Separation of 2(3),9(10),16(17),23(24)-Tetrasubstituted Phthalocyanines with Newly Developed HPLC Phases

Michael Sommerauer, Christine Rager, and Michael Hanack*

Contribution from the Lehrstuhl für Organische Chemie II, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received March 27, 1996[⊗]

Abstract: The synthesis of 2(3),9(10),16(17),23(24)-tetrasubstituted phthalocyanines from 1,2-dicyano-4-alkoxybenzenes or the corresponding isoindolines is reported. In each case, four isomers with D_{2h}, C_{4h}, C_{2v}, and C_s symmetry are obtained in the statistical expected yield. The separation of the C_{4h} and the D_{2h} isomers was achieved successfully for the first time from the other two isomers with newly developed HPLC phases based on $\pi-\pi$ interactions. In one case, phthalocyanine **12** could be separated into the isomers **12a**−**d** and characterized by UV/vis and ^{1}H-NMR spectroscopy. Due to line broadening at room temperature, T_1 and T_2 relaxation time measurements of two phthalocyanines (**3** and **12**) at different temperatures are carried out. Whether the broad peaks are due to aggregation or due to a short relaxation time is explained.

Introduction

Phthalocyanine and metallophthalocyanines have been investigated for many years in detail because of their wide application fields,[1,2] including use in chemical sensors,[1,2] liquid crystals,[1,2] Langmuir−Blodgett films,[1,2] nonlinear optics,[1,2] optical data storage,[1,2] and as carrier generation materials in near-IR.[1,2] Substituted derivatives can also be used for photodynamic cancer therapy and other processes driven by visible light.[1,2] Pure isomers may show interesting NLO properties, which cannot be investigated in the mixture of all four isomers. A decisive disadvantage of phthalocyanines and metal phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the pheripheral positions of the phthalocyanine framework.[3] Because of their lower degree of order in the solid state, tetrasubstituted phthalocyanines are more soluble than the corresponding octasubstituted ones. The synthesis of tetrasubstituted metallophthalocyanines and metal-free phthalocyanines substituted in the so-called 1(4),8(11), 15(18),22(25)- and 2(3),9(10),16(17),23(24)-positions (as shown in Figure 1) normally starts with a 1- or 2-substituted phthalodinitrile or the corresponding diiminoisoindolines with an appropriate metal salt in a suitable solvent.[1] By a statistical condensation reaction in all cases, a mixture of constitutional isomers of the symmetries given in Figure 1 is formed.

For the first time, we were able to separate these constitutional isomers by chromatographic methods (MPLC, HPLC) in the case of 1(4),8(11),15(18),22(25)-tetrakis[((2-ethylhexyl)oxy)-phthalocyaninato]nickel(II) (**1**). Separation was carried out on a commercially available nitrophenyl column, and the four isomers were completely characterized in terms of their symmetry by UV and ^{1}H-NMR spectroscopy.[4] Separation of these isomers by HPLC methods was possible, because the steric interaction of the peripheral substituents R = $OCH_2CH(C_2H_5)$-C_4H_9 in the 1(4),8(11),15(18),22(25)-position with each other and with the phthalocyanine core is comparatively strong. As a result of this, the planarity of the macrocycle is slightly disturbed.[4] This can be shown with the D_{2h} isomer of 1(4), 8(11),15(18),22(25)-tetrakis[((2-ethylhexyl)oxy)phthalocyani-

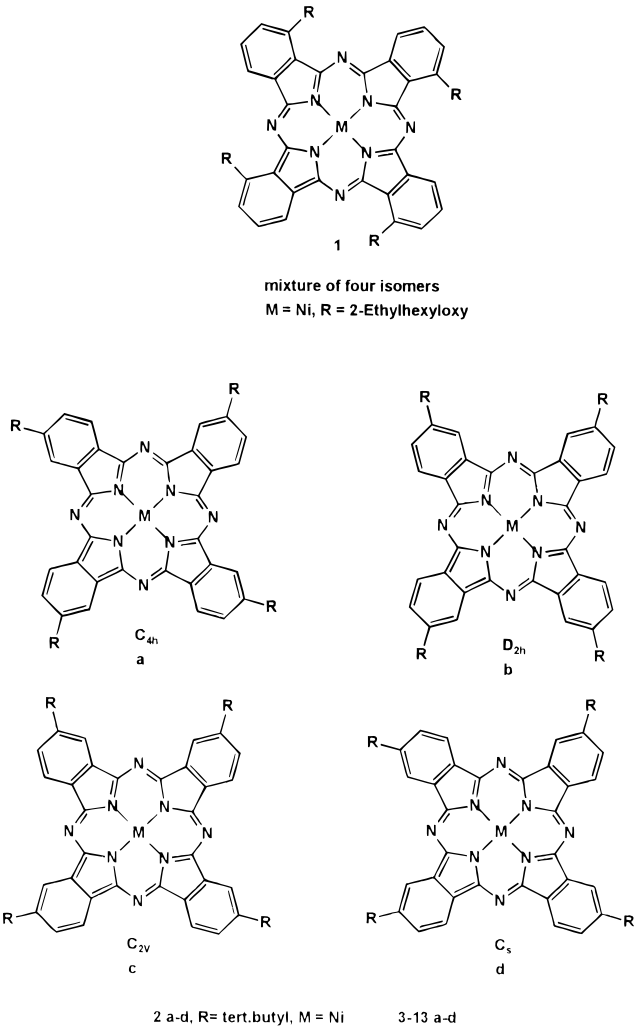


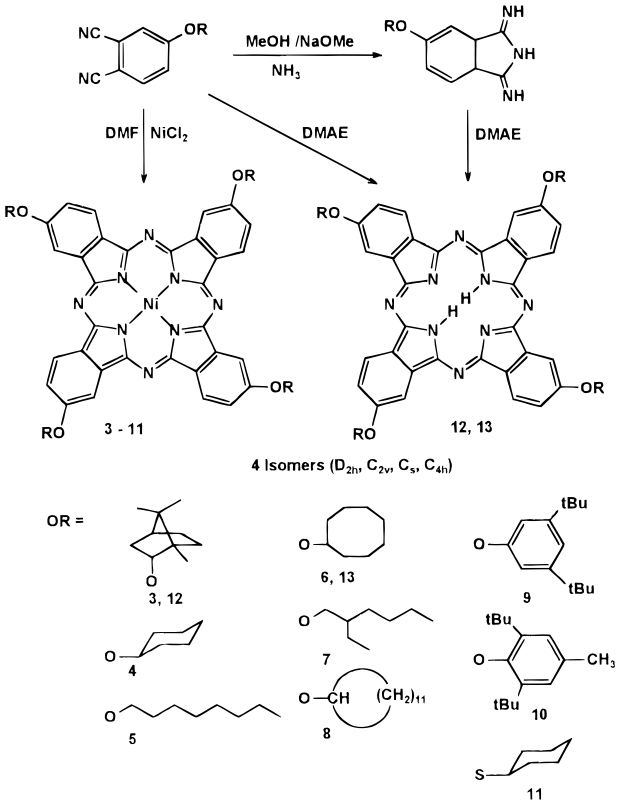
Figure 1. 1(4),8(11),15(18),22(25)-Tetrasubstituted phthalocyanines (top) and the four constitutional isomers of 2(3),9(10),16(17),23(24)-tetrasubstituted phthalocyanines.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) Hanack, M.; Lang, M. *Adv. Mater.* **1994**, *6*, 819.
(2) Leznoff, C. C. In *Phthalocyanines. Properties and Applications*, Vols. I−III; Lever, A. B. P., Ed.; VCH Publishers: New York, 1989 and 1993.
(3) Beck, A.; Mangold, K.-M.; Hanack, M. *Chem. Ber.* **1991**, *124*, 2315.
(4) Schmid, G.; Sommerauer, M.; Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1422.

S0002-7863(96)01009-8 CCC: $12.00

Scheme 1. Synthesis of 2(3),9(10),16(17),23(24)-Tetrasubstituted Phthalocyanines **3**−**13**



nato]nickel(II). The Q-band in its UV spectrum should be split, but this effect is not observable because the real symmetry is lower than D_{2h} while the macrocycle is nonplanar.[4]

Our first attempts to separate tetrasubstituted metallophthalocyanines using chromatographic methods were carried out with 2(3),9(10),16(17),23(24)-tetrasubstituted systems, tetrakis(*tert*-butylphthalocyaninato)nickel(II) (**2a**−**d**). However, only enrichment of the C_{2v} and C_s isomers **2c**,**d** using MPLC on a silica gel column was possible.[5]

Mixtures of different phthalocyanines obtained by a statistical condensation of two dinitriles have been completely separated by using phthalocyanined silica gels.[6] The authors report that it is not possible to separate constitutional isomers with these special phases.

In this paper, we now describe the separation of the four constitutional isomers of 2(3),9(10),16(17),23(24)-tetrasubstituted alkoxyphthalocyanines.

Results and Discussion

The investigated 2(3),9(10),16(17),23(24)-alkoxy-substituted phthalocyanines **3**−**13** and their synthesis are given in Scheme 1. For the preparation of the 4-alkoxyphthalodinitriles or the corresponding diiminoisoindolines, the appropriate 4-nitrophthalodinitriles are reacted with the corresponding alcohols, ROH, which are chosen to exhibit different steric hindrance according to R (R of different size).[7] From the 4-alkoxyphthalodinitriles and the corresponding alkoxy-substituted diiminoisoindolines, the nickel 2(3),9(10),16(17),23(24)-alkoxy-substituted phthalocyanines **3**−**11** and metal-free phthalocyanines **12** and **13** are obtained in yields between 11 and 80%.

All phthalocyanines **3**−**13**, prepared according to Scheme 1, form constitutional isomers as shown by NMR spectroscopy (vide infra), but it is not possible to separate them with commonly available HPLC columns or by recrystallization. Therefore, it is necessary to develop new HPLC phases to separate and characterize these isomers. Another question is whether the expected statistical distribution of 12.5% D_{2h}, 12.5% C_{4h}, 25% C_{2v}, and 50% C_s isomers occurs in all cases or if the nature of the side chains of the 2(3),9(10),16(17),23(24)-substituted phthalocyanines **3**−**13** changes this distribution.

The characterization of the 2(3),9(10),16(17),23(24)-alkoxy-substituted phthalocyanines **3**−**13** is carried out by ^{1}H-NMR spectroscopy.[4,5] This is possible without difficulty in the case of the recently described 1(4),8(11),15(18),22(25)-tetrakis[((2-ethylhexyl)oxy)phthalocyaninato]nickel(II) (**1**) compounds.[5] The 2(3),9(10),16(17),23(24)-substituted phthalocyanines **3**−**13**, however, exhibit very broad signals in the ^{1}H-NMR spectra, as known in general for many substituted phthalocyanines.[8] Broad signals in the ^{1}H-NMR spectra not only make characterization of the phthalocyanines impossible but also prevent the determination of the symmetry of these molecules.

There are two possible reasons for the broad signals of 2(3),9(10),16(17),23(24)-alkoxy-substituted phthalocyanines in the ^{1}H-NMR spectra. First, the T_1 or T_2 relaxation times of the phthalocyanines **3**−**13** are very short. This leads to broad signals in the recorded spectra (Heisenberg), because the transition energy is not well defined. Hence, the T_1 (inversion recovery technique) and T_2 relaxation time measurements (Carr−Purcell−Meiboom−Gill sequence) are carried out with the 2(3),9(10),16(17),23(24)-alkoxy-substituted phthalocyanines **3** and **12**. We may assume that the T_2 relaxation time is short and thus responsible for the broad signals at 300 K. There are strong dipolar interactions in and between rigid molecules. This leads to a quick defocusing of the magnetization after a NMR pulse, which means a short T_2 time.[9] The energy stays constant, and only the entropy increases. For the T_1 time, we have to discuss a process in which the transition energy of the molecule is released. Relaxation takes place only when the magnitude of the fluctuation fields is nearly the magnitude of the Larmor frequency. This depends on the correlation time τ_c. In the correlation time τ_c, all parameters (vibration, rotation, movement, etc.) of a molecule are united. According to theory, the correlation time τ_c of large and rigid molecules like phthalocyanines is long. The relaxation time T_1 has a minimum at a defined temperature for each molecule. At higher temperatures, the correlation time τ_c decreases. The spectral density of frequencies near the Larmor frequency becomes smaller, and the relaxation time T_1 increases. At lower temperatures, the correlation time τ_c increases, there are fewer magnetic fields in the magnitude of the Larmor frequency, and the relaxation time T_1 also increases.

The possible second reason for broad signals is aggregation of molecules in solution. This leads to a high-field shift of the signals in the ^{1}H-NMR spectra. The relaxation times T_1 and T_2 become shorter, because the correlation time τ_c increases and dipolar interactions are stronger, as in nonaggregated molecules.

To solve these problems, relaxation time measurements at different temperatures are carried out. For these measurements, a defined amount of 2(3),9(10),16(17),23(24)-tetrakis[((1*S*)-*endo*-(−)-bornyloxy)phthalocyaninato]nickel(II) (**3**) and 2(3),9(10),16(17),23(24)-tetrakis[((1*S*)-*endo*-(−)-bornyloxy)phthalocyanine (**12**) (mixture of the four isomers) in 0.5 mL of benzene-

(5) Hanack, M.; Meng, D.; Beck, A.; Sommerauer, M.; Subramanian, L. R. *J. Chem. Soc., Chem. Commun.* **1993**, 58.
(6) Leznoff, C. C.; McArthur, C. R.; Qin, Y. *Can. J. Chem.* **1993**, *71*, 1319.
(7) Leznoff, C. C.; Marcuccio, S. M.; Greenberg, S.; Lever, A. B. P.; Tomer, K. B. *Can. J. Chem.* **1985**, *63*, 623.
(8) Haisch, P.; Hanack, M. *Synthesis* **1995**, 1251.
(9) Derome, A. E. In *Modern NMR Technics for Chemical Research*; Baldwin, J. E., Magnus P. D., Eds.; Tetrahedron Organic Chemistry Series 6; Pergamon Press Ltd.: Oxford, 1987; pp 97−127.

Table 1. T_1 Measurement Data for 1 mg of $(BorO)_4PcNi$ (**3**): Not Aggregated, 250 MHz

	T_1 (ms)			
chem shift (ppm)	300 K	320 K	330 K	340 K
1.18−1.19	410	389	390	408
1.28−1.30	452	407	411	453
1.49−1.51	500	430	462	505
1.75−1.85	230	207	216	238
2.09	407	350	353	402
3.02	248	218	223	248
5.08	431	328	389	415
7.78−7.81	818	690	610	582
8.78−8.92	720	594	680	710
9.15−9.18	1550	1150	1070	1210
9.20−9.25	964	936	539	762

Table 2. T_1 Measurement Data for 1 mg of $(BorO)_4PcH_2$ (**12**): Not Aggregated, 250 MHz

	T_1 (ms)			
chem shift (ppm)	300 K	320 K	330 K	340 K
−1.8 ± 0.3	173	173	50	52
1.0−1.3	432	386	420	432
1.6	173	173	211	231
1.9	360	343	260	426
2.8	174	175	209	225
4.9	320	319	287	328
7.5−7.8	721	644	390	420
8.8−9.0	577	533	190	220
9.1−9.4	865	698	200	250

Table 3. T_2 Measurement Data for 1 mg of $(BorO)_4PcH_2$ (**12**): Not Aggregated, 250 MHz

	T_2 (ms)	
chem shift (ppm)	300 K	320 K
−1.8 ± 0.3	<10	<10
1.0−1.3	69	32
1.6	<10	<10
1.9	21	<10
2.8	<10	<10
4.9	<10	<10
7.5−7.8		31
8.8−9.0	33	13
9.1−9.4	33	22

Table 4. T_1 Measurement Data for 7 mg of $(BorO)_4PcH_2$ (**12**): Aggregated, 250 MHz

	T_1 (ms)				
chem shift (ppm)	300 K	310 K	320 K	330 K	340 K
−2.0					
1.0−1.3	398	353	375	372	396
1.6	385	360	395	405	440
1.9	340	309	330	348	373
2.8−3.0	205	185	189	197	209
5.0	236	230	242	257	278
7.4−7.6	300	297	314	336	361
8.4−8.5	137	120	120	130	156
8.8−9.2			103	166	182

d_6 are used. The phthalocyanines **3** and **12** are chosen because aggregation is less likely with these bulky side groups and the aggregates can be broken at higher temperatures. In Tables 1−5, the results of the T_1 and T_2 measurements of **3** and **12** between 300 and 340 K are shown.

As can be seen from Table 3 for **12**, the T_2 relaxation time is much shorter than the T_1 relaxation time. For **3**, T_2 relaxation times cannot be determined. Therefore, it is advantageous to increase the temperature, because then the T_2 relaxation time increases and the signals show less broadening, so that coupling constants below 2 Hz can be easily resolved. The determination

Table 5. T_1 Measurement Data for 3 mg of $(BorO)_4PcH_2$ (**12**): Aggregated, 250 MHz

	T_1 (ms)				
chem shift (ppm)	300 K	310 K	320 K	330 K	340 K
−2.0					
1.0−1.3	351	357	375	388	406
1.7	186	193	199	209	224
2.0	302	301	334	364	398
2.8−3.0	185	191	194	202	215
5.0	230	241	259	285	329
7.4−7.6	302	315	342	380	405
8.4−8.5	138	145	161	165	248
8.8−9.2	163	158	168	184	235

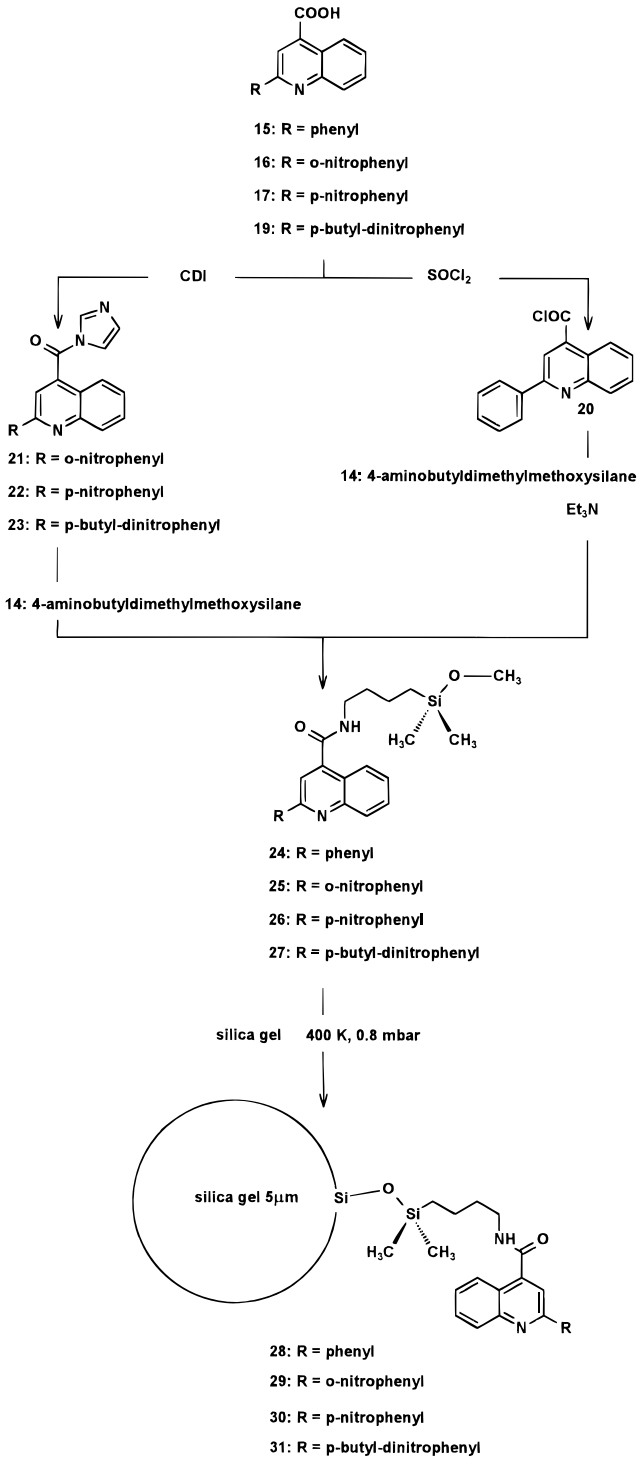
of these short T_2 times is not exact, because it is technically not possible to choose a shorter delay, as used between the 180° pulses (in pulse program cpmg, see Experimental Section). In most cases, the measured values cannot be fitted with an exponential function. Therefore, we can only conclude that the broad signals are due to the T_2 relaxation and the line width decreases with increasing temperature as assumed.

Both phthalocyanines **3** and **12** show a minimum of the T_1 time between 330 and 335 K without aggregation (1 mg of **3** or **12** in 0.5 mL of benzene, see Tables 1 and 2). At higher and lower temperatures, the relaxation time T_1 increases as predicted. If aggregation occurs, the T_1 time becomes shorter, but this depends on the concentration of the solution. At 340 K the T_1 time of 3 mg of **12** in 0.5 mL of benzene has the same value as that for the solution of 1 mg of **12** in 0.5 mL of benzene. But the solution of 3 mg of **12** in 0.5 mL of benzene shows a decreasing T_1 time and no minimum (Table 5). This is due to a commencement of aggregation at decreasing temperatures. The solution of 7 mg of **12** in 0.5 mL of benzene shows only a short T_1 time with a parabolic course (Table 4), because the concentration of phthalocyanine **12** is so high that the aggregates rearrange in a very short time, which is not detectable by NMR spectroscopy. Aggregation leads to a 0.2 ppm high-field shift of the aromatic signals of **12** and to additional broadening of the aromatic signals. In diluted solutions of **12**, the aggregates are not stable (Tables 1, 2, and 5). Well-resolved ^{1}H-NMR spectra at 330−340 K can be obtained from the nonaggregated form of **3** and **12**, as predicted by theory.

As mentioned, phthalocyanines **2**−**13** cannot be separated with commonly available HPLC phases. Only a nitrophenyl column (Macherey-Nagel ET250/8/4 5NO_2) shows a peak with two shoulders. The problem was solved by designing new HPLC phases based on $\pi-\pi$ interactions between the phthalocyanines and an aromatic part linked to silica gel to separate 2(3),9(10),16(17),23(24)-tetrasubstituted phthalocyanines. A monofunctionalized spacer, (4-aminobutyl)dimethylmethoxysilane (**14**), was used to synthesize HPLC phases based on silica gel. Activated carboxylic acids (imidazoles) **21**−**23** can easily be connected at this spacer (**14**) without dimerization or polymerization of the spacer molecule. Another advantage of monofunctional spacers is an easy purification of the connected products (**24**−**27**) by flash chromatography (Scheme 2). The part responsible for the $\pi-\pi$ interactions is the commericially available 2-phenylquinoline-4-carboxylic acid (**15**) and its derivatives **16**, **17**, and **19**. Scheme 2 shows the synthesis of the HPLC phases **28**−**31**.

Each phase (**28**−**31**) is identified by elemental analysis, thermogravimetry, and IR, ^{13}C-CP/MAS NMR, and ^{29}Si-CP/MAS spectroscopy. For the (*o*-nitrophenyl)quinoline phase **29**, a contact time variation with ^{29}Si-CP/MAS spectroscopy is carried out to determine the covering of this phase in comparison with the data from elemental analysis (EA) and thermogravimetry (TG).

Scheme 2. Synthesis of Phases **28**−**31**



The contact time variation gives information about all Si atoms which are on or near the silica gel surface (cross polarization). The used silica gel is totally porous, so that all Si atoms can be cross-polarized. The ^{29}Si-CP/MAS spectrum shows three signals: the signal at 13.4 ppm belongs to the Si atom (M) of the spacer, the one at −101 ppm (Q^3) to $SiO_{3/2}$(OH), and the one at −110 ppm (Q^4) to $SiO_{4/2}$. According to this measurement, the (*o*-nitrophenyl)quinoline phase **29** consists of 57.7 ± 4.5% Q^4, 32.3 ± 4.3% Q^3, and 10.0 ± 0.9% M groups. The covering can be calculated to 0.24 mmol/g (0.69 μmol/m^2) and is in good agreement with the results of the other methods, EA and TG.

With these phases, HPLC columns are packed and tested with 1,3,5-tri-*tert*-butylbenzene (1 μL of 10% solution of 1,3,5-tri-*tert*-butylbenzene in hexane) to obtain characteristic parameters for the comparison with other columns. Table 6 shows the characteristics of these columns.

The parameters for columns with good separation qualities are given in the literature[10] and are compared with the parameters of columns used in this report showing a good agreement (Table 6).

Separation of the phthalocyanines **3**−**13** is achieved analytically with phases **28**−**31** and on a preparative scale with phase **29**. As eluent, a mixture of either toluene or THF and hexane according to Table 7 is used.

Table 7 shows that the C_{4h} and D_{2h} isomers of **3a**,**b** (Figure 1) can be separated with phase **29** (Scheme 2) (comparable results were obtained with phase **30**). It is also possible to enrich the C_{2v} isomer of **3** to 58% and the C_s isomer to 86% after three repetitions with the same phase. The symmetries of the separated and enriched isomers of **3** are proved by UV/vis, ^{1}H-NMR, and ^{13}C-DEPT135-NMR spectroscopy. Generally, a separation can be achieved when the side chains or rings of the phthalocyanines contain six or more C atoms (**3**−**13**). The separation is better when bulky substituents in the periphery of the phthalocyanine ring (e.g., **3**, **12**, **6**, or **13**) are used.

As shown in Table 7, one possibility to achieve better separations of 2(3),9(10),16(17),23(24)-tetraalkoxy-substituted phthalocyanines is to vary the peripheral substituents of the macrocycle. Another possibility is to develop new HPLC phases. First, we improved the electronic situation of the phases by nitration of the phenyl ring of the phenylquinoline system **15** to obtain **16** and **17**. With both phases **29** and **30**, it is possible to separate the D_{2h} and C_{4h} isomers (Table 7 and Figure 2).

A further alteration of the phenylquinoline system **15** is carried out by introducing an additional nitro group and a butyl group. The second nitro group leads to a further increase of the $\pi-\pi$ interactions with the phthalocyanines. The more nitro groups added to the basic system **15**, the more the retention time of the compounds on the column was increased. An example is given in Table 8.

Therefore, the polarity of the eluent must be raised. The butyl group induces a steric effect. With this phase (**31**), for the first time it is possible to separate practically all four isomers of **12**, as shown in Figure 3.

The separation of the nickel phthalocyanines **3**−**11** using phase **31** is less successful: although a complete separation of the C_{2v} and C_s isomers of **12** is possible, the separation of the nickel phthalocyanines **3**−**11** shows only a shoulder between the C_{2v} and C_s isomers.

The aromatic region of the ^{1}H-NMR spectra recorded at 330−340 K of the phthalocyanines is used to determine the point group of the separated or enriched isomers. As discussed above, the elevated temperature is necessary to obtain well-resolved spectra. Each phthalocyanine contains four isoindoline units. The typical pattern is a doublet of doublets for H_a ($^3J_{Hab}$ = 9.2 Hz and $^4J_{Hab'}$ = 1.9 Hz) (Figure 4), a doublet for H_b ($^3J_{Hba}$ = 9.2 Hz), and a doublet for $H_{b'}$ ($^4J_{Hb'a}$ = 1.9 Hz). In the cases of the C_{4h} and D_{2h} isomers, all isoindoline units are equal, and the pattern of the three aromatic protons is shown only once. The C_{2v} isomer has two different units, leading to a double signal pattern, and in the C_s isomer, all four units are different (Table 9), and the pattern of the aromatic protons appears four times for this isomer. In the spectrum of the C_s isomer, signal overlap occurs, because of the low chemical shift difference of the different protons of the four units. The C_{4h} and D_{2h} isomers show nearly identical NMR spectra (Figure 4), and hence the

(10) Meyer, V. R. *Praxis der Hochleistungsflüssigkeitschromatographie*, 7th ed.; O. Salle Verlag, Verlag Sauerländer: Aarau, Frankfurt a. M., Salzburg, 1992; pp 96−121.

Table 6. Characteristics of the Prepared HPLC Columns

column	reduced separation height, H	reduced velocity, υ	flow resistance, ϕ	separation impedance, E
phenylquinoline (**28**)	5.1	3.0	1224	31 710
(*o*-nitrophenyl)quinoline (**29**)	4.3	3.9	1340	24 940
(*p*-nitrophenyl)quinoline (**30**)	4.1	4.1	1275	21 430
(dinitrobutylphenyl)quinoline (**31**)	3.3	2.25	1415	15 280
literature[9]	2−5	3−20	500−1000	2000−10^5

Table 7. Ratio of the Relative Retention Times α of the Phthalocyanines **3**−**13** with Phase **29**

Pc	eluent	$\alpha_{C_{4h}}/\alpha_{C_{2v},C_s}$	$\alpha_{C_{2v},C_s}/\alpha_{D_{2h}}$
3	THF/*n*-hexane 2:8	1.46	1.37
12	THF/cyclohexane 2:8	1.21	1.17
4	THF/*n*-hexane 2:8	1.26	1.12
5	toluene/*n*-hexane 7:3	1.45	1.25
6	THF/*n*-hexane 3:7	1.45	1.25
13	THF/*n*-hexane 2:8	1.50	1.23
7	THF/*n*-hexane 2:8	1.28	1.44
8	THF/*n*-hexane 2:8	1.41	1.46
9	THF/*n*-hexane 1:9	1.22	1.14
10	THF/*n*-hexane 1:9	1.30	1.30
11	toluene/*n*-hexane 7:3	1.20	1.11

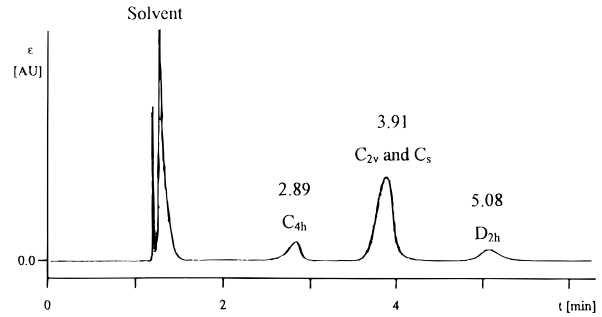


Figure 2. Separation of **3** with phase **29**. Flow, 1.5 mL/min; pressure, 75 bar; eluent, 20% THF and 80% *n*-hexane; peak detection, 330 nm.

Table 8. Relative Retention Times α of Phthalocyanine **7a**−**d** in the Used Columns **28**−**31** Using the Same Eluent, 60% Toluene and 40% *n*-Hexane

column	α of the C_{4h} isomer **7a**	α of the C_{2v} and C_s isomers **7c**,**d**	α of the D_{2h} isomer **7b**
phenylquinoline (**28**)	0.17	0.21	no separation
(*o*-nitrophenyl)quinoline (**29**)	0.63	0.92	1.20
(*p*-nitrophenyl)quinoline (**30**)	0.64	0.93	1.23
(dinitrobutylphenyl)quinoline (**31**)	3.70	4.95	5.90

UV/vis spectra are recorded in CH_2Cl_2 to determine the point groups. The spectrum with a split Q-band is assigned to the D_{2h} symmetry. The split Q-band is due to the symmetry reduction, which necessarily means that the phthalocyanines must be planar and the peripheral substituents do not hinder each other. The splitting of the Q-band is 17 nm. The C_{4h} isomer shows the smallest width of the Q-band at half-height, as predicted in theory. Table 9 shows the NMR, UV/vis, and IR data of the four isomers of $(BorO)_4PcNi$ (**3**). In the fingerprint region of the IR spectra of the separated and enriched isomers are differences depending on the symmetry of the isomers. The D_{2h} and C_{4h} isomers show fewer bands than the two other ones. Some IR bands of the enriched C_s isomer are broad in this region because vibration bands overlap. For the correct assignment of these bands, an analysis of the normal coordinates would be necessary. Figure 4 shows the ^{1}H-NMR and ^{13}C-DEPT135-NMR spectra of the pure isomers **3a**,**b**. The two protons b and b′ of **3b** show a low-field shift, because two alkoxy groups in the neighborhood decrease the electron density

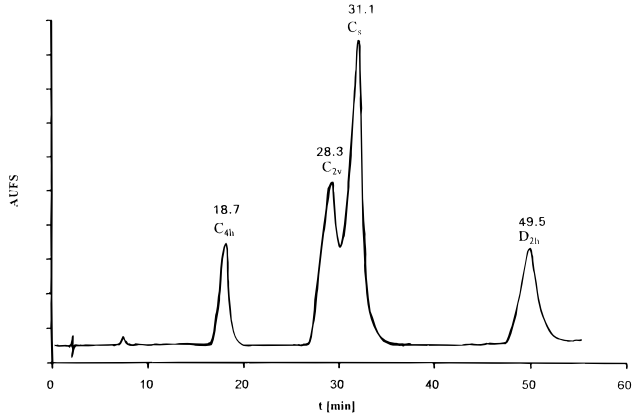


Figure 3. Separation of **12** with phase **31**. Flow, 1.5 mL/min; pressure, 78 bar; eluent, 5% THF and 95% *n*-hexane; peak detection, 330 nm.

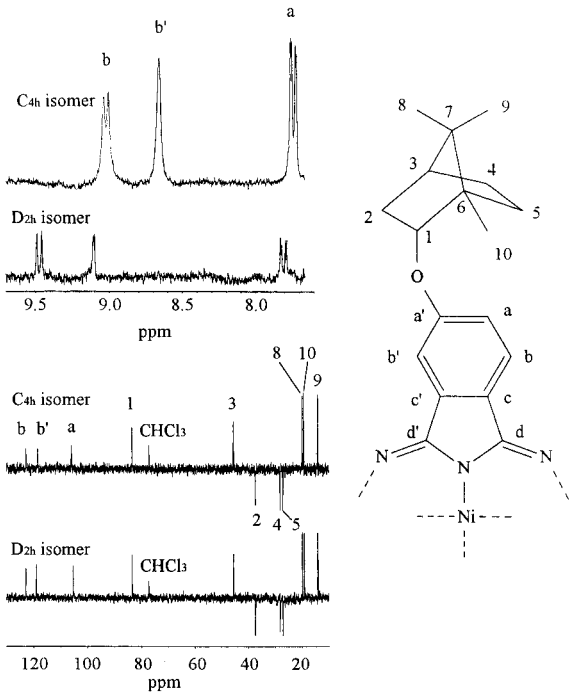


Figure 4. ^{1}H-NMR spectra (250.13 MHz, 330 K) of the aromatic region of the separated pure isomers **3a**,**b** in C_6D_6 and ^{13}C-DEPT-NMR spectra (62.89 MHz, 300 K) of **3a**,**b** in $CDCl_3$.

of the aromatic system more than only one group in the case of **3a**. For proton a, the influence of the aromatic system is less strong, and the influence of the alkoxy group is the same in both ortho positions; therefore, the shift difference is nearly zero between **3a** and **3b** (Figure 4).

Table 10 shows the comparable data for the metal-free phthalocyanine **12**. With these data, as explained above, the point groups are unequivocally determined. Table 10 and Figure 5 also show that, although the C_{2v} (**12c**) and C_s isomers (**12d**) are not separated to the baseline (Figure 3), pure samples of the C_{2v} and C_s isomers can be obtained (Figure 5).

Because all UV/vis spectra of the isomers show a split Q-band, the assignment of the D_{2h} and C_{4h} isomers is done by

Table 9. Spectroscopic Data for the Separated and Enriched Isomers of $(BorO)_4PcNi$ **(3)** (Assignment According to Figure 4)

	isomers			
	C_{4h} (**3a**)	C_{2v} (**3c**, 58% from integral $H_{b'}$)	C_s (**3d**, 86% from integral $H_{b'}$)	D_{2h} (**3b**)
^{1}H-NMR (C_6D_6, 250 MHz, 330 K, aromatic region only) 340 K (ppm)	H_a: 7.75, dd, $J = 9.2$, 1.9 Hz $H_{b'}$: 8.71 br H_b: 9.13−9.33, 6d, $J = 9.2$ Hz	H_a: 7.70−7.82, 6dd, $J = 9.2$, 1.9 Hz $H_{b'}$: 8.96 br, 8.82, 8.84, 8.87, 8.97 from C_s, $J = 1.9$ Hz H_b: 9.45, d, $J = 9.2$ Hz	H_a: 7.69−7.82, 6dd, $J = 9.2$, 1.9 Hz $H_{b'}$: 8.82, 8.84, 8.87, 8.97, d, $J = 1.9$ Hz, 8.96 br from C_{2v} H_b: 9.13−9.33, 6d, $J = 9.2$ Hz	H_a: 7.81, dd, $J = 9.2$, 1.9 Hz $H_{b'}$: 9.08, d, $J = 1.9$ Hz H_b: 9.45, d, $J = 9.2$ Hz
DEPT135 (C_6D_6/CS_2, 62.89 MHz, 300 K) (−, negative intensity; sp, split signals) (ppm)	14.45, 19.74, 20.26, 27.54−, 28.67−, 37.71−, 45.90, 83.83, 106.28, 118.74, 123.07	14.67, 19.79, 20.38, 27.92−, 28.94−, 37.86− (sp), 46.26, 84.11 (sp), 106.51 (sp), 119.47 and 119.28, 123.50 (sp)	14.71, 19.68 (sp), 20.40, 27.94−, 28.97−, 37.86− (sp), 46.28, 84.08 (sp), 106.55 (sp), 119.28 and 119.39 (sp), 123.34 and 123.50 (br)	14.51, 19.52, 20.24, 27.55−, 28.63−, 37.75−, 45.91, 83.90, 105.76, 119.35, 123.18
UV/vis (CH_2Cl_2) (nm)	676.0, 609.3, 385.2, 328.0, 307.6	677.5, 609.9, 385.2, 327.8, 305.2	677.5, 609.9, 385.2, 327.8, 305.2	685.3, 668.3, 608.3, 388.9, 328.2, 302.9
width of the Q-band at half-height (nm)	22.1	25.4	25.4	35.6
IR data (cm^{-1})	2951 (s), 2926 (s), 2872 (m), 1612 (s), 1533 (w), 1497 (w), 1470 (s), 1418 (m), 1388 (w), 1354 (m), 1271 (m), 1244 (s), 1121 (s), 1097 (s), 1067 (s), 1024 (m), 993 (m), 958 (w), 871 (w), 852 (w), 817 (w), 808 (w), 750 (m), 736 (w), 644 (w)	2951 (s), 2872 (m), 1612 (s), 1573 (w), 1531 (w), 1510 (w), 1477 (s), 1416 (m), 1391 (w), 1365 (w), 1352 (w), 1328 (w), 1304 (w), 1261 (m), 1242 (s), 1182 (w), 1164 (w), 1117 (s), 1094 (s), 1065 (s), 1051 (s), 1022 (s), 993 (m), 957 (w), 869 (w), 852 (w), 806 (s), 750 (m), 649 (w)	2963 (m), 2871 (w), 1612 (m, broad), 1571 (w), 1479 (m, broad), 1452 (w), 1416 (m), 1391 (w), 1365 (w), 1354 (w), 1330 (w), 1303 (w), 1261 (s), 1245 (w), 1096 (s), 1067 (s), 1053 (s), 1022 (s), 958 (w), 868 (m), 802 (s), 750 (m), 700 (w, broad)	2955 (s), 2930 (s), 2872 (m), 1614 (s), 1533 (w), 1483 (s), 1427 (w), 1406 (m), 1388 (w), 1354 (w), 1261 (s), 1242 (s), 1128 (w), 1092 (s), 1061 (s), 1022 (s), 964 (w), 854 (w), 802 (s), 750 (m), 678 (w)

Table 10. Spectroscopic Data for the Separated Isomers of $(BorO)_4PcH_2$ **(12)** (Assignment According to Figure 4)

	isomers			
	C_{4h} (**12a**)	C_{2v} (**12c**)	C_s (**12d**)	D_{2h} (**12b**)
^{1}H-NMR (C_6D_6, 250 MHz, 330 K, aromatic region only) (ppm)	H_a: 7.86, dd, $J = 8.4$, 1.9 Hz $H_{b'}$: 9.31, d, $J = 1.9$ Hz H_b: 9.64, d, $J = 8.4$ Hz	H_a: 7.82−7.9 $H_{b'}$: 9.3, 9.7, 2d, $J = 1.9$ Hz H_b: 9.68, dd, $J = 8.4$ Hz	H_a: 7.83−7.9 $H_{b'}$: 9.33, 9.35, 2d, $J = 1.9$ Hz H_b: 9.66, 9.65, 9.67, 3d, $J = 8.4$ Hz	H_a: 7.85, dd, $J = 8.4$, 1.9 Hz $H_{b'}$: 9.24, d, $J = 1.9$ Hz H_b: 9.61, d, $J = 8.4$ Hz
UV/vis (benzene) (nm)	707.2, 670.1, 650.8, 607.7, 395.0 sh, 352.5	706.7, 672.1, 646.3, 610.8, 398.1, 345.1, 290.5	706.9, 672.1, 646.3, 611.4, 397.9, 345.3, 290.6	711.0, 670.3, 641.3, 608.6, 390.0, 348.5
width of the *Q*-band at half-height (nm)	53.7	54.4	54.7	56.7
IR data (cm^{-1})	3296 (w), 3028 (m), 2953 (s), 1612 (m), 1502 (m), 1470 (m), 1391 (m), 1365 (w), 1346 (w), 1323 (w), 1259 (m), 1242 (m), 1215 (w), 1115 (s), 1097 (m), 1055 (m), 1022 (m), 939 (w), 871 (w), 846 (w), 746 (w), 612 (m)	3296 (m), 3064 (w), 2953 (s), 2877 (m), 1612 (s), 1500 (w), 1477 (s), 1452 (w), 1427 (w), 1391 (m), 1366 (w), 1344 (w), 1321 (m), 1259 (s), 1163 (w), 1115 (s), 1097 (s), 1072 (s), 1053 (s), 1014 (s), 939 (w), 873 (w), 854 (w), 808 (m), 750 (m)	3294 (w), 3064 (w), 2953 (s), 2873 (m), 1614 (s), 1500 (w), 1477 (s), 1454 (w), 1427 (w), 1391 (m), 1365 (w), 1344 (w), 1323 (m), 1259 (s), 1242 (s), 1163 (w), 1114 (s), 1097 (s), 1072 (s), 1053 (s), 1015 (s), 939 (w), 871 (w), 854 (w), 808 (m), 748 (m), 717 (w)	3294 (w), 2953 (s), 2926 (s), 2870 (m), 2854 (m), 1612 (s), 1479 (s), 1452 (m), 1427 (w), 1390 (w), 1365 (w), 1326 (w), 1261 (s), 1240 (s), 1164 (m), 1115 (s), 1097 (s), 1055 (s), 1030 (s), 937 (w), 804 (m), 743 (m)

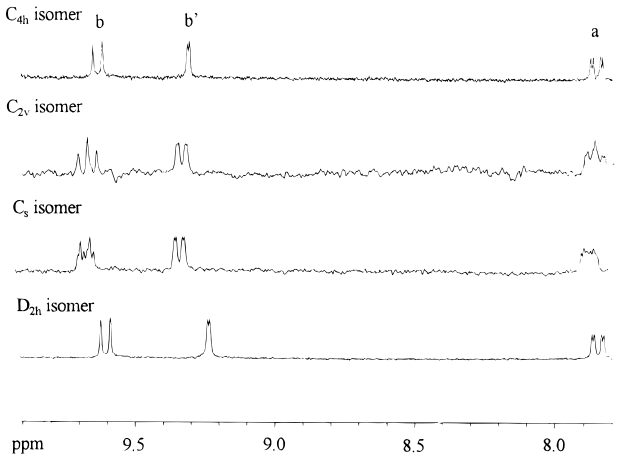


Figure 5. ^{1}H-NMR spectra (250.13 MHz, 330 K) of the aromatic region of the separated pure isomers **12a**−**d** in C_6D_6.

analogy to the corresponding nickel phthalocyanine **3**. Another link for the right assignment is the small Q-band of the C_{4h} isomer **12a**. For all investigated phthalocyanines **3**−**13**, we find the same distribution of the four isomers (by NMR spectroscopy): 12.5% C_{4h}, 25% C_{2v}, 50% C_s, and 12.5% D_{2h} isomer (Table 7). The peak areas in the HPLC chromatograms of the phthalocyanines **3**−**13**, detected with UV light at 330 nm, are valid, because all four isomers have the same extinction coefficient at this wavelength. Normally, the C_{2v} and the C_s isomers **3**−**11** and **13** are not separated completely from each other, but the peak area of both isomers (C_{2v} and C_s) in the chromatograms has, in each case, 75% accumulation. The aromatic regions in the ^{1}H-NMR spectra show always a pattern which is due to 25% C_{2v} and 50% C_s isomer.

Conclusion

In conclusion, we have shown that, by developing new HPLC phases **28**−**31**, which consist of π-acceptor molecules linked by a spacer (**14**) to the silicon surface, it is possible for the first time to separate or enrich the four constitutional isomers of 2(3),9(10),16(17),23(24)-tetrasubstituted alkoxyphthalocyanines **3**−**13** using a comparatively large alkoxy group (e.g., bornyloxy). The determination of the symmetry of the four isomers is carried out by a combination of ^{1}H-NMR, ^{13}C-DEPT-NMR, IR, and UV/vis spectroscopy, as we have achieved earlier with 1(4),8(11),15(18),22(25)-tetrasubstituted alkoxyphthalocyanines (e.g., **1**). The best conditions for ^{1}H-NMR measurements of **3** and **12** are determined by investigation of T_1 and T_2 relaxation times, depending on temperature and concentration.

Table 11. Experimental Data for the Preparation of the Nickel Phthalocyanines **3**−**6** and **8**−**11**

R_4PcNi	reaction time (h)	solvent	solvent for chromatograhy	yield (%)
(1S)-*endo*-(−)-bornyloxy (**3**)	120	DMF	$CHCl_3$	11.4
cyclohexyloxy (**4**)	60	DMF	Et_2O	49.8
octyloxy (**5**)	24	DMAE	$CHCl_3$/*n*-hex 1:1	48.2
cyclooctyloxy (**6**)	22	DMAE	toluene	48.8
cyclododecyloxy (**8**)	48	DMF	toluene	19.1
(3,5-di-*tert*-butylphenyl)-oxy (**9**)	22	DMF	toluene	79.7
(2,6-di-*tert*-butyl-4-methylphenyloxy (**10**)	66	DMF	toluene	55.3
cyclohexylthio (**11**)	72	DMF	$CHCl_3$	11.0

Experimental Section

General. All reactions were performed under dry nitrogen, and all solvents were dried according to standard methods. Commercially available reagents were used as purchased. The 4-substituted 1,2-dicyanobenzenes were synthesized according to reported procedures.[7,11] NMR spectra were recorded on Bruker AMX 400, ASX 300, or ARX 250, IR spectra on a Bruker IFS 48, mass spectra on a Varian MAT 711, and UV/vis spectra on Shimadzu UV-365 and UV-3102 PC spectrometers. Elemental analysis were carried out using a Carlo Erba elemental analyzer 1106 and thermogravimetry on a Netsch STA 409 apparatus. HPLC were conducted using Beckmann System Gold (Autosampler 507, programmable solvent module 126 and diode array detector module 168) and Kronlab systems (Mastercron 4 high-performance pump, Dynamax absorbance detector module UV-1, and Gilson fraction collector Model 201). Melting points were taken on a Gallenkamp melting point apparatus and were uncorrected.

The T_1 and T_2 measurements were carried out on a Bruker ARX 250. Acquisition and processing of the data were done with the software of Bruker UXNMR 941002.2 and XWINNMR 1.1. For each T_1 measurement, the inversion recovery technique is used (pulse program, Bruker t1ir ARX version). The relaxation delay is 5 s, and the delay between the 180° and 90° pulses is incremented with 40 ms and 64 increments. For each T_2 measurement, the Carr−Purcell−Meiboom−Gill sequence is used (pulse program, Bruker cpmg ARX version). The relaxation delay is 5 s, and the delay between the 180° pulses (fixed echo time) is 2 ms. The length of the 180° pulse train is incremented with 10 ms and 64 increments. All relaxation time measurements were carried out in benzene-d_6 without degassing the solution. A degassed (nitrogen) sample of **3** shows the same relaxation times as a nondegassed solution.

The separation of the isomers of **3** and **12** was carried out by preparative HPLC. Portions of 10 mg of phthalocyanine in 10 mL of eluent were given on the preparative column (250 mm × 16 mm with a precolumn, 30 mm × 16 mm). The separation was repeated eight times to get enough pure isomers for ^{13}C-NMR spectroscopy. The samples of pure or enriched isomers were collected with a fraction collector (see above). The samples were evaporated to dryness and washed with methanol to remove impurities of the used solvents.

For ^{1}H-NMR spectroscopy, 1 mg of each sample was dissolved in $CDCl_3$ and measured at high temperature (330−340 K). For ^{13}C-DEPT-NMR spectroscopy, 4 mg of each sample was dissolved in $CDCl_3/CS_2$ (3:1) and measured at 300 K.

General Procedure for the Synthesis of Phthalocyanines 3−11. 1,2-Dicyano-4-alkoxybenzene (2 mmol) and nickel chloride (64.95 mg, 0.5 mmol) were dissolved in 5 mL of absolute solvent (DMF or DMAE). This mixture was heated under reflux for several hours (Table 11). After the reaction, the solvent was distilled and the residue purified by chromatography over silica gel as shown in Table 11. Then purified product was then dissolved in a small amount of dichloromethane (DCM) and precipitated with methanol.

Tetrakis[(1S)-*endo*-(−)-bornyloxy)phthalocyaninato]nickel(II) (3): dark blue powder; MS (FD) *m*/*e* 1178.4 (M^+); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.11, 1.12 (s, 12H), 1.23, 1.26, 1.28 (s, 24H), 1.6 (br, 12H), 2.01 (br, 8H), 2.59 (br, 4H), 2.83 (br, 4H), 4.87 (br, 4H), 7.30−7.48 (m, 4H), 8.02−8.71 (m, 8H); ^{13}C-NMR ($CDCl_3/CS_2$, 62.89 MHz) δ 14.17, 19.18, 19.38, 19.91, 27.25, 28.34, 37.38, 45.59, 47.79, 49.75, 49.78, 49.85, 83.37, 83.49, 105.24, 105.55, 105.67, 118.51, 122.29, 122.61, 129.16, 129.44, 138.07, 144.55 (m), 160.32; IR (KBr disk) ν 2951 (s), 2951 (m), 1612 (s), 1531 (m), 1477 (s), 1416 (m), 1391 (w), 2352 (m), 1329 (m), 1281 (m), 1238(s), 1126 (s), 1096 (s), 1065 (s), 1024 (s), 993 (w), 892 (m) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 677.5 (1.648), 610.0 (0.356), 388.5 (0.289), 328.0 (0.403), 302.5 (0.605), 280.0 (0.553), 241.0 (0.291) nm. Anal. Calcd for $C_{72}H_{80}N_8O_4Ni$: C, 73.31; H, 6.84; N, 9.51. Found: C, 71.88; H, 6.77; N, 9.18.

Tetrakis[(cyclohexyloxy)phthalocyaninato]nickel(II) (4): dark blue powder; MS (FD) *m*/*e* 962.4 (M^+); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.5−2.0 (m, 24H), 2.19 (m, 8H), 2.43 (br, 8H), 4.74 (br, 4H), 6.82−7.36 (br, 4H), 7.6−7.90 (br, 8H); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ 24.08, 26.11, 29.73, 32.12, 32.21, 74.92, 74.99, 75.12, 75.33, 75.48, 104.39, 105.54, 117.59, 118.04, 121.62 (m), 128.01 (m), 136.65 (m), 142.23 (m), 158.16; IR (KBr disk) ν 3067 (w), 2930 (s), 2854 (m), 1610 (s), 1477 (m), 1468 (s), 1413 (m), 1339 (m), 1234 (s), 1121 (m), 1094 (s), 1020 (m), 972 (m), 750 (m) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 676 (3.195), 613 (0.896) sh, 385 (0.636), 364 (0.608), 328 (1.024), 301 (1.653) sh, 283 (1.642), 244 (1.122) nm. Anal. Calcd for $C_{56}H_{56}N_8O_4Ni$: C, 69.83; H, 5.86; N, 11.62. Found: C, 68.96; H, 6.08; N, 11.60.

Tetrakis[(octyloxy)phthalocyaninato]nickel(II) (5): dark blue powder, MS (FD) *m*/*e* 1084.5 (M^++1), 541.3 (M^{2+}); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 0.96 (br, 12H), 1.36 (br, 40H), 1.66 (br, 8H), 3.5 (br, 8H), 5.9−6.9 (br, 12H); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ 14.21, 22.86, 26.19, 26.23, 29.47, 29.80, 32.03, 67.29 (m), 101.08 (m), 116.20 (m), 120.36 (m), 127.42 (m), 135.14 (m), 141.5 (m), 158.34 (m); IR (KBr disk) ν 3068 (w), 2924 (s), 2854 (m), 1612 (s), 1485 (m), 1468 (s), 1352 (m), 1242 (s), 1123 (m), 1097 (s), 750 (m) cm^{-1}; UV (CH_2Cl_2), λ (ϵ) 676 (0.539), 625 (0.203) sh, 381 (0.154), 363 (0.158), 328 (0.252), 302 (0.378) sh, 280 (0.413), 243 (0.322) nm. Anal. Calcd for $C_{64}H_{80}N_8O_4Ni$: C, 70.94; H, 7.45; N, 10.35. Found: C, 69.64; H, 8.00; N, 9.37.

Tetrakis[(cyclooctyloxy)phthalocyaninato]nickel(II) (6): dark blue powder; MS (FD) *m*/*e* 1074.4 (M^+), 2150.7, 3225.9; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.9 (br, 16H), 2.1−2.3 (br, 16H), 4.8 (br, 4H), 7.0−7.2 (br, 4H), 7.4−8.0 (br, 8H); ^{13}C-NMR ($CDCl_3/CS_2$, 62.89 MHz) δ 23.31, 23.39, 25.89, 25.98, 27.64, 27.70, 31.56, 31.70, 77.76, 77.91, 104.85, 118.09, 121.65, 128.32, 136.94, 141.90, 142.20, 142.75, 158.18, 158.25; IR (KBr disk) ν 3068 (w), 2920 (s), 2853 (m), 1610 (s), 1533 (m), 1477 (m), 1416 (m), 1350 (m), 1236 (s), 1124 (m), 1094 (s), 1063 (s), 976 (m), 820 (w), 750 (m) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 677.5 (1.702), 610.5 (0.437) sh, 386.0 (0.329), 327.5 (0.510), 301.5 (0.786), 286.0 (0.762), 244.5 (0.518) nm. Anal. Calcd for $C_{64}H_{72}N_8O_4Ni$: C, 71.44; H, 6.74; N, 10.41. Found: C, 70.31; H, 6.68; N, 10.20.

Tetrakis[(cyclododecyloxy)phthalocyaninato]nickel(II) (8): dark blue powder; MS (FD) *m*/*e* 1300.3 (M^+ + 1); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.3−2.2 (br, 44H), 4.9 (br, 4H), 7.5 (br, 4H), 8.3−9.0 (br, 8H); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ 19.46, 20.34, 22.35, 22.99, 25.15, 27.28, 28.17, 75.94, 105.62, 119.24, 122.82, 128.86, 129.38, 129.59, 138.45, 143.9 (m), 159.68; IR (KBr disk) ν 2934 (s), 2862 (m), 1612 (m), 1533 (w), 1472 (m), 1414 (m), 1348 (m), 1277 (w), 1234 (m), 1123 (m), 1094 (s), 1062 (m), 997 (w), 752 (w) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 678.0 (1.561), 625.0 (0.367) sh, 610.5 (0.304), 386.5 (0.232), 328.5 (0.392), 302.0 (0.639) sh, 244.5 (0.392) nm. Anal. Calcd for $C_{80}H_{104}N_8O_4Ni$: C, 73.92; H, 8.07; N, 8.63. Found: C, 73.30; H, 9.31; N, 8.61.

Tetrakis[((3,5-di-*tert*-butylphenyl)oxy)phthalocyaninato]nickel-(II) (9): dark blue powder; MS (FD) *m*/*e* 1387.0 (M^+), 2776.4, 4164.6; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.36, 1.38, 1.40, 1.41 (all s, 72H), 7.26, 7.27, 7.30, 7.32 (all s, 8H), 7.50 (m, 4H), 8.20−8.53 (m, 8H); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ 31.46, 34.91, 34.94, 109.76, 110.23, 113.97, 114.08, 114.17, 117.42, 117.54, 119.57, 122.52, 130.39, 137.25, 144.52 (m), 152.41, 152.43, 152.47, 156.56, 156.71, 158.64; IR (KBr disk) ν 2963 (s), 2905 (w), 2867 (w), 1607 (m), 1587 (s), 1485 (m), 1475 (s), 1416 (s), 1298 (m), 1232 (s), 1123 (m), 1094 (s), 970 (m) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 676.5 (1.147), 645.5 (0.293) sh, 608.5 (0.287), 382.5 (0.194), 332.0 (0.326), 299.5 (0.530), 285.5 (0.514), 253.0 (0.393) nm. Anal. Calcd for $C_{88}H_{96}N_8O_4Ni$: C, 76.15; H, 6.98; N, 8.08. Found: C, 74.89; H, 6.88; N, 8.01.

Tetrakis[((2,6-di-*tert*-butyl-4-methylphenyl)oxy)phthalocyaninato]-nickel(II) (10): dark blue powder; MS (FD) *m*/*e* 1442.7 (M^+); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.24, 1.40 (all s, 72H), 2.10, 2.16 (all s, 12H), 6.96, 6.98, 6.99, 7.01 (all s, 8H), 7.74−7.94 (m, 4H), 8.80−

(11) Siegl, W. O. *J. Heterocycl. Chem.* **1981**, *18*, 1613.

8.91 (br, 4H), 9.03−9.31 (m, 4H); ^{13}C-NMR ($CDCl_3/CS_2$, 62.89 MHz) δ 25.30, 25.48, 29.49, 34.72, 44.15, 44.21, 118,92, 119.20, 122.41 (m), 128.63, 135.80 (m), 137.80 (m), 144.64, 144.73, 145.24, 145.99, 185.75; IR (KBr disk) ν 3068 (w), 2924 (s), 2854 (m), 1612 (s), 1485 (m), 1468 (s), 1352 (m), 1242 (s), 1123 (m), 1097 (s), 750 (m) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 670.0 (1.082), 643.0 (0.179) sh, 604.0 (0.171), 365.0 (0.162) sh, 336.0 (0.259), 297.5 (0.287), 274.0 (0.260), 246.5 (0.350) nm. Anal. Calcd for $C_{92}H_{104}N_8O_4Ni$: C, 76.52; H, 7.26; N, 7.76. Found: C, 75.74; H, 7.22; N, 7.47.

Tetrakis[(cyclohexylthio)phthalocyaninato]nickel(II) (11): dark blue powder; MS (FD) *m*/*e* 1026.2 (M^+), 513.0 (M^{2+}); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 1.7 (br), 1.9 (br), 2.1 (br), 2.3 (br), 3.5 (br, 4H), 6.9−7.7 (br, 12H); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ 26.18 (2 peaks), 33.49, 45.78, 46.11, 46.47, 120.02 (m), 121.70 (m), 122.60 (m), 129.43 (m), 130.08 (m), 131.48 (m), 133.79 (m), 136.11 (m); IR (KBr disk) ν 2928 (s), 2853 (m), 1605 (s), 1533 (w), 1448 (m), 1400 (m), 1313 (m), 1261 (m), 1144 (m), 1099 (m), 1087 (m), 1043 (w), 997 (w), 935 (m), 818 (w), 750 (m) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 683.0 (0.735), 650.5 (0.364) sh, 622.5 (0.308) sh, 412.5 (0.145) sh, 364.0 (0.188) sh, 334.0 (0.325), 301.5 (0.571), 261.5 (0.401) nm. Anal. Calcd for $C_{56}H_{56}N_8NiS_4$: C, 65.43; H, 5.49; N, 10.89; S, 12.47. Found: C, 64.06; H, 5.39; N, 10.66; S, 12.40.

Tetrakis((1S)-*endo*-(−)-bornyloxy)phthalocyanine (12). 5-[((1S)-*endo*-(−)-bornyloxy)-1,3-dihydro-1,3-diiminoisoindoline (0.5 g, 1.68 mmol) was dissolved in 10 mL of DMF and heated under reflux for 60 h. The solvent was evaporated to dryness, and the residue was dissolved in chloroform and purified by column chromatography (silica gel, $CHCl_3$). The product was dissolved in a small amount of DCM and precipitated with methanol to provide 85 mg (18.1%) of **12** as a blue powder: MS (FD) *m*/*e* 1123.0 ($M^+ + 1$); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ −1.59 (br, 2H), 1.09 (s, 12H), 1.22, 1.27 (s, 24H), 1.6 (br, 12H), 1.99 (br, 8H), 2.59 (br, 4H), 2.83 (br, 4H), 4.94 (br, 4H), 7.48−7.65 (m, 4H), 8.35−8.50 (m, 4H), 8.80−9.12 (m, 4H); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ 13.54, 14.07, 19.10, 19.28, 19.50, 19.84, 26.72, 27.18, 27.87, 28.26, 36.43, 37.19, 45.54, 49.71, 49.79, 83.55, 84.02, 106.38, 106.70, 108.98, 118.86, 121.25, 123.47, 128.78, 137.91, 148.78 (m), 160.73, 160.95; IR (KBr disk) ν 3290 (w), 3068 (w), 2951 (s), 2873 (m), 1614 (s), 1475 (s), 1391 (w), 1366 (w), 1258 (s), 1115 (m), 1096 (s), 1053 (m), 1008 (w), 824 (w), 748 (m), 716 (w) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 707.0 (0.952), 671.5 (0.828), 645.5 (0.312), 610.5 (0.200), 395.0 (0.249), 343.0 (0.483), 292.0 (0.273), 256.0 (0.207) nm. Anal. Calcd for $C_{72}H_{82}N_8O_4$: C, 76.96; H, 7.36; N, 9.98. Found: C, 75.41; H, 7.35; N, 9.83.

Tetrakis(cyclooctyloxy)phthalocyanine (13). 1,2-Dicyano-4-(octyloxy)benzene (0.45 g, 1.77 mmol) was dissolved in 5 mL of DMAE and heated under reflux for 40 h. The solvent was distilled, and the residue was purified by column chromatography (silica gel, $CHCl_3$). The product was dissolved in THF/diethyl ether (1:1) and precipitated with methanol to provide 80 mg (17.6%) of **13** as a blue powder: MS (FD) *m*/*e* 1019.3 ($M^+ + 1$), 2038.9; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ −4.2 (br, 2H), 1.87−2.34 (m, br, 60H), 4.84 (br, 4H), 7.11−7.27 (m, 4H), 7.74 −7.83 (m, 4H), 8.09−8.28 (m, 4H); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ 23.34, 23.46, 25.93, 26.01, 27.55, 27.60, 31.75, 31.91, 78.42, 78.47, 78.55, 78.61, 106.36, 106.40, 106.45, 106.51, 106.59, 106.62, 118.79, 118.85, 118.91, 122.88, 122.92, 123.00, 123.05, 128.30, 128.35, 137.29, 127.32, 137.36, 137.46, 147.5 (br), 159.21, 159.26; IR (KBr disk) ν 3292 (w), 3068 (w), 2920 (s), 2852 (m), 1612 (s), 1477 (s), 1340 (m), 1257 (m), 1236 (s), 1096 (s), 1049 (m), 1011 (s), 973 (m), 822 (w), 748 (m) cm^{-1}; UV (CH_2Cl_2) λ (ϵ) 707.0 (1.203), 672.0 (1.032), 644.0 (0.400), 610.5 (0.265), 394.5 (0.330), 344.0 (0.644), 291.0 (0.402) nm. Anal. Calcd for $C_{64}H_{74}N_8O_4$: C, 75.40; H, 7.32; N, 11.00. Found: C, 74.25; H, 7.09; N, 11.00.

(Mononitrophenyl)quinolinecarboxylic acids (16, 17). 2-Phenylquinoline-4-carboxylic acid (**15**, 4 g, 16 mmol) was slowly added to a cold solution of 5 mL of 65% HNO_3 and 7 mL of 100% H_2SO_4. The cooling bath was removed, and the mixture stirred for 2 h at room temperature. The mixture was heated to 50 °C and stirred again for 2 h. The solution was cooled and poured into ice water. The obtained residue was washed with water until pH 7, dried at 60 °C, and recrystallized from ethanol. The first fraction contained pure (*o*-nitrophenyl)quinoline-4-carboxylic acid (**16**), and all other fractions contained both possible products **16** and **17**. Fractionated recrystallization from acetone gave (*p*-nitrophenyl)quinoline-4-carboxylic acid (**17**): yield 3g (63.8%) as yellow powder, decomposes at 200 °C (CO_2 evolution).

For 16: yield 1.2 g; MS *m*/*z* (relative intensity) 294.1 (M^+), 249.0, 204.0 (100), 176.0, 124.5, 101.0, 87.9, 74.9; ^{1}H-NMR (DMSO, 250 MHz) δ 7.75 (t, 1H), 7.88 (t, 1H), 8.19 (d, 1H), 8.36 (d, 2H), 8.53 (d, 2H), 8.56 (s, 1H), 8.64 (d, 1H), 14.01 (s, br, 1H); ^{13}C-NMR (DMSO, 62.89 MHz) δ 119.46, 123.83, 124.01, 125.43, 128.43, 128.62, 129.98, 130.56, 138.02, 143.67, 148.16, 148.31, 153.53, 167.35; IR (KBr disk) ν 3093 s, 2921 s, 2530 s, 1717 (s), 1595 (m), 1531 (s), 1348 (s), 1244 (m), 1200 (m), 798 (m), 762 (m), 696 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{10}N_2O_4$: C, 65.31; H, 3.43; N, 9.52. Found: C, 65.33; H, 3.63; N, 9.60.

For 17: yield 0.55 g; MS *m*/*z* (relative intensity) 294.1 (M^+), 249.0, 204.0 (100), 176.0, 124.5, 101.0, 87.9, 74.9; ^{1}H-NMR (DMSO, 250 MHz) δ 7.76 (t, J = 7.0 Hz, 1H), 7.85 (t, J = 8.0 Hz, 1H), 7.92, (dd, J = 7.0, 2.2 Hz, 1H), 8.19 (d, J = 8 Hz, 1H), 8.34 (dd, J = 7.5, 2.2 Hz, 1H), 8.56 (s, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 7.6 Hz, 1H), 9.05 (t, J = 1.8 Hz, 1H), 14.10 (s, br, 1H); ^{13}C-NMR (DMSO, 62.89 MHz) δ 119.04, 121.51, 123.79, 124.30, 125.39, 128.34, 129.85, 130.49 (2C), 133.36, 138.03, 139.36, 148.22, 148.44, 153.35, 167.38; IR (KBr disk) ν 3001 (w), 2932 (w), 2850 (w), 2642 (w), 1699 (s), 1514 (s), 1416 (m), 1348 (s), 1319 (m), 1277 (m), 1259 (m), 860 (m), 847 (m), 762 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{10}N_2O_4$: C, 65.31; H, 3.43; N, 9.52. Found: C, 64.63; H, 3.51; N, 9.31.

***N*-[(2-Phenyl-4-quinolyl)carbonyl]-4-(dimethylmethoxysilyl)butanamide (24).** Triethylamine (1.9 mL, 13.6 mmol) and **14** (1.2 mL, 6.2 mmol) were dissolved in 20 mL of DCM under cooling in an ice bath. To this solution was added 2-phenylquinoline-4-carboxylic acid chloride (**20**) (1.9 g, 6.2 mmol) in 20 mL of DCM. The cooling bath was removed and the solution stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness, and the residue was dissolved in DCM/acetonitrile (10:1). The crude product was purified with flash chromatography (silica gel 40−63 μm) in DCM/acetonitrile (10:1): yield 1.3 g (53.4%) as colorless oil; MS *m*/*z* (relative intensity) 392.3 (M^+), 363.2, 349.2, 317.1, 261.1, 232.1, 204.1 (100), 176.0, 149.0, 89.0; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 0.0 (s, 6H, $SiCH_3$), 0.56 (m, 2H, $SiCH_2$), 1.37 (m, 2H, CH_2), 1.60 (qi, 2H, J = 7.3 Hz, CH_2), 3.30 (s, 3H, OCH_3), 3.39 (q, 2H, J = 6.22 Hz, NCH_3), 6.5 (s, 1H, NH), 7.30 (m, 4H, ArH), 7.57 (m, 2H, ArH), 7.93 (m, 4H, ArH); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ −2.6, 15.6, 20.7, 33.0, 39.8, 50.2, 116.3, 123.3, 125.0, 127.2, 127.4 (2C), 128.8 (2C), 129.7, 129.9, 130.1, 138.7, 143.2, 148.5, 156.6, 167.6; ^{29}Si-NMR ($CDCl_3$, 49.69 MHz) δ 11.2; IR (KBr disk) ν 3273 (m), 3062 s, 2932 s, 1643 (s), 1591 (m), 1549 (s), 1495 s, 1350 (m), 1288 s, 1252 (m), 1088 (s), 841 (m), 771 (m), 694 (w) cm^{-1}. Anal. Calcd for $C_{23}H_{28}N_2O_2Si$: C, 70.37; H, 7.19; N, 7.14. Found: C, 70.82; H, 6.83; N, 6.92.

***N*-[(2-(*o*-Nitrophenyl)-4-quinolyl)carbonyl]-4-(dimethylmethoxysilyl)butanamide (25).** (a) **16** (1.2 g, 4.1 mmol) was suspended in 30 mL of DCM. Under cooling with ice water, 1,1′-carbonyldiimidazole (0.67 g, 4.13 mmol) in 30 mL of DCM was added, and the mixture was stirred for 2 h. During the reaction, a clear yellow solution containing **21** was obtained. (b) Without further purification, this solution was slowly added to an equimolar solution of **14** in 20 mL of DCM, and the mixture was stirred overnight. The mixture was evaporated to dryness and the residue dissolved in DCM/acetonitrile (10:1). The crude product was purified by flash chromatography (silica gel 40−63 μm) in DCM/acetonitrile (10:1) (R_f = 0.29): yield 1.08 g (60.3%) as yellow powder; mp 144−146 °C; MS *m*/*z* (relative intensity) 436.4 (M^+), 422.3, 405.3, 362.3, 332.3, 306.2, 277.2, 249.2, 203.2, 176.9, 89.0 (100), 59.0; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.09 (s, 6H, $SiCH_3$), 0.67 (m, 2H, $SiCH_2$), 1.51 (m, 2H, CH_2), 1.72 (qi, 2H, J = 7.3 Hz, CH_2), 3.37 (s, 3H, OCH_3), 3.56 (q, 2H, J = 6.22 Hz, NCH_3), 6.31 (s, 1H, NH), 7.56 (2d, 1H, J = 7.7 Hz, ArH), 7.63 (2d, 2H, J = 7.7 Hz, ArH), 7.75 (2d, 1H, J = 7.7 Hz, ArH), 7.86 (s, 1H, ArH), 8.14 (dd, 2H, J = 7.7, 8.2 Hz, ArH), 8.27 (m, 2H, ArH), 8.47 (d, 1H, J = 7.7 Hz, ArH), 8.96 (s, 1H); ^{13}C-NMR ($CDCl_3$, 100.61 MHz) δ −2.7, 15.6, 20.7, 32.9, 39.9, 50.2, 115.7, 122.2, 123.7, 124.2, 125.0, 128.0, 129.8, 130.2, 130.6, 133.1, 140.4, 143.8, 148.7, 148.9, 153.8, 167.1; ^{29}Si-NMR ($CDCl_3$, 49.69 MHz) δ 19.44; IR (KBr disk) ν 3277 (m), 3073 (w), 2930 (m), 1641 (s), 1589 (m), 1547 (s), 1527 (s), 1346 (s), 1288 (w), 1252 (m), 1088 (m), 845 (m), 762 (w), 689 (w) cm^{-1}. Anal.

Calcd for $C_{23}H_{28}N_3O_4Si$: C, 62.99; H, 6.44; N, 9.59. Found: C, 63.10; H, 7.31; N, 9.60.

***N*-[(2-(*p*-Nitrophenyl)-4-quinolyl)carbonyl]-4-(dimethylmethoxysilyl)butanamide (26).** (a) **17** (1 g, 3.4 mmol) was suspended in 40 mL of DCM. The reaction and purification were carried out as described for compound **25**: yield 1.2 g (80.7%) as light yellow powder; mp 136−138.5 °C; MS *m*/*z* (relative intensity) 437.5 (M^+), 394.4, 362.3, 308.3, 277.2, 250.3, 203.2, 149.1, 89.1 (100), 59.1; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 0.09 (s, 6H, $SiCH_3$), 0.67 (m, 2H, $SiCH_2$), 1.51 (m, 2H, CH_2), 1.72 (qi, 2H, J = 7.3 Hz, CH_2), 3.37 (s, 3H, OCH_3), 3.55 (q, 2H, J = 6.22 Hz, NCH_3), 6.32 (s, 1H, NH), 7.58 (2d, 1H, J = 7.2 Hz, ArH), 7.76 (2d, 1H, J = 7.2 Hz, ArH), 7.86 (s, 1H, ArH), 8.16 (d, 2H, J = 7.2 Hz, ArH), 8.29 (s, 4H, ArH); ^{13}C-NMR ($CDCl_3$, 62.89 MHz) δ −2.7, 15.6, 20.7, 32.9, 39.9, 50.3, 116.1, 123.8, 124.0, 125.0, 128.2, 129.8, 130.4, 130.6, 143.7, 144.5, 148.5, 148.7, 153.9, 167.1; ^{29}Si-NMR ($CDCl_3$, 49.69 MHz) δ 19.47; IR (KBr disk) ν 3278 (m), 3072 (w), 2916 (m), 2841 (w), 1641 (s), 1587 (m), 1548 (s), 1521 (s), 1346 (s), 1292 (w), 1250 (m), 1089 (m), 856 (m), 761 (w), 698 (w) cm^{-1}. Anal. Calcd for $C_{23}H_{28}N_3O_4Si$: C, 62.99; H, 6.44; N, 9.59. Found: C, 62.68; H, 6.27; N, 9.52.

Phenylquinoline-Modified Silica Gel (28). Silica gel (5 g) and **24** (1.3 g, 3.3 mmol) were suspended in 20 mL of DCM. The modified silica gel was dried in vacuo at 80 °C: yield 5.03 g; coverage 0.37 mmol/g determined by thermogravimetry (30 mL/min N_2, 1 h room temperature, ΔT = 2 K/min to 1000 °C, 1 h at 1000 °C); 0.33 mmol/g determined by elemental analysis; decomposition begins at 295 °C; ^{13}C-TOSS/MAS-NMR (75.03 MHz, rf = 10 kHz) δ −1.8, 15.2, 30.9, 38.6, 48.0,128.3; ^{29}Si-CP/MAS-NMR (59.58 MHz, rf = 10 kHz) δ 13.4, −101.3, −110.4; IR (KBr/silica gel disk) ν 2937 (w), 1649 (w), 1593 (w), 1551 (w) cm^{-1}. Anal. Found for the modified silica gel: C, 8.7; H, 1.8; N, 0.9.

(*o*-Nitrophenyl)quinoline-Modified Silica Gel (29). Silica gel (2.8 g) and **25** (0.8 g, 1.83 mmol) were suspended in 30 mL of DCM. The reaction and purification were carried out as described for compound **28**: yield 2.92 g; coverage 0.30 mmol/g determined by thermogravimetry (30 mL/min N_2, 1 h room temperature, ΔT = 2 K/min to 1000 °C, 1 h at 1000 °C); 0.43 mmol/g determined by elemental analysis; decomposition begins at 295 °C; ^{13}C-CP/MAS-NMR (75.03 MHz, rf = 10 kHz) δ −1.5, 20.1, 33.1, 40.6, 48.0,123.9, 129.1, 142.0, 148.3, 167.7; ^{29}Si-CP/MAS-NMR (59.58 MHz, rf = 10 kHz) δ 13.4, −101.0, −110.2; IR (KBr/silica gel disk) ν 2960, 1647, 1593, 1533, 1352 cm^{-1}. Anal. Found for the modified silica gel: C, 11.3; H, 2.7; N, 1.9.

(*p*-Nitrophenyl)quinoline-Modified Silica Gel (30). Silica gel (3 g) and **26** (1.1 g, 2.48 mmol) were suspended in 30 mL of DCM. The reaction and purification were carried out as described for compound **28**: yield 3.14 g; coverage 0.37 mmol/g determined by thermogravimetry (30 mL/min N_2, 1 h room temperature, ΔT = 2 K/min to 1000 °C, 1 h at 1000 °C); 0.36 mmol/g determined by elemental analysis; decomposition begins at 295 °C; ^{13}C-CP/MAS-NMR (75.03 MHz, rf = 10 kHz) δ −1.9, 19.7, 32.4, 39.8, 49.8, 123.7, 127.6, 141.9, 147.6, 167.7; ^{29}Si-CP/MAS-NMR (59.58 MHz, rf = 10 kHz) δ 12.2, −101.5, −110.9; IR (KBr/silica gel disk) ν 3283 (w), 3066 (w), 2935 (m), 2864 (m), 1647 (s), 1596 (m), 1550 (s), 1523 (s), 1348 (s), 763 (m), 702 (m) cm^{-1}. Anal. Found for the modified silica gel: C, 9.4; H, 2.1; N, 1.7.

2-(*p*-Butylphenyl)quinoline-4-carboxylic Acid (18). Isatin (5.6 g, 0.038 mol) and *p*-butylacetophenone (6.7 g, 0.038 mol) were added to a saturated solution of KOH (6.4 g, 0.114 mol). Enough ethanol (20−40 mL) was added to render the mixture homogeneous, and the mixture was heated to 70−80 °C for 48 h. The reaction mixture was evaporated and the residue dissolved in H_2O. The aqueous solution was acidified with 50% acetic acid. The creamy precipitate was purified by recrystallization from ethanol: yield 4.9 (43%) as light red powder; mp 212 °C; MS *m*/*z* (relative intensity) 306 (M^+), 276, 262 (100), 215; ^{1}H-NMR (acetone, 250 MHz) δ 0.96 (t, 3H), 1.39 (sx, 2H), 1.68 (q, 2H), 2.73 (t, 2H), 7.43 (d, 2H), 7.68 (t, 1H), 7.84 (t, 1H), 8.2 (d, 1H), 8.28 (d, 2H), 8.57 (s, 1H), 8.84 (d, 1H); ^{13}C-NMR (acetone, 250 MHz) δ 13.7, 22.5, 33.8, 35.5, 120.0, 124.4, 126.0, 127.6, 127.8, 129.3, 130.2, 130.4, 136.5, 136.9, 145.3, 149.6, 156.7, 165.1; IR (KBr disk) ν 2956 (m), 2928 (s), 2858 (m), 1722 (m), 1645 (w), 1616 (m), 1591 (s), 1418 (m), 1393 (m), 1245 (w) cm^{-1}. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.65; H, 6.28; N, 4.59. Found: C, 78.69; H, 6.13; N, 4.48.

2-(*p*-Butyldinitrophenyl)quinoline-4-carboxylic Acid (19). **18** (4.5 g, 14.7 mmol) was slowly added to a cold solution of 5 mL of 100% HNO_3 and 7 mL of 100% H_2SO_4 and worked up analogously to (mononitrophenyl)quinolinecarboxylic acid **16** or **17**. The yellow powder was recrystallized from toluene: yield 2.5 g (42.8%) of yellow powder; mp 182 °C; several constitutional isomers; MS *m*/*z* (relative intensity) 396 (M^+), 378 (100%), 361, 336, 308, 204; ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 0.91 (t, 3H), 1.36 (sx, 2H), 1.59 (q, 2H), 2.85 (t, 2H), 7.51 (d, 1H), 7.7 (t, $^1/_2$H), 7.84 (t, $^1/_2$H), 8.04 (d, $^1/_2$H), 8.22 (d, $^1/_2$H), 8.35−8.53 (m, 2H), 8.6 (d, $^1/_2$H), 8.65 (s, $^1/_2$H), 8.75 (d, $^1/_2$H), 9.07 (d, $^1/_2$H); ^{13}C-NMR (DMSO, 250 MHz) δ 13.6, 22.0, 31.4, 32.2, 115.2, 120.7, 122.9, 124.7, 124.8, 125.2, 128.3, 129.4, 131.5, 132.7, 135.9, 138.4, 138.9, 146.7, 148.2, 149.8, 155.1, 166.8; IR (KBr disk) ν 3101 (w), 2957 (m), 2930 (m), 1713 (m), 1624 (w), 1595 (m), 1531 (s), 1416 (w), 1346 (s), 1261 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{17}N_3O_6$: C, 60.74; H, 4.34; N, 10.63. Found: C, 60.78; H, 4.36; N, 10.01.

***N*-[(2-(*p*-Butyldinitrophenyl)-4-quinolyl)carbonyl]-4-(dimethylmethoxysilyl)butanamide (27).** (*p*-Butyldinitrophenyl)quinolinecarboxylic acid (**19**, 2.2 g, 5.6 mmol) was suspended in 40 mL of DCM. The reaction and purification were carried out as described for compound **25**: yield 0.6 g (20%) as yellow powder; mp 162−165 °C; MS *m*/*z* (relative intensity) 539 (M^+), 450, 418, 392, 332, 200 (100); ^{1}H-NMR ($CDCl_3$, 250 MHz) δ 0.17 (s, 6H), 0.74 (t, 2H), 1.01 (t, 3H), 1.51−1.85 (m, 8H), 2.98 (t, 2H), 3.44 (s, 3H), 3.64 (q, 2H), 6.37 (s, 1H), 7.53 (d, 1H), 7.67 (t, 1H), 8.07−8.11 (m, 2H), 8.38−8.59 (m, 3H); ^{13}C-NMR (DMSO, 250 MHz) δ 0.8, 1.1, 1.3, 14.5, 18.4, 20.6, 21.3, 22.9, 32.3, 33.1, 49.5, 119.1, 121.8, 123.8, 124.9, 125.1, 125.2, 125.3, 127.6, 128.4, 130.1, 132.2, 132.3, 133.7, 136.7, 137.2, 137.9, 139.3, 139.6, 139.7, 139.8, 144.8, 148.9, 149.1, 150.6, 150.7, 156.1, 166.2, 166.3; IR (KBr disk) ν 3271 (s), 2957 (m), 2932 (m), 1641 (m), 1593 (m), 1523 (s), 1340 (m), 1259 (w), 1090 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{34}N_4O_6Si$: C, 60.20; H, 6.37; N, 10.41. Found: C, 61.11; H, 6.35; N, 11.00.

(*p*-Butyldinitrophenyl)quinoline-Modified Silica Gel (31). Silica gel (3 g) and *N*-[(2-(*p*-butyldinitrophenyl)-4-quinolyl)carbonyl]-4-dimethylmethoxysilyl)butanamide (**27**, 0.6 g, 1.1 mmol) were suspended in 20 mL of DCM. The reaction and purification were carried out as described for compound **29**: yield 3.5 g, coverage 0.2 mmol/g determined by thermogravimetry (30 mL/min N_2, 1 h room temperature, ΔT = 2 K/min to 1000 °C, 1 h at 1000 °C); 0.29 mmol/g determined by elemental analysis; ^{13}C-CP/MAS-NMR (75.03 MHz, rf = 10 kHz) δ −2.8, 11.7, 21.8, 33.3, 128.3, 135.6, 143.6, 157.3, 168.8; ^{29}Si-CP/MAS-NMR (59.58 MHz, rf = 10 kHz) δ −111.1, −101.3, 12.9; IR (KBr/silica gel disk) ν 2935, 2862, 1651, 1595, 1549 cm^{-1}.

Acknowledgment. Thanks are expressed to the Deutsche Forschungsgemeinschaft DFG for financial support.

JA961009X