good accordance with the UV/ Vis spectroscopic data indicating the presence of individual non-aggregated phthalocyanine molecules anchored to the pore walls. Consequently, the observed dark spots in the TEM micrographs are evenly spread over the pore walls but are not found in the pore volume.

Experimental Section

Spectroscopic Methods

The UV/Vis absorption spectra were recorded with a Hitachi-U310 spectrophotometer in chloronaphthalene for phthalocyanine derivatives and as solid pellets for (PcTi@SBA-15) and (PcTi/TiOx@SBA-15) materials. IR spectra were recorded with a Bruker IFS 588 spectrophotometer with KBr pellets. The following abbreviations were used to identify the intensities of the bands: vs. (very strong), s (strong), m (medium), w (weak), vw (very weak), br (broad), and sh (shoulder). \tilde{v} = Wave-number /cm⁻¹. EI-mass spectra were measured with a CH7 mass spectrometer, Varian MAT (450 °C, 10⁻⁶ Torr, 70 eV), MALDI-TOF measurements were carried out by using a Bruker Flex III, in dry MeCN, without addition of an energy transfer matrix, the m/z-values refer to the isotopic ratio according to the natural abundance of the isotopes. Elemental analysis was carried out by using Elementar-Vario EL, burning of samples was carried out at 950 °C. TGA measurements were recorded on TGA/SDTA 851 by Mettler-Toledo.



Figure 11. (A) on-top view of the hexagonal pore array with dark contrasts showing the presence of titanium phthalocyanine in the pores; (B) cross-section of the ordered pore system where dark spots originating from the dye can be seen on the pore wall.

Crystal data	(2)	(5)
Molecular formula	C ₆₈ H ₄₆ N ₈ O ₂ Si ₂ Ti	$C_{32}H_{16}N_8S_2Ti$
Formula mass	1111.21	624.55
Crystal description	prism, dark green	block, black
Crystal size /mm	$0.38 \times 0.32 \times 0.27$	$0.045 \times 0.03 \times 0.03$
Crystal system	triclinic	monoclinic
Space group	ΡĪ	$P2_1/n$
Unit cell a /Å	10.4160(8)	13.114(3)
b /Å	11.2160(8)	9.752(2)
c /Å	13.1495(9)	20.975(5)
$\alpha /^{\circ}$	114.124(5)	
βΙ°	99.452(6)	100.46(2)
γ /°	96.174(6)	
Volume /Å ³	1356.7(2)	2637.9(10)
Ζ	1	4
$D_{\rm calcd} / \rm g \cdot \rm cm^{-3}$	1.360	1.573
Absorption μ /mm ⁻¹	0.259	0.524
Data collection		
Diffractometer	IPDS-II (Stoe)	
Radiation	MoK _a graphite mo	nochromator
	$(\lambda = 0.71073 \text{ Å})$	
Temperature /K	193(2)	100(2)
$\theta_{\rm max}/^{\circ}$	25.14	25.00
Reflections total	19504	16523
Refinement		
Reflections unique. $>2\sigma(I)$	4490, 3751	4643, 912
Parameters	459	188
Residuals R, wR_2 (all refl.)	0.0401, 0.0852	0.444, 0.349
(observed refl.)	0.0315, 0.0823	0.198, 0.225
Goodness of fit S	1.050	1.001
$\delta \rho$ (max, min) /e· Å ⁻³	0.283, -0.370	0.5680.947

Table 6. Crystallographic data, measurement and refinement conditions of 2 and 5.

Syntheses

All manipulations of reagents and products were carried out under an inert atmosphere of nitrogen by using a glove box (Type MB 150 BG II or LABMASTER 130 Braun) or on a vacuum line by using standard Schlenk technique. All solvents were thoroughly dried in an appropriate manner, distilled, and kept under nitrogen over molecular sieves. All organic reagents were purchased as a pure grade from Acros and used as received. Chloronaphthalene was purchased as a mixture of 90 % α - and 10 % β -chloronaphthalene. [PcTiO] was prepared according to the literature procedure [28].

(i) N,N'-Di-4-tolylureato(phthalocyaninato)titanium(IV) (1): This compound was prepared as described elsewhere [17] by reaction of [PcTiO] with an excess of 4-tolylisocyanate in chloronaphthalene.

(ii) Synthesis of *trans*-[PcTi(OSiPh₃)₂] (2): A mixture of (1) (400 mg, 0.5 mmol) and triphenylsilanol (550 mg, 2 mmol) was refluxed in chlorobenzene (40 mL) for 1 hr. The reaction mixture was gradually cooled from 130 °C to room temperature within 3 hrs giving dark-green crystals suitable for X-ray structure determination. Afterwards the crystals were filtered off, washed with MeCN, toluene, and pentane and dried under vacuum to give *trans*-bis(triphenylsiloxy)phthalocyaninatotitanium(IV) (2). Yield: 620 mg (92 %), C₆₈H₄₆N₈O₂Si₂ Ti (1111.2): calcd. C 73.50 H 4.17 N 10.08; found C 72.75 H 4.65 N 9.50. **MS** (MT): *m/z* = 1111 [M⁺]. **UV/Vis** (CIN): $\lambda_{max} = 741.5$ (m), 698.0 (s), 663.5 (sh), 627.0 (w), 356.5 (m) nm. **IR** (KBr): $\tilde{v} = 1590(m)(v_{C=Carom.})$, 1429(m), 1305(s), 1104(m), 1043(s), 998(w), 971(w), 944(w), 886(vs),

Crystal Structure Determinations

All crystals were isolated under scrupulously oxygen-free conditions and their X-ray crystallographic data were collected on an IPDS-2 area detector system using a graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). For 4 only very small crystals could be obtained. Thus, only about 20 % of the reflections were $>2\sigma(I)$ and the quality of the structural data is rather low, therefore. The structures were solved by direct methods using the program SIR2002 [26] and refined on F^2 by full-matrix least-squares using SHELXL-97 [27]. The crystal data and experimental conditions are collected in Table 6. For 2 all non-hydrogen atoms were refined using anisotropic displacement parameters, for 4 the titanium and sulfur atoms only. The hydrogen atoms were kept riding on calculated positions with isotropic displacement factors taken as 1.2 times (1.5 times for CH₃) the U_{eq} value of the corresponding carbon atom. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-287958 (2) and -287959 (4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. Code +44(1223)336-033; E-Mail: deposit@ccdc.cam.ac.uk].



 $821(w)(v_{\rm O-Sioop}),\ 800(w),\ 766(w),\ 736(m),\ 711(m),\ 707(m),\ 697(s)$ $cm^{-1}.$

(iii) Synthesis of [PcTi{(NH)₂C₆H₄] (3): A mixture of (1) (400 mg, 0.5 mmol) and 1,2-phenylenediamine (220 mg, 2 mmol) in chloronaphthalene (20 mL) was heated at 160 °C for 2 hours. The product was precipitated by addition of hexane (20 mL). The precipitate was filtered off and washed by successive extractions with refluxing MeCN, toluene (5x50ml), and washed with pentane and dried under vacuum to give 1,2-phenylenediimino(phthalocyaninato)titanium(IV) (3). Yield: 270 mg (82 %), $C_{38}H_{22}N_{10}Ti$ (666.5): calcd. C 68.48, H 3.33, N 21.01; found C 67.63, H 3.35, N 20.26. MS (MT): m/z = 666 [M⁺]. UV/Vis (ClN): $\lambda_{max} = 698.5(s)$ (Q_{0,0}), 668.0(sh) (Q_{1,0}), 629.5(m) (Q_{2.0}), 337.0(s) (B) nm. IR (KBr): $\tilde{v} = 3450(m)(v_{NH})$, 1606(w), 1491(w), 1476(w), 1414(w), 1330(s), 1283(m), 1230(w), 1160(w), 1117(s), 1074(vs), 892(m), 826(w), 748(s), 724(vs) cm⁻¹.

(iv) Preparation of Sulfido(phthalocyaninato)titanium(IV) (4) a) By Reaction of 1 with H₂S Gas: Into a solution of 400 mg (0.5 mmol) of (1) in chloronaphthalene (20 mL) in a sealed teflon valve container, dry H₂S gas (1 bar) was bubbled for five minutes under a cover of nitrogen gas. The container was tightly closed and the solution was stirred at 160 °C for 3 hours. After cooling and removing of the gas, the product was precipitated by addition of hexane (about 10 mL). The produced bluish-green solid was collected on a glass frit and washed with MeCN (5×50 mL) and finally with pentane. The product PcTi=S (4) was dried at 120 °C / 10^{-3} mbar for 3 hours. The product (4) yield: 160 mg (50 %), C₃₂H₁₆N₈STi (592.4): calcd. C 64.87, H 2.72, N 18.91, S 5.42; found C 64.60, H 3.20, N 18.44, S 4.17. MS (MALDI-TOF): m/ $z = 592.3 \text{ (M}^+\text{)}, 560.3 \text{ (M}^+\text{-S)}.$ UV/Vis (ClN): $\lambda_{\text{max}} = 696.0 \text{ (s)}$ (Q_{0.0}), 667.0 (w) (Q_{1.0}), 635.5 (w) (Q_{2.0}), 339.0 (s) (B) nm. IR (KBr): $\tilde{v} = 1647(m), 1608(w), 1553(br), 1491(s), 1415(m), 1332(vs),$ 1287(m), 1160(w), 1118(vs), 1071(vs), 1053(vs), 894(s), 778(m), 751(s), 730(vs), 563(m) ($v_{Ti=S}$), 501(w), 411(vw) cm⁻¹.

¹H NMR (500 MHz, C₆D₅Br, 373 K): $\delta = 8.03 - 8.11$ [m, 8H(α)], 9.45-9.59 [m, 8H(β)].



b) By Reaction of [PcTiO] with P_4S_{10} : A mixture of [PcTiO] (300 mg, 0.52 mmol) and P_4S_{10} (230 mg, 0.52 mmol) in chloronaphthalene (10 mL) was heated at 160 °C for 10 hours. The color turns dark green. After cooling, the product was precipitated by addition of hexane (20 mL). The precipitate was collected on a glass frit and washed by extraction from refluxing MeCN (3 × 50ml), refluxing toluene (3x50ml) and finally washed with pentane. The solid was dried at 120 °C/10⁻³ mbar for 1 hour. A sample (200 mg) of this product (mixture of PcTiS and PcTiS₂) was heated with Ph₃P (1 g) to a melt (160 °C) under nitrogen atmosphere for 4 hours. The blue-green mass was washed by successive extractions from refluxing MeCN (5 × 50 mL) and refluxing toluene (5 × 50 mL). The product (4) was finally washed with 50 mL of ether and dried at 120 °C/10⁻³ mbar for 3 hours. Yield: 170 mg (57 %).

(v) Preparation of Disulfido(phthalocyaninato)titanium(IV) (5): The same procedure as applied in the preparation of PcTi=S with H_2S

gas was followed but in presence of air and heating at 180 °C for 6 hours. The final product was identified as [PcTiS₂] (**5**), yield 210 mg (67 %), $C_{32}H_{16}N_8S_2Ti$ (624.53): calcd. C 61.54, H 2.58, N 17.94, S 10.30; found C 62.68, H 2.97, N 18.16, S 7.74. **MS** (MT): m/z = 624.2 [M⁺]. **UV/Vis** (ClN): $\lambda_{max} = 699$ (s) (Q_{0,0}), 665.4 (w) (Q_{0,1}), 337.1 (s) (B band) nm. **Raman spectra:** $\tilde{v} = 1606.5$, 1515.8, 1430.8, 1386.4, 1334.5, 1105.0, 1026.8, 833.9, 677.2, 590.2, 559.2, 548.4(v_{S-S}), 484.1, 424.6(v_{Ti-S}), 560.0 cm⁻¹.

¹H NMR (500 MHz, C₆D₅Br, 373 K): $\delta = 8.32 - 8.38$ [m, 8H(α)], 9.72-9.83 [m, 8H(β)].



(vi) Preparation of SBA-15: SBA-15 was prepared according to the procedure given in literature [23]. The material was dried at 200 °C, 10^{-3} mbar for 20 hours before use.

(vii) Preparation of (TiO_x@SBA-15): A sample of the previously synthesized and dried SBA-15 (200 mg) was suspended in dry ethanol (20 mL) for 30 min. Afterwards, excess of TBOT (1 mL) was added and the mixture was stirred at room temperature for 24 hours. The solid was filtered and washed with dry methanol (3×30 mL) and finally dried at $120 \,^{\circ}\text{C}/10^{-3}$ mbar for 2 hours. The solid was calcined in air at 600 °C for 24 hours to give TiO_x@SBA-15 (Ti = 2.66 wt%).

(viii) Anchoring of Titanium Phthalocyanine Dye on SBA-15 and (TiO_x@SBA-15): A solution of N,N'-di-4-tolylureato(phthalocyaninato)titanium(IV) (1) (200 mg) in chloronaphthalene (30 mL) was heated at 373 K under inert atmosphere until the solution was clear. About 20 mL of this solution were filtered using a microfilter (0.45 μ L) and then added to dried silica SiO₂ (100 mg) (Sample A), SBA-15 (100 mg) (Sample B) or TiO_x@SBA-15 (100 mg) (Sample C). The mixture was stirred at 150 °C for 6 hours. The faint-green solid was filtered and washed with refluxing chlorobenzene, toluene, MeCN, and with pentane and dried at 120 °C/10⁻³ mbar for 2 hours.

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