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Synthesis, characterization and HPLC-applications of novel phthalocyanine modified silica gel materials

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2(3)-Tetrakisalkenyloxy substituted phthalocyanines **3**–**6** are synthesized from the corresponding 1,2-dicyano-4-alkenyloxybenzenes **2a**–**c**. These phthalocyanines were hydrosilylated with trimethoxysilane to yield the phthalocyanines **7**–**10** which were reacted immediately with tetramethoxysilane (TMOS) as co-condensation agent or HPLC silica gel to obtain the new stationary phases **11**–**16** based on phthalocyanines. The phthalocyanines **3**–**10** and the corresponding stationary phases **11**–**16** were characterized by MS, UV/Vis, IR, EA and NMR spectroscopy. Additionally, the stationary phase **16** was measured by suspended state NMR spectroscopy. With the PcInCl stationary phase **13c**, scanning and transmission electron microscopic investigations were performed to obtain information about the morphology of the stationary phases. The modified HPLC silica gels **14**–**16** were tested successfully for the separation of two different aromatic test mixtures using methanol–water as eluent.

Introduction

Phthalocyanines (Pcs) and metallophthalocyanines (PcMs) have been investigated in detail for many years because of their wide range of applications, such as chemical sensors,[1–3] liquid crystals,[1–3] Langmuir–Blodgett films,[1–3] and others. It has been shown that substituted phthalocyanines are more soluble in common organic solvents than unsubstituted phthalocyanines.[1–3] Axially substituted metallophthalocyanines, *e.g.* indium phthalocyanines, show interesting nonlinear optical properties (*e.g.* optical limiting).[4,5] Tetrasubstituted phthalocyanines are obtained as a mixture of constitutional isomers in different proportions by tetramerization of monosubstituted phthalonitriles. Such constitutional isomers have been separated recently by chromatographic methods (MPLC, HPLC) using special modified silica gels.[6,7]

The immobilization of phthalocyanines on silica gel is an area of intense research, *e.g.* for their use as HPLC materials. The stationary phases can be prepared by surface coverage of silica gel[8,9] or by sol–gel processing to yield organic–inorganic hybrid materials. The properties of the products obtained by sol–gel polycondensation strongly depend on the reaction conditions such as concentration of the monomer, solvents and type of catalyst.[10] The modified silica gels presented here together with a mobile phase can be called "interphases".[11–13] The stationary phase consists of a main interaction centre (phthalocyanines as a π-electron system), a spacer (*n*-alkyl or *n*-alkyloxy chains which are connected to a solid phase) and a matrix (silica gel). A solvent increases the mobility of the organic ligands in these interphases by solvation and causes a higher interaction affinity. The spacer length determines the mobility of the macrocycle and therefore influences the availability of the reactive centre.

In general, HPLC is one of the most widespread analytical methods.[14] Therefore, investigations to find optimum stationary phases for successful HPLC separations are essential. One of the most conventionally used reversed phase materials is the C_{18} *n*-alkyl phase,[15] in which the hydrophobic interactions between the *n*-alkyl chains, solvated molecules and the organic solvent are responsible for the separation. Further reversed phase materials, *e.g.* modified with anthracene,[16] acridine[17] or fluorene,[12,18] have been described. For these aromatic phases, the most important separation effect is the π–π-interaction between the soluble aromatic analytes and the modified stationary phases.[19] Porphyrin or phthalocyanine systems have been used linked *via* sulfonic ester groups to the silica surface.[20,21]

We report here the synthesis of several 2(3)-tetrakisalkenyloxy substituted phthalocyanines **3**–**6** from the corresponding phthalonitriles **2a**–**c**, which are hydrosilylated at the terminal double bond with trimethoxysilane and then subsequently bound to the surface of HPLC silica gel or reacted with tetramethoxysilane (TMOS) as co-condensation agent to obtain new stationary phases **11**–**16**. Detailed information about the structure of these amorphous and insoluble materials is obtained by multinuclear cross-polarization magic-angle spinning (CP/MAS) solid-state NMR spectroscopy.[22,23] ^{13}C-CP/MAS NMR spectroscopy is used to establish the integrity of the organic moiety. The high resolution technique HR/MAS NMR is also a powerful technique to investigate the stationary phases under similar conditions as for chromatographic separations and allows a complete assignment of the proton signals. The structure of the T–Q matrices is characterized by ^{29}Si solid-state NMR spectroscopy studies.[11] In order to obtain information about the morphology of the materials analytical electron microscopy is employed. Additionally, the modified HPLC stationary phases **14**–**16** are tested with two different test mixtures.

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Results and discussion

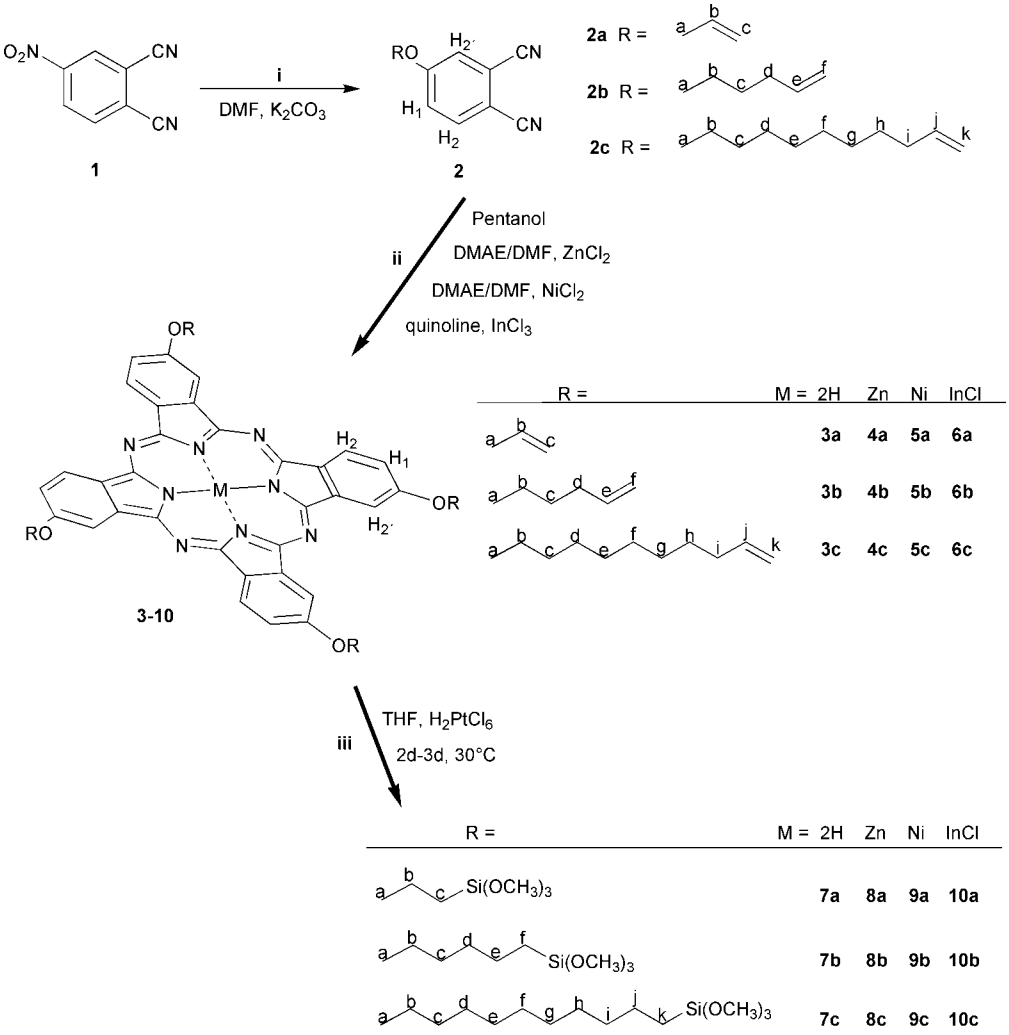
Preparation and characterization of the phthalonitriles (2a–c), the corresponding phthalocyanines (3a–6c; 7a–10c) and their stationary phases (11–16)

The phthalonitriles [4-(prop-2-enyloxy)- (**2a**), 4-(hex-5-enyloxy)- (**2b**), 4-(undec-10-enyloxy)-phthalonitrile (**2c**)], which are required for the preparation of the phthalocyanines **3a**–**6c**, were synthesized by a typical base catalyzed nucleophilic aromatic substitution with the commercially available 4-nitrophthalonitrile (**1**) and the corresponding alkenol[24] (Scheme 1).

Base catalyzed tetramerization of the phthalonitriles **2a**–**c**[2] with the appropriate metal salt yielded the required tetrakis-alkenyloxy substituted phthalocyanines **3a**–**6c** as a mixture of structural isomers[6,7] (Scheme 1). The phthalocyanines **3a**–**6c** were purified by column chromatography with $CHCl_3$ as eluent and recrystallized from dichloromethane–methanol to obtain green-blue to dark blue, analytically pure products which dissolved readily in common organic solvents. The phthalocyanines **3a**–**6c** were completely characterized by elemental analysis (EA), UV/Vis, IR, mass, ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy (see Experimental section).

The ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra of the tetrasubstituted phthalocyanines **3a**–**6c** are fully consistent with the expected structure and showed their typical signal pattern in the aromatic region.[1,2,6,7] All spectra exhibited the characteristic signals of the vinyl protons. The aromatic region, for example of **6a**, displays three typical signals at $\delta = 8.55$, 7.82, 7.35 ppm for H_2, $H_{2'}$ and H_1 (Scheme 1). The terminal alkenyl group in **6a** appears with its typical splitting pattern sequence at $\delta = 6.20$ ppm and 5.43 ppm for H_b and H_c. The remaining signal belongs to the H_a protons of the methyleneoxy group at $\delta = 4.62$ ppm. Also, all phthalocyanines **3a**–**6c** with longer alkyl chains showed nearly the same chemical shifts for these significant groups. The proton signals for the methylene groups of the phthalocyanines with the longer alkenyl chains appear in the aliphatic region as expected. The NH-hydrogens of the metal-free phthalocyanines **3a**–**c** appear shifted to high field to about δ −5.0 to −6.4 ppm. The $^{13}C\{^1H\}$-NMR spectra of **3a**–**6c** showed the expected seven signals of the macrocyclic carbons for tetrasubstituted phthalocyanines in the aromatic region. Besides the signals of the aromatic carbons, there are also two signals for the terminal double bond in this region. The chemical shifts of the aliphatic carbons appear as expected (see Experimental section).

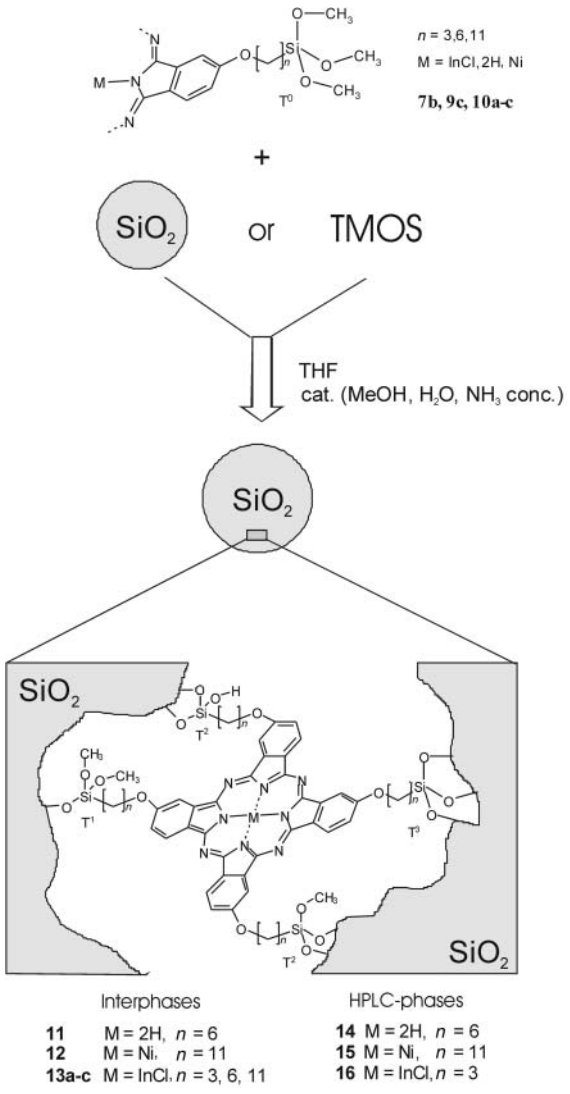
Hydrosilylation of the phthalocyanines **3a**–**6c** was carried out in dry THF with an excess of trimethoxysilane ($HSi(OCH_3)_3$) using hexachloroplatinic acid as catalyst under dry argon at room temperature for two days, to obtain the corresponding hydrosilylated phthalocyanines **7a**–**10c** (Scheme 1). To obtain the required derivatives **7a**–**10c** the excess of trimethoxysilane was evaporated under argon, and the residue was redissolved in dry THF. The terminal double bonds of the phthalocyanines **3a**–**6c** can then be hydrosilylated. In the case of the phthalocyanines **7a**, **7c**, **8a**–**c**, **9a** and **9b** it was impossible to redissolve them after evaporation in common organic solvents such as THF, and therefore spectroscopic data



Scheme 1 *Reagents*: i (a) prop-2-en-1-ol, (b) hex-5-en-1-ol, (c) undec-10-en-1-ol; ii (a) lithium pentanolate, (b) $ZnCl_2$, DMF–dimethylaminoethanol (DMAE), (c) $NiCl_2$, DMF–DMAE, (d) $InCl_3$, quinoline (only the C_s-isomer is shown); iii $HSi(OCH_3)_3$, H_2PtCl_6, THF.

are not available. The other hydrosilylated phthalocyanines **7b**, **9c**, and **10a–c** were purified over a short silica gel column under argon atmosphere. After spectroscopic characterization, they were reacted with tetramethoxysilane (TMOS) as co-condensation agent to yield **11–13**, or with HPLC silica gel to yield **14–16**. Some isomerization of the terminal double bond for the hydrosilylated products **7b**, **9c**, **10a–c** to the neighbouring carbon atom was also observed. The migration of the double bond was proven by ^{1}H- and ^{13}C{^{1}H}-NMR spectra after hydrosilylation and before sol–gel processing or surface modification. The rearrangement of the double bond is less than 6% for all phthalocyanines.

The sol–gel process with the hydrosilylated phthalocyanines **7b**, **9c** and **10a–c** was carried out in a mixture of THF, methanol, water, conc. NH_3 solution as catalyst and TMOS or HPLC silica gel (Scheme 2). The insoluble blue and greenish blue phases were subsequently characterized by solid state NMR spectroscopy. Surface information about the immobilized HPLC silica gel-containing phthalocyanine subunits is available from ^{29}Si-CP/MAS spectroscopy.[25–27] The ^{29}Si-CP/MAS spectra of the stationary phases show signals of various substructures of the T and Q silane units, which indicate an incomplete condensation process. The T groups of silicon atoms in the polysiloxane matrices contain protons at distances that are close enough to get an efficient Hartmann–Hahn match.[22,28] The T and Q groups are shifted to a higher field with increasing degree of condensation. The characteristic



Scheme 2 Preparation of the phthalocyanine substituted silica gels **11–16**, and their possible binding to the surface (T^1, T^2, T^3).

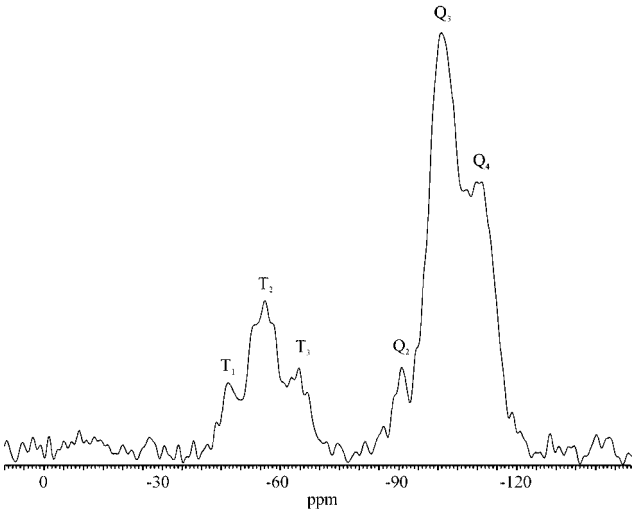
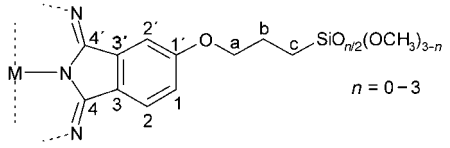


Fig. 1 ^{29}Si-CP/MAS spectrum of **16**.

NMR signals of unmodified silica gel are silanediol groups (Q^2), silanol groups (Q^3) and siloxane groups (Q^4), which appear at −92, −101 and −110 ppm.[13,25,27] The characteristic active silane group (T^0) of hydrosilylated phthalocyanines **7b**, **9c**, **10a–c** appears in the average chemical shift region between −48 and −68 ppm after surface preparation. The ratios between T^1, T^2 and T^3 exhibit information about the degree of binding of the phthalocyanines to the surface and therefore indicate the degree of the condensation reaction. In Fig. 1 the ^{29}Si spectrum of **16** is shown.

^{13}C-CP/MAS NMR spectroscopy[26] provides information about the structure of the silica bound phthalocyanines. The resonances in the solid state spectrum are broadened due to the attachment of the molecules to the silica gel. A solid state ^{13}C-CP/MAS NMR spectrum of **16** is shown in Fig. 2. The signals in the aromatic region between 161.4 ppm and 107.3 ppm resemble those of phthalocyanine **3a** excluding the two signals of the terminal double bond. The signal of the carbon C_a next to the ether oxygen atom appears at 69.9 ppm. The two resonances of the terminal double bond of the carbon atoms C_b and C_c are now shifted to high field. The carbon C_c which is directly bound to the silicon atom appears at 7.5 ppm and the



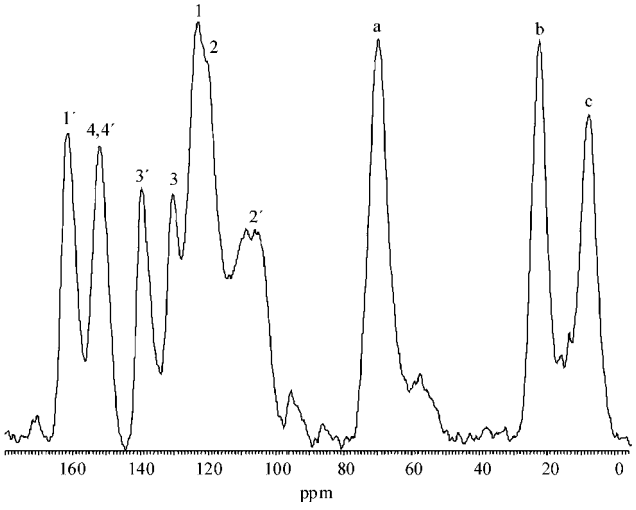


Fig. 2 ^{13}C-CP/MAS spectrum of **16**.

resonance at 22.0 ppm is due to the carbon C_b in the β-position to the silicon atom. For the other stationary phases **11**–**15**, the carbon atoms next to the silicon atom appear at about 13 ppm. In general, the structures of the stationary phases **11**–**16** correlate well with the structures of the phthalocyanines **7b**, **9c**, **10a**–**c** described above. In fact each carbon (even the quaternary aromatic ones) appears clearly in the ^{13}C-CP/MAS NMR spectra (*cf.* Fig. 2) and the sharpness of the alkyl and aromatic signals increases as the alkyl chain length increases. For more details about the ^{13}C-CP/MAS spectra of the stationary phases **11**–**16** see the Experimental section.

For stationary phase **16**, ^{1}H-MAS (Fig. 3a) and ^{1}H-HR/MAS NMR spectra (Fig. 3b)[29,30] were measured. HR/MAS NMR spectroscopy enables the acquisition of spectra with high resolution from insoluble substances. Increasing the sample mobility achieved by suspended or swollen states of the stationary phases, will eliminate residual dipole–dipole and susceptibility induced interactions of the protons and consequently the resolution of the spectra is improved. The technique of suspended state NMR, measured with different solvents, allows acquisition of the detected nuclei under similar conditions as for HPLC and gives additional information about the swelling properties of the sample.

Most stationary phases are based on silica which is not soluble in organic solvents. This leads to strong dipole–dipole interactions of the silanol protons and to broad signals in the NMR spectra, which even overlap significant signals of the ligands. By using the CPMG (Carr–Purcell–Meiboom–Gill) pulse sequence, which is applied to measure the T_2 relaxation time the broad silica signals are eliminated without suppressing considerable signals of other groups in the molecule. The comparison of a ^{1}H solid state NMR spectrum (Fig. 3a) with a ^{1}H-HR/MAS NMR spectrum (Fig. 3b) shows the essential advantages of this experiment. In the ^{1}H-HR/MAS spectrum of **16** (*cf.* Fig. 3b), all protons, aliphatic as well as aromatic, can be identified. The aromatic protons appear between 7.75 and 7.19 ppm. The two resonances at 3.87 and 3.58 ppm are due to the protons of the methyleneoxy group. The signals at 1.97 and 1.66 ppm are generated by the protons of the methylene group in the β-position and the signals at 0.90 and 0.73 ppm by the protons of the methylene group in the α-position to the silicon atom. This signal multiplicity has two different potential reasons. Firstly, different structural isomers of tetrasubstituted phthalocyanines[6,7] may be responsible, which explains the differences in the chemical shifts. Secondly, the more detailed and sharp pattern of the mobile T^1 groups in the ^{29}Si solid state NMR spectrum could be caused by the degree of condensation between the trimethoxysilyl groups and the hydroxy groups at the surface of the silica gel. But also both reasons could be responsible for the signal multiplicity.

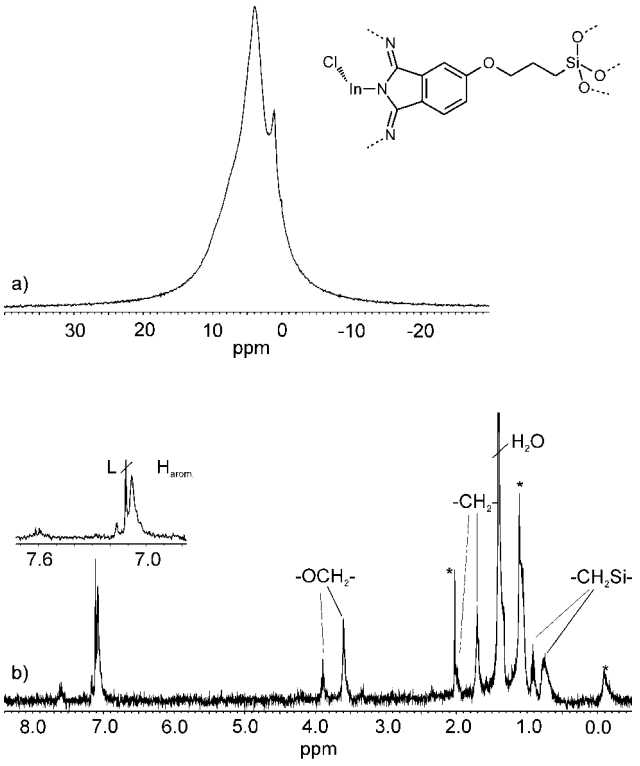


Fig. 3 (a) ^{1}H-MAS NMR spectrum and (b) ^{1}H-HR/MAS spectrum of **16** in $CDCl_3$ (* indicates signals of the rotor inlay).

UV/Vis[31] spectral data (in $CHCl_3$) of the soluble phthalocyanines **3a**–**6c** and the UV/Vis results of the stationary phases **11**–**16** are given in the Experimental section. The UV/Vis spectra of the insoluble materials were recorded as a suspension of the material in $CHCl_3$, which was prepared by ultrasonication. Spectra of **6a** and **16** are shown in Fig. 4. Compound **6a** shows the characteristic π–π*-transition (Q-band) at 699.5 nm and the B-band at 356 nm. In the case of the metal-free phthalocyanines **3a**–**c** all electronic states are non-degenerate due to reduced D_{2h} symmetry. Hence, the Q-band transition splits into two bands with similar intensities. The silica bound phthalocyanines **11**–**16** show different UV/Vis spectra compared to the precursor phthalocyanines **7b**, **9c**, **10a**–**c** (Fig. 4). The Q-bands of the modified stationary phases **11**–**16** appear very broad with a bathochromic shift of the maxima. The red-shift and broadening of the maxima occur due to aggregation of the phthalocyanines in the stationary phases and are also due to the binding of the phthalocyanines to the silica gel matrix.

In order to study the influence of stoichiometry on material properties, stationary phase **13c** was synthesized by self-condensation of **10c** and by co-condensation of **10c** with TMOS in a TMOS : phthalocyanine ratio 1 : 350. The obtained stationary phase was investigated by scanning (SEM) and energy filtering transmission electron microscopy (EFTEM). Scanning and transmission electron micrographs of **13c** are displayed in Fig. 5.

The self-condensation product of **13c** has a smooth surface and exhibits sharp edges and large faces which prove that the compound is hard and brittle. In contrast, the rough surface of the co-condensation product indicates a high porosity.

With respect to the grain size, SEM only probes the surface of the sample. To provide a view into the stationary phases, TEM samples were prepared by ultramicrotomy. EFTEM images clearly reveal the higher porosity of the mainly inorganic stationary phase, the pore size being in the order of 20–50 nm. An electron diffraction pattern is given as an overlay in Fig. 5. It shows that, despite the high aggregation

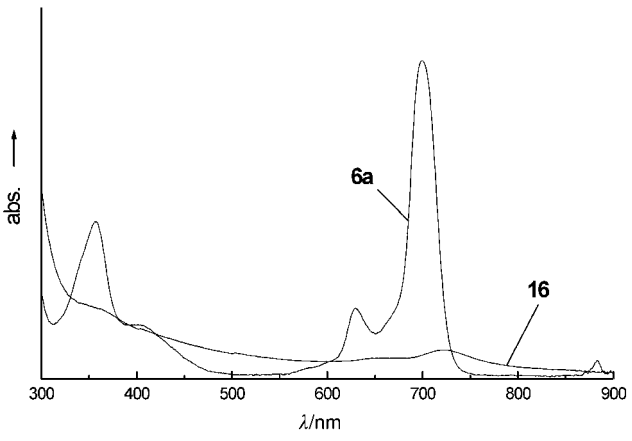


Fig. 4 UV/Vis absorption spectra ($CHCl_3$) of **6a** (dilute solution, $CHCl_3$) and **16** (suspension).

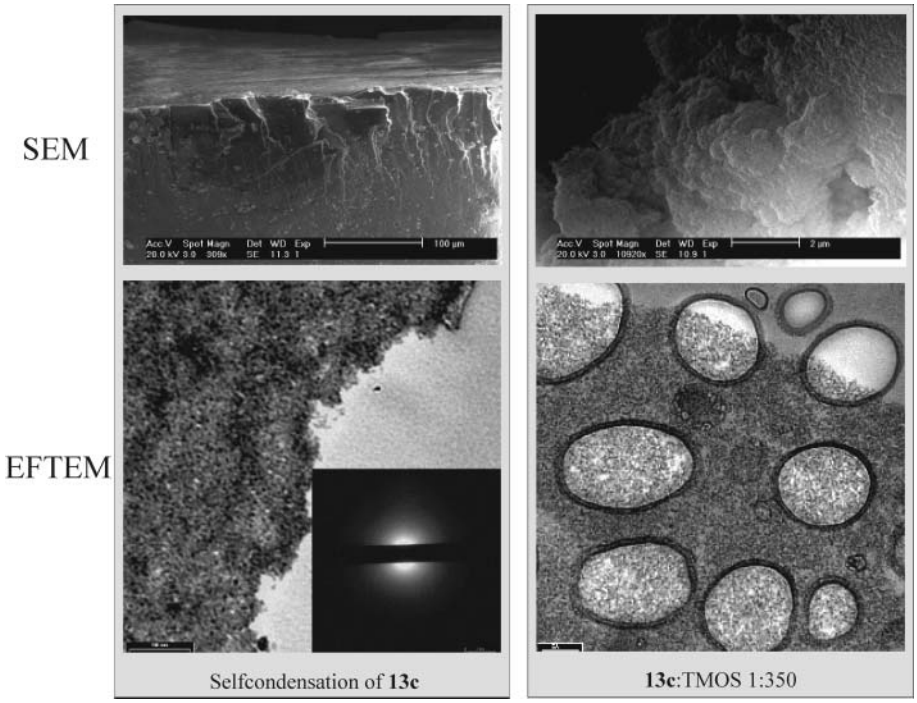


Fig. 5 Effect of stoichiometry on stationary phases, compared on the scale of electron microscopy. The self-condensation product appears more brittle and less porous. In the TEM micrograph of the co-condensation product the perforated carbon foil which serves as specimen support is also imaged. TEM specimens were prepared by ultramicrotomy.

tendency of phthalocyanines, crystalline domains are not observed. The stationary phases are amorphous solids in terms of electron diffraction.

HPLC applications of the surface modified silica gels 14–16

The stationary phases **14**–**16** obtained by surface modification of HPLC silica gel with the tetrasubstituted phthalocyanines **7b**, **9c** and **10a** were packed in commercially available steel columns. Before packing of the columns, the surface coverage of the modified stationary phases was determined by elemental analysis (EA) and thermal gravimetric analysis (TGA). The coverage determined by TGA measurements is normally lower than that measured by elemental analysis, because the combustion of the organic part is not totally complete. The surface coverage of the stationary phases determined by elemental analysis was 0.21 mmol g^{-1} for **14**, 0.05 mmol g^{-1} for **15** and 0.17 mmol g^{-1} for **16**.

The engaged HPLC silica gel possesses a particle size of 5 μm and a pore size of 200 Å and hence a surface area of 200 m^2 g^{-1}. A scanning electron micrograph of **15** is shown in Fig. 6.

The surface coverage of phase **15** is the lowest, but no difference in the retention times and separation effect for the aromatic test mixtures could be found in comparison to the phases **14** and **16**. The column efficiencies of the three phases **14**–**16** were estimated from the elution of toluene with a methanol–water mixture 1 : 1.[18] The column efficiency (N) was calculated from the retention time of the toluene peak (t_R) and the peak width at base line (t_W) according to eqn. (1).

$$N = 16(t_R/t_W)^2$$

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The efficiency of the Pc2H column **14** was 3300, for the PcNi column **15** 1600 and for the PcInCl column **16** 5100 theoretical plates, respectively. These column efficiencies are lower than those of commercially packed columns and may be caused by the lower surface coverage or by the missing end-capping of the free hydroxy groups of the silica gel. Another reason leading to weaker column efficiencies is the heterogeneity of the stationary phases. For example, some phthalocyanines are covalently linked at all four substituents, whereas others are linked to the silica in only one, two or three positions.

The packed columns **14**–**16** were tested with two different aromatic test mixtures. The chromatograms were recorded

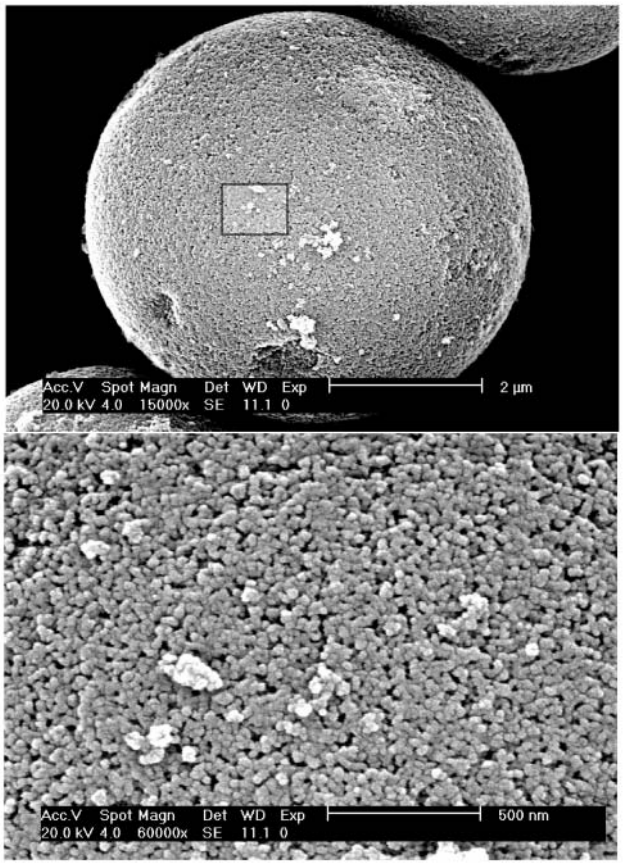

Fig. 6 Scanning electron micrograph of PcNi coated HPLC phase **15**. The enlarged view of the indicated area shows the porosity of the surface, the pore size being about 20 nm.

Table 1 Retention times t_R/min of benzene, naphthalene, fluorene, phenanthrene and anthracene

Stationary phase	Benzene	Naphthalene	Fluorene	Phenanthrene	Anthracene
InCl **4a**(T^n) $(Q^m)_y$	3.50	4.42	6.48	9.71	10.60
H_2 **4b**(T^n) $(Q^m)_y$	3.75	6.19	7.70	14.93	17.15
Ni **4c**(T^n) $(Q^m)_y$	3.57	4.47	6.90	10.93	11.75

with a UV detector at 254 nm, a flow rate of 1 ml min^{-1} and a mobile phase consisting of methanol–water at room temperature. The first test mixture consisted of five different aromatic compounds: benzene, naphthalene, fluorene, phenanthrene and anthracene. The retention data obtained from the three phthalocyanine columns **14**–**16** are summarized in Table 1 and an example for the PcInCl column **16** is given in Fig. 7. For every column **14**–**16** the five compounds of the test mixture are well separated and the elution order is the same. The best separation factors, calculated from the recorded chromatograms, were observed for benzene–naphthalene and naphthalene–fluorene. This leads to the assumption that the separation of smaller aromatic compounds is more effective. The main retention mechanism on these columns is based on the π–π interaction between the aromatic rings of the test mixture and the macrocycles of the phthalocyanines as described above. Hence π–π overlap for the separation of bulkier aromatic systems is more effective and therefore retention time increases.

As reported above, separation factors of small aromatic compounds are high on these columns. Therefore, the second test mixture consisted of *o*- and *p*-xylene, mesitylene and tri-*tert*-butylbenzene. The elution order of *o*- and *p*-xylene for the PcInCl column **16** differs from the two other columns **14** and **15**, but is the same as for the C_{18} columns. First, *p*-xylene is eluted, followed by *o*-xylene, mesitylene and tri-*tert*-butylbenzene (Table 2). This result is probably due to the axial substituent of the PcInCl system, which decreases the interaction between the aromatic compounds and the phthalocyanine systems. For the Pc2H **14** and PcNi **15** columns the elution order of the test mixture has changed. First, *o*-xylene is eluted followed by mesitylene, *p*-xylene and tri-*tert*-butylbenzene. The retention times of the columns **14**–**16** are summarized in Table 2. A chromatogram for the separation of the test mixture on the Pc2H column **14** is shown in Fig. 8. However, all columns **14**–**16** show good separation of the test compounds within short retention times.

Table 2 Retention times t_R/min of *o*-, *p*-xylene, mesitylene and tri-*tert*-butylbenzene

Stationary phase	*o*-Xylene	Mesitylene	*p*-Xylene	Tri-*tert*-butylbenzene
InCl **4a** (T^n) $(Q^m)_y$[a]	5.63	6.21	5.44	6.56
H_2 **4b** (T^n) $(Q^m)_y$	8.10	8.50	9.53	13.96
Ni **4c** (T^n) $(Q^m)_y$	5.10	5.50	5.61	7.62

[a]Mobile phase: 70% methanol–30% water.

Conclusion

The synthesis of 2(3)-tetrakisalkenyloxy substituted phthalocyanines **3a**–**6c** from the corresponding phthalonitriles **2a**–**c** has been carried out successfully. After hydrosilylation of the alkenyloxy substituted phthalocyanines and sol–gel processing with TMOS as co-condensation agent or surface modification of HPLC silica gel, a new class of functionalized stationary phases **11**–**16** was obtained. The precursor phthalocyanines were fully characterized by spectroscopic methods (EA, MS, IR, UV/Vis ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectroscopy). The hydrosilylated phthalocyanines were directly bound to the silica gel surface with a high degree of cross linkage, as shown by their ^{29}Si-CP/MAS NMR spectra. The organic part of the phthalocyanine modified stationary phases was characterized by ^{13}C-CP/MAS NMR spectroscopy and also for the first time with ^{1}H-HR/MAS NMR spectroscopy, and reveals the typical structure.

SEM and EFTEM investigations show that the stationary phases are porous solids. The properties of the materials strongly depend on the amount of co-condensation agent involved in their synthesis. Enlargement of the inorganic part of the compound **13c** leads to an enhanced porosity. Stationary phases are amorphous solids in terms of electron diffraction.

Separation of π-electron rich compounds with the phthalocyanine modified stationary phases **14**–**16** was tested. Two different aromatic test mixtures were used to demonstrate the separation ability of the columns. A clear separation was found for the first test mixture, containing five different aromatic compounds, the elution order is the same for all three phases. The highest separation factor was found between benzene and naphthalene. The three stationary phases **14**–**16** were tested with a second test mixture containing *o*- and *p*-xylene, mesitylene and tri-*tert*-butylbenzene. The separation of these smaller aromatic compounds is much more efficient. The PcIn phase **16** showed a different elution order for the separation of *o*- and *p*-xylene from phases **14** and **15**, which is attributed to the axial substituent present in the case of the indium phthalocyanine. The preparation of stationary phases based on phthalocyanines containing other metals, and showing a higher homogeneity of the materials in respect to the linked spacers, is currently in progress.

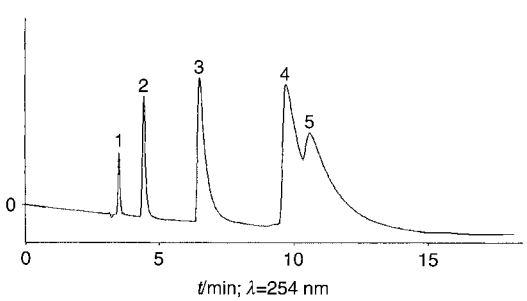

Fig. 7 Separation of five aromatic compounds with PcInCl **16**: 1 benzene, 2 naphthalene, 3 fluorene, 4 phenanthrene and 5 anthracene. *Conditions*: mobile phase 90% methanol–10% water; temperature 23 °C; flow rate 1 ml min^{-1}; wavelength 254 nm.

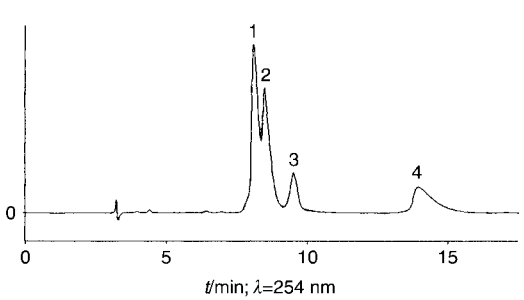

Fig. 8 Separation of *o*-, *p*-xylene, mesitylene and tri-*tert*-butylbenzene with **15**: 1 *o*-xylene, 2 mesitylene, 3 *p*-xylene and 4 tri-*tert*-butylbenzene. *Conditions*: mobile phase 80% methanol–20% water; temperature 23 °C; flow rate 1 ml min^{-1}; wavelength 254 nm.

Experimental

Equipment and measurements

The elemental analyses for C, H and N were carried out using a Carlo Erba Elemental Analyzer 1104 and 1106. FT-IR spectra were recorded on a Bruker IFS 48 spectrometer as KBr pellets. The UV/Vis-spectra were taken in $CHCl_3$ using a Perkin Elmer Lambda 2 spectrometer. EI mass spectra were obtained on a Finnigan ISQ 70 (200 °C, 70 eV), the FD spectra using a Varian MAT 711 A and reported in mass/charge (*m*/*z*). High resolution NMR spectra were measured with a Bruker 250 ARX spectrometer. The ^{1}H-NMR spectra were acquired at 250.1 MHz, $^{13}C\{^1H\}$ at 62.9 MHz, respectively. The chemical shifts in these spectra were measured relative to partially deuterated solvent ($CDCl_3$) and are recorded relative to TMS. The CP/MAS (cross polarization/magic angle spinning) solid state NMR spectra were recorded on a Bruker DSX 200 (^{29}Si) and a Bruker ASX 300 (^{13}C) multinuclear spectrometer equipped with wide bore magnets (field strength: 4.7 and 7.05 T). Magic angle spinning was applied at 3.5 kHz (^{29}Si) and 10 kHz (^{13}C). Frequencies for ^{29}Si were 39.8 MHz and for ^{13}C 75.5 MHz. The cross polarization time for ^{29}Si and ^{13}C was 2 ms. ^{1}H-HR/MAS NMR spectra were acquired on a Bruker ARX 400 spectrometer operating at 400.13 MHz for protons (field strength 9.4 T). A 4 mm HR-MAS probe was used together with a rotor containing an inner bottom spacer so that spinning stability was improved. Typically, data were acquired for 512 transients using an acquisition time of 1.52 s into 16384 data points. For the CPMG experiment, the total relaxation delay was 40 ms, and the spin rate 4500 Hz.

Scanning electron micrographs were recorded on a Philips XL 30 scanning electron microscope, detecting secondary electrons generated by a probe current of about 150 pA at 20 keV primary beam energy. Energy filtering transmission electron microscopic (EFTEM) investigations were performed on a LEO 912 Ω microscope equipped with Köhler illumination, a micro-dose focussing system, and a cooled high speed slow scan CCD (charge coupled device) camera. The EFTEM micrographs displayed were recorded with zero-loss electrons at 120 keV beam energy.

Chromatography

HPLC separations were carried out with a Beckmann (model 126) pump, a variable wavelength detector (Beckmann model 168) and an auto sampler (Beckmann model 507). The stationary phases were packed into 250 × 4 mm stainless steel tubes (Bischoff, Leonberg, Germany) in a high pressure slurry packing procedure on a Knauer Pneumatic HPLC Pump (Berlin, Germany). The tubes were packed with a suspension of propan-2-ol (25 ml) and modified silica gel under ultrasonication for 15 minutes and then packed with 500 bar pressure of methanol. The wavelength used for the UV detection was 245 nm and the temperature was maintained at 23 °C.

Electron microscopy

For SEM investigations, the sample powder was placed on a specimen stub covered with a conductive adhesive tab and subsequently provided with a sputtered 20 nm gold layer to avoid specimen charging.

Samples for transmission electron microscopy purposes were prepared by ultramicrotomy. The sample powder was embedded in Embed 812 epoxy resin which was allowed to infiltrate the sample grains for 24 hours and subsequently polymerized at 60 °C for 48 hours. For ultrathin sectioning, an 8800A Ultrotome III by LKB equipped with a diamond knife by Diatome was used. For mechanical support, the ultrathin sections were placed onto a perforated foil of amorphous carbon with a thickness of about 10 nm.

General synthesis of phthalonitriles 2a–c

4-Nitrophthalonitrile (**1**) and the corresponding alcohol were heated in 200 ml of dry DMF to 70 °C while stirring. Freshly ground potassium carbonate (30 g) was added in portions over 1 h and the heating continued for a further 60 h. The reaction mixture was allowed to cool to room temperature, filtered and the filtrate washed with dichloromethane (3 × 150 ml). The combined organic layers were washed with water (2 × 250 ml), brine (2 × 250 ml) and once again with water (2 × 250 ml). The organic extract was dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. The light brown-yellow crude product was dissolved in $CHCl_3$ and purified by column chromatography (SiO_2–toluene–$CHCl_3$) to yield a colourless pure product.

4-(Prop-2-enyloxy)phthalonitrile (2a). 16 g (0.092 mol) of **1** were reacted with 6 g (0.104 mol) of prop-2-en-1-ol, to yield 9.32 g (0.05 mol, 55%) of a white solid (mp: 91–93 °C): *m*/*z*: 184.0 (M^+); ν/cm^{-1}: 2232 (CN); ^{1}H δ[ppm]: 7.69 (d, 1H, H2), 7.25 (d, 1H, H2′), 7.18 (dd, 1H, H1), 6.07–5.91 (m, 1H, Hb), 5.45–5.34 (m, 2H, Hc), 4.62 (d, 2H, Ha); $^{13}C\{^1H\}$ δ[ppm]: 161.6 (C1′), 135.2 (C2), 131.0 (Cb), 119.8 (C2′), 119.6 (C1), 119.3 (Cc), 117.4 (C3′) 155.6 (C4′), 115.2 (C4), 107.4 (C3), 69.7 (Ca); found: C 71.79, H 4.46, N 15.11, $C_{11}H_8N_2O$ requires: C 71.73, H 4.38, N 15.21%.

4-(Hex-5-enyloxy)phthalonitrile (2b). 16 g (0.092 mol) **1** were reacted with 9 g (0.104 mol) of hex-5-en-1-ol, to yield 8.2 g (0.036 mol, 39.4%) of a pale yellow oil (mp: 4–6 °C): *m*/*z*: 226.1 (M^+); ν/cm^{-1}: 2232 (CN); ^{1}H δ[ppm]: 7.70 (d, 1H, H2), 7.23 (d, 1H, H2′), 7.16 (dd, 1H, H1), 5.84–5.71 (m, 1H, He), 5.05–4.95 (m, 2H, Hf), 4.03 (t, 2H, Ha), 2.01 (dd, 2H, Hd), 1.85–1.77 (m, 2H, Hb), 1.61–1.52 (m, 2H, Hc); $^{13}C\{^1H\}$ δ[ppm]: 162.1 (C1′), 138.0 (Ce), 135.1 (C2), 119.5 (C2′), 119.3 (C1), 117.3 (C3′), 115.7 (C4′), 115.3 (C4), 115.1 (Cf), 107.0 (C3), 69.1 (Ca), 33.1 (Cb), 28.1 (Cc), 25.0 (Cd); found: C 73.94, H 5.73, N 12.42, $C_{14}H_{14}N_2O$ requires: C 74.31, H 6.24, N 12.38%.

4-(Undec-10-enyloxy)phthalonitrile (2c). 16 g (0.092 mol) of **1** were reacted with 17.7 g (0.104 mol) of undec-10-en-1-ol, to yield 5.8 g (0.02 mol, 21.3%) as a white solid (mp: 37–39 °C): *m*/*z*: 296.1 (M^+); ν/cm^{-1} 2230 (CN); ^{1}H δ[ppm]: 7.67 (d, 1H, H2), 7.23 (d, 1H, H2′), 7.15 (dd, 1H, H1), 5.83–5.72 (m, 1H, Hj), 5.00–4.87 (m, 2H, Hk), 4.02 (t, 2H, Ha), 2.01 (dd, 2H, Hi), 1.82–1.73 (m, 2H, Hb), 1.45–1.28 (m, 12H, Hc–Hh); $^{13}C\{^1H\}$ δ[ppm]: 162.2 (C1′), 139.1 (Cj), 135.1 (C2), 119.5 (C2′), 119.3 (C1), 117.3(C3′), 115.7 (C4′), 115.3 (C4), 114.1 (Ck), 106.9 (C3), 69.3 (Ca), 33.7 (Cb), 29.5–28.7 (Cc–Ch), 25.7 (Ci); found: C 76.52, H 8.10, N 9.35, $C_{19}H_{24}N_2O$ requires: C 76.99, H 8.16, N 9.45%.

General procedure for the synthesis of phthalocyanines 3–6

1,2-Dicyano-4-alkyloxybenzene **2a**–**c** (0.02 mol) and the metal salt (0.006 mol of $NiCl_2$, $ZnCl_2$ or $InCl_3$) were dissolved in 50 ml of the absolute solvent (DMF–DMAE, pentanol or quinoline) with 5 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The mixture was heated under reflux for several hours (Table 3). After the reaction, the mixtures of **3**–**5** were diluted with methanol–water (90 : 10) and filtered. In the case of **6a**, the solvent was distilled. The residue was purified by chromatography over silica gel as shown in Table 3 and reprecipitated twice from dichloromethane in methanol–water.

2,9,16,23-Tetrakis(prop-2-enyloxy)phthalocyanine (3a). Dark green-blue powder: *m*/*z*: 738.3 (M^+); λ/nm: 703.5, 666.5, 645, 610, 386, 342; ν/cm^{-1}: 3290, 2939, 1612, 1485, 1502, 1481, 1423, 1364, 1325, 1223, 1097, 924; ^{1}H δ[ppm]: 7.74–6.20 (m, 12H, H2, H2′, H1), 6.17–6.05 (m, 4H, Hb), 5.57–5.38 (m, 8H, Hc), 3.32 (m,

Table 3 Experimental data for the preparation of the Pcs **3–6**

Pc	Reaction time/h	Solvent	Solvent for chromatography	Yield (%)
3a	1	Li pentanolate–pentanol	CH_2Cl_2–THF 20 : 1	41.6
3b	1	Li pentanolate–pentanol	CH_2Cl_2–THF 20 : 1	32.9
4a	16	DMF–DMAE 2 : 1	CH_2Cl_2–THF 20 : 1	36.6
4b	16	DMF–DMAE 2 : 1	CH_2Cl_2–THF 20 : 1	54.9
5b	16	DMF–DMAE 2 : 1	CH_2Cl_2–THF 20 : 1	67.6
5c	16	DMF–DMAE 2 : 1	CH_2Cl_2–THF 20 : 1	56.1
6a	10	Quinoline	CH_2Cl_2–THF 10 : 1	45.2

8H, Ha), −6.64 to −6.72 (m, 2H, N–H); $^{13}C\{^1H\}$ δ[ppm]: 159.1 (C1′), 145.7 (C4,C4′), 135.6 (C3′), 133.5 (Cb), 127.5 (C3), 121.8 (C2), 117.7 (Cc), 117.2 (C2′), 103.0 (C1), 68.6 (Ca); found: C 70.65, H 4.63, N 14.90, $C_{44}H_{34}N_8O_4$ requires: C 71.53, H 4.64, N 15.17%.

2,9,16,23-Tetrakis(hex-5-enyloxy)phthalocyanine (3b). Dark green-blue powder: *m*/*z*: 906.5 (M^+); λ/nm: 705, 668, 608, 388, 344; ν/cm^{-1}: 3296, 3074, 2939, 1612, 1502, 1485, 1429, 1389, 1323, 1257, 1097, 1009, 912, 833, 752; ^1H δ[ppm]: 7.84–7.18 (m, 4H, H2), 6.88–6.10 (m, 8H, H2′, H1), 6.07–5.93 (m, 4H, He), 5.26–5.13 (m, 8H, Hf), 3.84 (t, 8H, Ha), 2.56 (br, 8H, Hd), 1.91 (br, 8H, Hb), 1.73 (br, 8H, Hc), −5.36 to −5.84 (m, Hx); $^{13}C\{^1H\}$ δ[ppm]: 159.9 (C1′), 146.3 (C4,C4′), 138.7 (Ce), 136.2 (C3′), 127.8 (C3), 121.9 (C1), 117.0 (C2), 115.0 (Cf), 103.4 (C2′), 67.8 (Ca), 33.8 (Cb), 29.1 (Cc), 25.6 (Cd); found: C 73.13, H 6.55, N 11.87, $C_{56}H_{58}N_8O_4$ requires: C 74.15, H 6.44, N 12.35%.

2,9,16,23-Tetrakis(prop-2-enyloxy)phthalocyaninatozinc (4a). Dark blue powder: *m*/*z*: 801.9 (M^+); λ/nm^{-1}: 680, 613, 350; ν/cm^{-1}: 3074, 2866, 1710, 1647, 1609, 1489, 1423, 1238, 1096, 1049, 997, 824; ^1H δ[ppm]: 8.82–8.66 (m, 4H, H2), 8.39–8.25 (m, 4H, H-2′), 7.57–7.45 (m, 4H, H1), 6.58–6.43 (m, 4H, Hb), 5.87–5.53 (m, 8H, Hc), 5.10 (m, 8H, Ha); $^{13}C\{^1H\}$ δ[ppm]: 161.2 (C1′), 152.2 (C4,C4′), 141.1 (C3′), 135.2 (Cb), 132.5 (C3), 124.0 (C2), 118.4 (C2′), 117.5 (Cc), 106.2 (C1), 70.2 (Ca); found: C 64.29, H 4.34, N 13.38, $C_{44}H_{32}N_8O_4Zn$ requires: C 65.88, H 4.02, N 13.97.

2,9,16,23-Tetrakis(hex-5-enyloxy)phthalocyaninatozinc (4b). Dark blue powder: *m*/*z*: 968.4 (M^+); λ/nm^{-1}: 681.5, 614, 350; ν/cm^{-1}: 3074, 2924, 2856, 1641, 1609, 1491, 1387, 1240, 1094, 910, 852; ^1H δ[ppm]: 9.00–8.49 (m, 4H, H2), 8.56 (m, 4H, H2′), 7.59 (br, 4H, H1), 6.16–5.99 (m, 4H, He), 5.29–5.11 (m, 8H, Hf), 4.56 (br, 8H, Ha), 2.50–2.38 (br, 8H, Hd), 2.18 (br, 8H, Hb), 2.00–1.86 (m, 8H, Hc); $^{13}C\{^1H\}$ δ[ppm]: 160.7 (C1′), 151.7 (C4,C4′), 140.1 (C3′), 138.7 (Ce), 131.2 (C3), 122.9 (C2), 116.9 (C2′), 114.2 (Cf), 105.0 (C1), 68.2 (Ca), 33.7 (Cb), 29.2 (Cc), 25.7 (Cd); found: C 68.46, H 4.09, N 11.56, $C_{56}H_{56}N_8O_4Zn$ requires: C 69.11, H 5.82, N 11.56%.

2,9,16,23-Tetrakis(hex-5-enyloxy)phthalocyaninatonickel (5b). Blue-green powder: *m*/*z*: 962.2 (M^+); λ/nm^{-1}: 673.5, 623.5, 381, 328.5; ν/cm^{-1}: 3074, 2939, 2866, 1639, 1610, 1533, 1418, 1350, 1242, 1097, 962, 908; ^1H δ[ppm]: 7.14–6.09 (br, 12H, H2, H2′, H1), 5.94 (m, 4H, He), 5.07 (m, 8H, Hf), 3.47 (br, 8H, Ha), 2.18 (br, 8H, Hd), 1.78 (br, 8H, Hb), 1.63 (br, 8H, Hc); $^{13}C\{^1H\}$ δ[ppm]: 158.6 (C1′), 141.7 (C4,C4′), 138.6 (Ce), 135.8 (C3′), 127.7 (C3), 120.7 (C2), 116.3 (C2′), 114.8 (Cf), 101.7 (C1), 67.4 (Ca), 33.7 (Cb), 29.9 (Cc), 25.4 (Cd); found: C 69.32, H 5.81, N 11.57, $C_{56}H_{56}N_8O_4Ni$ requires: C 69.79, H 5.86, N 11.57%.

2,9,16,23-Tetrakis(undec-10-enyloxy)phthalocyaninatonickel (5c). Dark blue-green powder: *m*/*z*: 1242.7 (M^+); λ/nm^{-1}: 673, 622, 379, 362, 328; ν/cm^{-1}: 3074, 2924, 2853, 1612, 1533, 1485, 1486, 1420, 1352, 1244, 1126, 1096, 1076, 993, 908, 822, 750; ^1H δ[ppm]: 7.66–6.42 (br, H2, H2′, H1), 5.98–5.82 (m, 4H, Hj), 5.20–4.99 (m, 8H, Hk), 3.72 (br, 8H, Ha), 2.14 (br, Hi), 1.87 (br, Hb), 1.46 (br, Hc–Hh); $^{13}C\{^1H\}$ δ[ppm]: 159.0 (C1′), 141.7 (C4,C4′), 139.2 (Cj), 136.3 (C3′), 127.9 (C3), 120.9 (C1), 116.8 (C2), 114.3 (Ck), 101.9 (C2′), 67.8 (Ca), 33.9 (Cb), 29.9–29.1 (Cc–Ch), 26.3 (Ci); found: C 73.53, H 7.43, N 9.02, $C_{76}H_{96}N_8O_4Ni$ requires: C 73.36, H 7.78, N 9.01%.

2,9,16,23-Tetrakis(prop-2-enyloxy)phthalocyaninatoindium(III) chloride (6a). Green powder: *m*/*z*: 886.1 (M^+); λ/nm^{-1}: 699, 630, 402, 356; ν/cm^{-1}: 3076, 2914, 1606, 1485, 1450, 1363, 1240, 1228, 1118, 1047, 1024, 962, 825, 742; ^1H δ[ppm]: 8.65–8.46 (m, 4H, H2), 8.03–7.61 (m, 4H, H2′), 7.41–7.29 (m, 4H, H1), 6.33–6.13 (m, 4H, Hb), 5.71–5.15 (m, 8H, Hc), 4.87–4.37 (m, 8H, Ha); $^{13}C\{^1H\}$ δ[ppm]: 160.6 (C1′), 151.0 (C4,C4′), 139.0 (C3′), 132.9 (Cb), 129.7 (C3), 123.8 (C1), 119.1 (C2), 118.1 (Cc), 105.2 (C2′), 69.4 (Ca); found: C 58.81, H 3.58, N 12.28, $C_{44}H_{32}N_8O_4InCl$ requires: C 59.58, H 3.64, N 12.63%.

General hydrosilylation procedure for 7b, 9c, 10a–c

In a typical procedure, the phthalocyanines **3b**, **5c**, **6a–c** were reacted with an excess of trimethoxysilane and a catalytic amount of hexachloroplatinic acid (0.1 ml, 0.1 mol l^{-1} solution) in dry THF (60 ml) under argon. The reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue dissolved in THF (10 ml). The dark green/blue solutions were purified under argon on a short silica gel column with THF and then the solvent removed again under reduced pressure to yield the hydrosilylated phthalocyanines **7b**, **9c**, **10a–c**.

All phthalocyanines **7b**, **9c**, **10a–c** were reacted directly with the calcined HPLC silica gel or TMOS as co-condensation agent to obtain the modified stationary phase **11–16**.

General preparation of the stationary phases 11–13

80 mg of the phthalocyanines **7b**, **9c**, **10a–c** were dissolved in THF and 3 ml (0.02 mol) of TMOS was added. After stirring for 5 min at room temperature, 0.5 ml water, 1.5 ml methanol and 5 drops of a dilute NH_3 solution (as catalyst) were added. The reaction mixture was stirred for 16 h at 30 °C, filtered and the residue washed with ethanol, acetone, THF, chloroform and hexane. The stationary phases **11–13** were dried overnight at 50 °C.

Pc2H stationary phase (11). ^{13}C-CP/MAS δ[ppm]: 168.5, 159.5, 146.4, 128.1, 117.6, 67.7, 59.5, 51.1, 28.6, 25.1, 16.1; ^{29}Si-CP/MAS δ[ppm]: −51.8 (T^2), −62.4 (T^3), −91.3 (Q^2), −101.3 (Q^3), −109.3 (Q^4); ν/cm^{-1}: 3314, 2986, 1691, 1614, 1485, 1398, 1367, 1109, 951, 802.

PcNi stationary phase (12). ^{13}C-CP/MAS δ[ppm]: 163.8, 139.3, 128.5, 120.7, 106.9, 98.8, 68.3, 50.9, 29.5, 22.4, 13.4, 6.1; ^{29}Si-CP/MAS δ[ppm]: −38.5 (T^1), −52.9 (T^2), −62.4 (T^3), −90.7 (Q^2), −100.2 (Q^3), −109.1 (Q^4); ν/cm^{-1}: 3667, 1772, 1616, 1083, 943, 802.

PcInCl stationary phase (13a). ^{13}C-CP/MAS δ[ppm]: 160.9, 151.5, 138.7, 129.5, 123.0, 119.8, 105.3, 70.1, 22.3, 9.2; ^{29}Si-CP/MAS δ[ppm]: −54.7 (T^2), −63.6 (T^3), −90.9 (Q^2), −100.4 (Q^3), −109.3 (Q^4); ν/cm^{-1}: 3148, 1717, 1616, 1456, 1402, 1086, 943, 802.

PcInCl stationary phase (13b). ^{13}C-CP/MAS δ[ppm]: 161.1, 152.5, 139.9, 129.8, 123.1, 106.1, 68.4, 49.35, 28.8, 12.9; ^{29}Si-CP/MAS δ[ppm]: −47.6 (T^1), −54.1 (T^2), −64.1 (T^3), −91.7 (Q^2), −100.8 (Q^3), −109.4 (Q^4); ν/cm^{-1}: 3348, 2926, 2854, 1610, 1489, 1394, 1339, 1092, 914, 802.

PcInCl stationary phase (13c). ^{13}C-CP/MAS δ[ppm]: 168.7, 162.0, 152.6, 139.7, 129.6, 122.7, 105.9, 67.7, 50.6, 29.5, 25.0, 11.9; ^{29}Si-CP/MAS δ[ppm]: −54.9 (T^2), −66.1 (T^3), −100.8 (Q^3), −110.4 (Q^4); ν/cm^{-1}: 3404, 2928, 2856, 1616, 1506, 1489, 1387, 1367, 1092, 943, 804.

General preparation of the phthalocyanine modified HPLC-phases 14–16

HPLC silica gel (3 g) (200 Å, 5 μm with 4 μmol m^{-2} reactive surface hydroxy groups) was dried under vacuum at 140 °C for 4 h. After cooling to room temperature, the flask was aerated, treated with 30 ml of THF and a solution of **7b**, **9c** or **10a** in THF. After stirring for 15 minutes at room temperature, a mixture of 1 ml of water, 3 ml of methanol and 4 drops of conc. NH_3-solution (as catalyst) was added and the mixture was stirred for another 12 h under reflux. Afterwards the products were filtered on a sintered glass funnel (grade 4) and the residue was washed twice with THF, ethanol, $CHCl_3$ and hexane (50 ml). Finally the greenish blue modified stationary phase (**14–16**) was dried under vacuum at 60 °C for 6 h.

Pc2H HPLC phase (14). ^{13}C-CP/MAS δ[ppm]: 160.0 (C1′), 146.5 (C4,C4), 138.3 (C3′), 129.2 (C3), 122.6 (C1), 119.4 (C2), 103.9 (C2′), 67.9 (Ca), 26.2 (Cb–Ce), 12.7 (Cf); ^{29}Si-CP/MAS δ[ppm]: −46.9 (T^1), −55.5 (T^2), −63.8 (T^3), −90.6 (Q^2), −100.9 (Q^3), −108.9 (Q^4); λ/nm^{-1} (suspension): 735, 628, 425; ν/cm^{-1}: 3670, 2937, 1884, 1717, 1616, 1487, 1099, 804, 752.

PcNi HPLC phase (15). ^{13}C-CP/MAS δ[ppm]: 161.4 (C1′), 143.9 (C4,C4′), 137.7 (C3′), 130.8 (C3), 123.3 (C1), 118.8 (C2), 103.6 (C2′), 68.3 (Ca), 29.9 (Cb–Cj), 12.1 (Ck); ^{29}Si-CP/MAS δ[ppm]: −48.6 (T^1), −55.6 (T^2), −65.0 (T^3), −91.4 (Q^2), −101.0 (Q^3), −110.3 (Q^4); λ/nm^{-1} (suspension): 683, 631, 384; ν/cm^{-1}: 3676, 1772, 1616, 1084, 943, 804.

PcInCl HPLC phase (16). ^{13}C-CP/MAS δ[ppm]: 161.4 (C1′), 152.0 (C4,C4′), 139.6 (C3′), 130.4 (C3), 123.0 (C1), 120.3 (C2), 107.3 (C2′), 69.9 (Ca), 22.2 (Cb), 7.6 (Cc); ^{29}Si-CP/MAS δ[ppm]: −46.7 (T^1), −56.1 (T^2), −64.7 (T^3), −90.7 (Q^2), −100.9 (Q^3), −110.5 (Q^4); λ/nm^{-1} (suspension): 777, 642, 446, 378; ν/cm^{-1}: 3663, 2963, 1877, 1720, 1612, 1489, 1366, 1339, 1103, 804, 744.

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