Synthesis, Separation and Characterization of Unsymmetrically Substituted Phthalocyanines☆

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Unsymmetrically substituted (phthalocyaninato)nickel(II) complexes **3**–**7** were synthesized by statistical condensation of 4,5-dipentoxy- (**2a**), 4,5-diheptyl- (**2b**), 3,6-dihexoxy- (**2c**), and 3,6-diheptylphthalonitrile (**2d**) with 3,4,5,6-tetraphenylphthalonitrile (**1**) and separated by column chromatography. The obtained phthalocyanines **3**–**7** were characterized by UV-, IR-, and ^{1}H-NMR spectroscopy.

In the last few years tetra- and symmetrically octa- and hexadeca-substituted phthalocyanines (Pcs) have been investigated intensively with respect to their electrical conductivities, optical or liquid-crystalline properties as well as their use as LB films[1]. However, in contrast to symmetrically substituted phthalocyanines reports on Pcs with lower symmetry have appeared scarcely, mainly because of the problems associated with their preparation. Phthalocyanines with lower symmetry show interesting properties in nonlinear optics and are important materials for Langmuir-Blodgett films[2] and ladder polymers[3]. They are also useful in understanding the nature of Pcs. For example, fine tuning of the position of the absorption band of Pcs can be achieved by the stepwise introduction of peripheral substituents or by the stepwise adjustment of the size of the π-conjugated macrocyclic systems[4].

To obtain unsymmetrical phthalocyanines several strategies can be applied: the polymer support route[5], the subphthalocyanine route[6], and the statistical condensation route[7] including the separation of the statistical mixture of the constitutional isomers which are normally formed in the synthesis of Pcs starting from either unsymmetrically substituted phthalonitriles (e.g. *tert*-butylphthalonitrile)[8] or phthalonitriles of different structure. Recently, we have reported for the first time on the successful separation of the constitutional isomers of [tetra-*tert*-butyl- and tetrakis(2-ethylhexyloxy)phthalocyaninato]nickel(II) by using MPLC and HPLC[8].

The strategy of our synthesis of unsymmetrical phthalocyanines is based on the statistical condensation reaction of two differently substituted phthalonitriles. In a statistical condensation of two different phthalonitriles A and B six kinds of phthalocyanines are expected: phthalocyanines containing four A or B units (AAAA or BBBB), three A units and one B unit (AAAB), three B units and one A unit (ABBB), and two A units and two B units (two isomers: ABAB and AABB). It has been reported that such product mixtures are difficult to separate by common chromatographic methods due to their tendency toward aggregation[9].

A procedure which reduces the number of possible Pcs by using a phthalonitrile bearing in 3,6-positions bulky groups such as phenyl as starting material has been described recently[10]. Two units of such a phthalonitrile cannot be adjacent and coplanar due to steric hindrance. The result is that one should obtain only three types of phthalocyanines, when treating a phthalonitrile with bulky substituents in 3,6-positions (A) with phthalonitriles having no bulky substituents (B): four B units (BBBB), three B units and one A unit (BBBA), and two B and A units with only the D_{2h} isomer (BABA).

In this paper we report on a statistical condensation of tetraphenylphthalonitrile (**1**) with various alkyl- and alkoxy-substituted phthalonitriles **2a**–**d** (see Scheme 1). The substituted phthalonitriles used have enabled us to separate the obtained phthalocyanines for the first time by using common column chromatography.

Results and Discussion

Tetraphenylphthalonitrile (**1**) is obtained by condensation of tetraphenylcyclopentadienone with chloromaleonitrile and subsequent removal of HCl and CO[11]. The following phthalodinitriles have been used for the statistical condensation with **1**: 4,5-dipentoxy- (**2a**)[12], 4,5-diheptyl- (**2b**)[13], 3,6-dihexoxy- (**2c**)[14], and 3,6-diheptylphthalonitrile (**2d**)[15] (Scheme 1). The statistical condensation is carried out by reactions of equimolar amounts of **1** and the appropriate dinitriles **2a**–**d**, with nickel acetate in *n*-pentanol in the presence of catalytic amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 140°C for 24 h[16]. The mixtures of phthalocyanines obtained are separated by chromatography on silica gel with toluene/hexane mixtures as eluent. All phthalocyanines **3**–**7** prepared (Scheme 1) show good solubility in common organic solvents, e.g. chloroform, toluene, except the symmetrical (octaheptylphthalocyaninato)nickel (**3b**).

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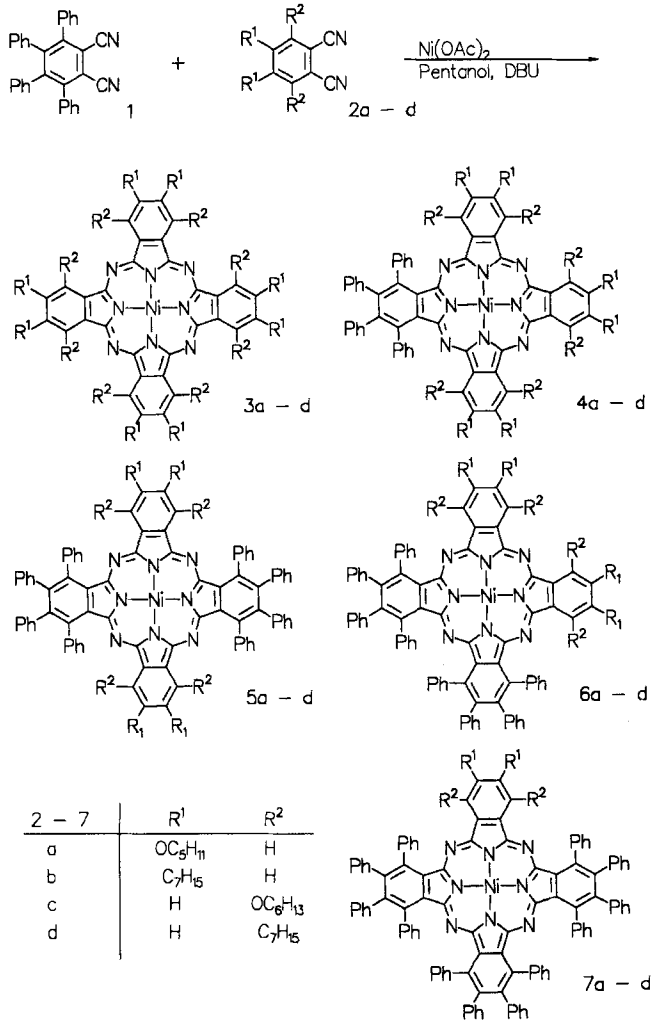
Scheme 1



2 – 7	R^1	R^2
a	OC_5H_{11}	H
b	C_7H_{15}	H
c	H	OC_6H_{13}
d	H	C_7H_{15}

The chromatographic behavior of the phthalocyanines **3**–**7** is as follows: within the series of alkoxy-substituted phthalocyanines **3a**–**7a** and **3c**–**7c**, compounds **7a**, **c** are eluted first, followed by the isomers **6a**, **c** and **5a**, **c**, ending with the symmetrical phthalocyanines **3a**, **c**. In contrast, the order of elution of the alkyl-substituted NiPcs **3b**–**7b** and **3d**–**7d** reverses. The first fraction contains the symmetrical phthalocyanines **3b**, **d** formed from four molecules of **2b**, **d** (BBBB), the last fraction elutes the phthalocyanines **7b**, **d** consisting of three molecules of **1** and one molecule of **2b**, **d** (AAAB), respectively. For the exact order of elution see experimental part.

In all statistical condensations of tetraphenylphthalonitrile (**1**) with **2a**–**d**, we have observed in accordance with ref.[17] that **1** does not form (1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecaphenylphthalocyaninato)-nickel(II) by selfcondensation due to steric hindrance of the phenyl groups. In contrast to ref.[17], but in agreement with reported data[18], we have obtained relatively large quantities of phthalocyanines **6a**–**d** and **7a**–**d** in which two tetraphenyl units are in neighboring positions. The product ratio of the four groups of phthalocyanine mixtures (**a**–**d**) based on NMR data for the product mixtures are given in Table 1. The relative ratio was determined by ^{1}H-NMR spectroscopy using the methylene protons (Ar-CH_2-) with $CHCl_3$ as internal standard. In addition the relative ratio was estimated by weighing the isolated products.

Table 1. Relative yields (in %) of the NiPcs **3a**–**7d**

R	3	4	5	6	7
a	30	45	19	5	1
b	14	53	20	8	5
c	17	48	16	15	4
d	15	38	18	18	11

UV/Vis Spectroscopy: The UV/Vis spectra of the (phthalocyaninato)nickel complexes **3**–**7** recorded in toluene show the typical pattern of a phthalocyanine, mainly the π–π^* transition within the heteroaromatic 18-π electron system. The Q bands appear between λ = 670 and 760 nm and the Soret bands between λ = 300 and 360 nm (Table 2).

Table 2. UV/Vis data (in toluene) of the NiPcs **3a**–**7d**

Compound	λ_{max}(nm)
3a	670, 641, 410, 312
4a	684, 671, 609, 440, 391, 335, 311
5a	700, 669, 638, 605, 452, 343, 301
6a	698, 628, 394, 347, 311
7a	726, 654, 377, 353, 310
3b	678, 649, 610, 365, 339, 301
4b	690, 675, 642, 614, 345, 303
5b	706, 672, 642, 607, 349, 304
6b	703, 672, 633, 350, 307
7b	728, 657, 459, 351, 309
3c	734, 659, 439, 327, 304
4c	738, 664, 422, 353, 309
5c	745, 671, 441, 351, 312
6c	748, 674, 442, 354, 311
7c	758, 684, 470, 358, 313
3d	702, 669, 632, 458, 347, 300
4d	711, 639, 459, 349, 305
5d	738, 706, 639, 462, 354, 310
6d	728, 655, 464, 354, 308
7d	745, 670, 470, 359, 313

The absorption spectra for each symmetry of the phthalocyanines **3**–**7** are given in Figures 1 to 4 for comparison. They can be classified into three groups by the splitting mode in the Q bands[6a,19]:

(1) in which each Q band has only one sharp peak,

(2) in which the Q bands show a slightly split profile,

(3) with large splitting of the Q band like a metal-free phthalocyanine.

In the first group, it is well-known that the symmetrical phthalocyanines **3a–d** give rise to single Q bands due to the degeneracy of the LUMO (e_g) of phthalocyanines with D_{4h} symmetry. Phthalocyanines **6a–d** exhibit similar types of spectra (see Figure 3) in spite of the lowered symmetry (C_{2v}) which could give rise to non-degenerate electronic states. The degeneracy of the LUMO is probably slightly dissolved by the perturbation of the substituents. In the UV/Vis spectra of the phthalocyanines **7a–d** (see Figure 4) the Q bands do not split either, but the bands appear broader than observed in the spectra of **6a–d**.

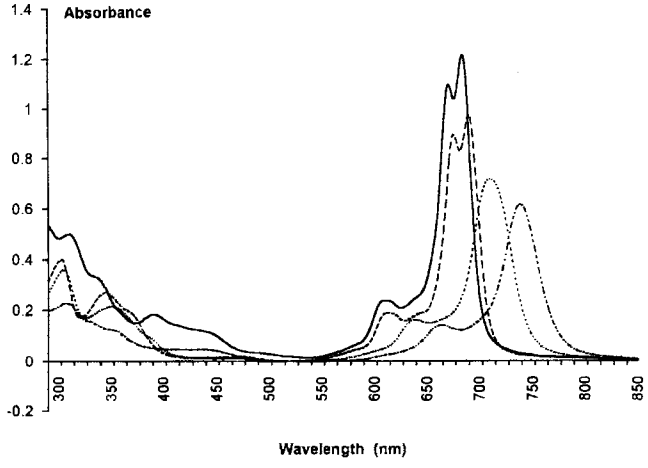


Figure 1. Absorption spectra of NiPc **4a** (solid line), **4b** (dashed line), **4c** (dashed/dotted line), and **4d** (dotted line) in toluene

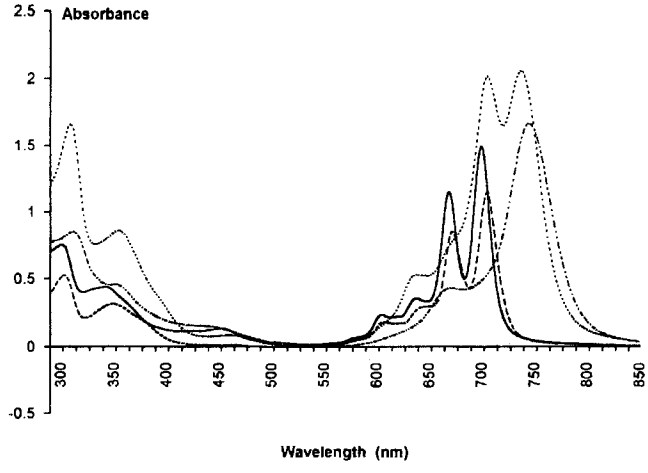


Figure 2. Absorption spectra of NiPc **5a** (solid line), **5b** (dashed line), **5c** (dashed/dotted line), and **5d** (dotted line) in toluene

Although the phthalocyanines **4a–d** have the same symmetry (C_{2v}) as the phthalocyanines **7a–d**, the Q bands split in the case of **4a** and **4b** whereas the NiPcs **4c** and **4d** show broad Q bands without splitting (see Figure 1). This means that the extent of the degeneracy of the LUMO depends on the type and position of the substituents. Probably the compounds **4c**, **d** are not planar in comparison with **4a**, **b**[20].

The large splitting of the Q band of **5a–c** (the Q band of NiPc **5d** shows no splitting, see Figure 2) is readily understood. Considering the anisotropic structure (D_{2h}

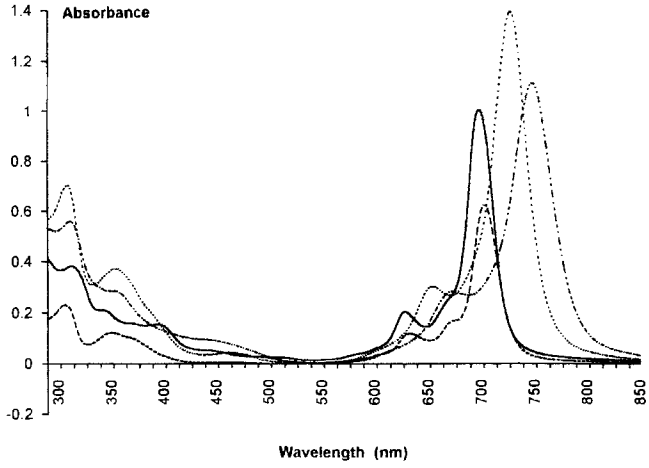


Figure 3. Absorption spectra of NiPc **6a** (solid line), **6b** (dashed line), **6c** (dashed/dotted line), and **6d** (dotted line) in toluene

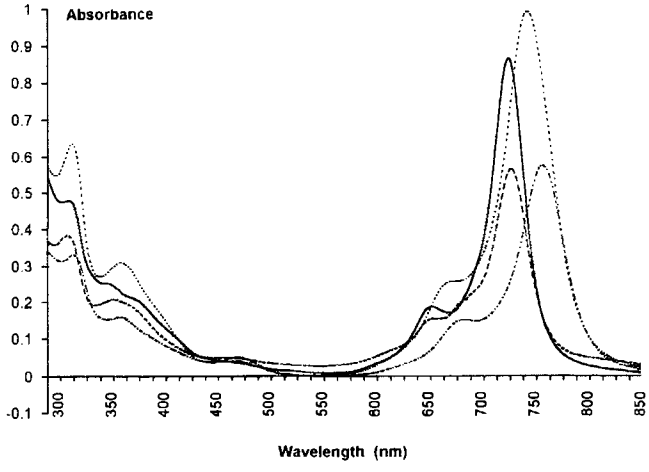


Figure 4. Absorption spectra of NiPc **7a** (solid line), **7b** (dashed line), **7c** (dashed/dotted line), and **7d** (dotted line) in toluene

symmetry) of these compounds, they have the same symmetry as metal-free symmetrical phthalocyanines. At present no explanation can be given why no splitting is observed in the case of **5d**.

IR Spectroscopy: The IR spectra of the unsymmetrical phthalocyanines **4–7** are almost similar, whereas the spectra of the symmetrically substituted NiPcs **3** clearly differ from those of **4–7**. The number of absorption bands is lower than in the case of the unsymmetrical phthalocyanines.

The spectra of **4–7** are dominated by the absorption of the aromatic valence vibration (3100–3000 cm^{-1}), the C–H out-of-plane (700 cm^{-1}) and the ring deformation vibration (740 cm^{-1}) whereas in the spectra of **3** these vibrations are not observed or have a very low intensity.

All spectra described above show strong C–H valence vibrations which are due to the methylene and methyl groups of the substituents.

Figure 5 shows the different intensities of the C–H valence vibrations due to the aromatic $\nu(C-H)_{aromatic}$ and alkyl $\nu(C-H)_{alkyl}$ groups in **3d–7d**. The intensity of aro-

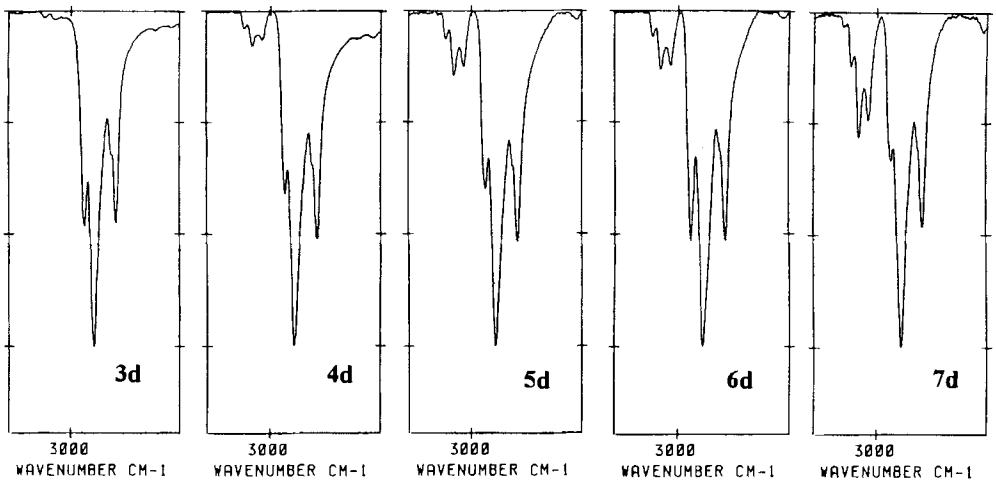


Figure 5. IR spectra of the NiPcs **3d**–**7d** in the range of C–H valence vibrations

matic ν(C–H) increases with increasing number of phenyl substituents. The different ratio of the intensities of $\nu(C-H)_{aromatic}/\nu(C-H)_{alkyl}$ allows us to assign the spectra to the differently substituted phthalocyanines **3d**–**7d** except for the two structural isomeres **5d** and **6d**. All the other phthalocyanines, namely **3a**–**7a**, **3b**–**7b**, and **3c**–**7c**, have been identified by using the same procedures (see Experimental).

^{1}H-NMR Spectroscopy: ^{1}H-NMR spectroscopy is a very useful tool to determine the structure of unsymmetrically substituted phthalocyanines[8]. It is obvious that the aromatic protons are not suitable for this case, because the broad signals of the phenyl protons make a distinction and an integration of the different resonances in this range difficult. The most characteristic differences in the spectra of the phthalocyanines **3**–**7** described above are observed between δ = 3.0 and 5.5. The resonances are assigned to the first methylene group adjacent to the aromatic ring system (Ar–CH_2– and Ar–OCH_2–, respectively).

The range between δ = 3.0 and 5.5 of the ^{1}H-NMR spectra of compounds **3c**–**7c** is shown in Figure 6.

The symmetrical octaalkoxy-substituted NiPc **3c** shows only one triplet at δ = 4.75. In compound **4c** two methylene groups are adjacent to phenyl substituents, and the remaining four methylene groups are next to an alkoxy group. Different sterical interactions are responsible for the different chemical shift of these protons. The integration ratio of 8:4 is a further evidence of this fact. The D_{2h} isomer **5c** shows just one triplet at δ = 4.0 because all methylene groups are positioned next to the phenyl substituents, hence they are equivalent. In contrast to compound **5c**, the isomer **6c** with C_{2v} symmetry has two triplets in the ratio of 4:4 at δ = 4.0 and 4.6. This can be explained again by the different neighborhood of the methylene groups. Analogously to compound **5c**, the resonances of the methylene protons in the spectrum of **7c** appear at δ = 3.94 as a triplet.

In general, the signals of the protons of the methylene groups adjacent to the phenyl substituents appear at higher field in contrast to the methylene protons which are not

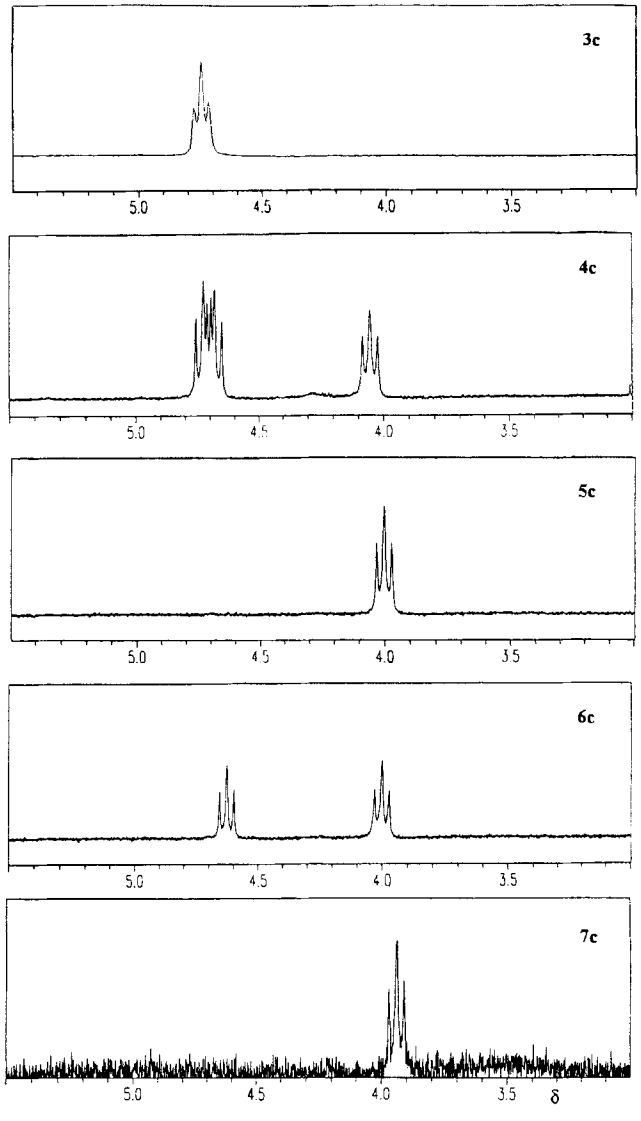


Figure 6. ^{1}H-NMR spectra of the NiPcs **3c**–**7c** in the range of δ = 3.5 to 5.0

close to phenyl groups. The pattern of the first methylene groups next to the aromatic ring system in the ^{1}H-NMR spectra and the integration of the aromatic protons allow an exact identification of the phthalocyanines **3**–**7** (see Experimental). All the other phthalocyanines, namely **3a**–**7a**, **3b**–**7b**, and **3d**–**7d**, have been identified in a similar way.

In summary, we have carried out four statistical syntheses of phthalocyanines by reaction of tetraphenylphthalonitrile (**1**) with various phthalonitriles bearing alkoxy (**2a**, **c**) and alkyl substituents (**2b**, **d**) in differnt positions. For the first time all phthalocyanines formed **3**–**7** have been separated by simple column chromatography and characterizied by several spectroscopic methods. The differences in the UV/Vis, IR, and ^{1}H-NMR spectra obtained are discussed in detail.

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Experimental

The starting materials **1**[11], **2a**[12], **2b**[13], **2c**[14], and **2d**[15] were prepared by literature procedures. – ^{1}H NMR: Bruker AC 250, $CDCl_3$ as solvent and $CHCl_3$ as internal standard. – IR: Bruker IFS 48 FT-IR, KBr pellets. – UV/VIS: Shimadzu UV-310 PC. – MS: Varian MAT 711, FD technique. – Elemental analyses: Carlo Erba Elemental Analyser 1104, 1106. – R_f values: Merck silica gel 60 F_{254}, chamber of size 20 × 4 × 7 cm. – Column chromatographic separations: Merck silica gel 60 (60–200 Mesh), column 60 × 3.5 cm.

Preparation and Separation of Compounds **3a**–**7a**: A mixture of tetraphenylphthalonitrile (**1**) (100 mg, 0.23 mmol), 4,5-dipentoxyphthalonitrile (**2a**) (69 mg, 0.23 mmol), nickel acetate (35 mg, 0.2 mmol), and catalytic amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 3 ml of *n*-pentanol was heated under nitrogen for 24 h under reflux. The cooled blue-green solution was poured into methanol/water (5:1; 50 ml), and the precipitate formed was centrifuged, washed with methanol, and dried in vacuo. The separation of the prepared compounds was performed by column chromatography with toluene/hexane (1:1). The fractions were collected and the solvent evaporated. The order of elution was **7a**, **5a**, **6a**, **4a**, and **3a**.

(2,3,9,10,16,17,23,24-Octapentoxyphthalocyaninato)nickel(II) (**3a**): Yield 9 mg (1.6%). – ^{1}H NMR: δ = 1.04–1.23 (m, 40H, CH_2 and CH_3), 1.66 (m, 16H, CH_2), 1.83 (m, 16H, CH_2), 2.19 (m, 16H, CH_2), 4.49 (t, 16H, CH_2), 8.12 (s, 8H, arom.). – IR: $\tilde{\nu}$ = 2955 cm^{-1}, 2934, 2860, 1608, 1531, 1501, 1481, 1466, 1429, 1391, 1362, 1279, 1204, 1105, 1074, 1063, 926, 851, 748. – UV: See Table 2. – FD-MS, *m/z*: 1260.3 [M^+]. – $C_{72}H_{96}N_8NiO_8$ (1260.3): calcd. C 68.6, H 7.7, N 8.9; found C 68.4, H 8.0, N 9.2. – R_f (toluene): 0.03.

(2,3,9,10,16,17-Hexapentoxy-22,23,24,25-tetraphenylphthalocyaninato)nickel(II) (**4a**): Yield 15 mg (2.3%). – ^{1}H NMR: δ = 1.05 (m, 18H, CH_3), 1.55–1.73 (m, 24H, CH_2), 2.13 (m, 12H, CH_2), 4.12 (t, 4H, CH_2), 4.44 (m, 8H, CH_2), 6.96–7.65 (m, 22H, arom.), 8.37 (d, 4H, arom.). – IR: $\tilde{\nu}$ = 3055 cm^{-1}, 2957, 2932, 2870, 1605, 1460, 1435, 1394, 1362, 1273, 1263, 1207, 1109, 1063, 1024, 804, 746, 698. – UV: see Table 2. – FD-MS, *m/z*: 1392.4 [M^+]. – $C_{86}H_{92}N_8NiO_6 \cdot 2\ H_2O$ (1428.5): calcd. C 72.3, H 6.8, N 7.8; found C 72.1, H 7.1, N 7.4. – R_f (toluene): 0.09.

(2,3,16,17-Tetrapentoxy-8,9,10,11,22,23,24,25-octaphenylphthalocyaninato)nickel(II) (**5a**): Yield 7.5 mg (1.4%). – ^{1}H NMR: δ = 1.05 (m, 12H, CH_3), 1.49–1.69 (m, 16H, CH_2), 2.05 (m, 8H, CH_2), 4.19 (t, 8H, CH_2), 6.82–7.66 (m, 44H, arom.). – IR: $\tilde{\nu}$ = 3055 cm^{-1}, 3026, 2954, 2927, 2856, 1502, 1493, 1443, 1362, 1273, 1258, 1126, 1107, 1072, 1061, 1026, 1001, 800, 745, 696. – UV: see Table 2. – FD-MS, *m/z*: 1524.5 [M^+]. – $C_{100}H_{88}N_8NiO_4 \cdot 2\ H_2O$ (1560.6): calcd. C 77.0, H 5.9, N 7.2; found C 76.0, H 6.0, N 6.6. – R_f (toluene): 0.30.

(2,3,9,10-Tetrapentoxy-15,16,17,18,22,23,24,25-octaphenylphthalocyaninato)nickel(II) (**6a**): Yield 2 mg (0.5%). – ^{1}H NMR: δ = 1.02 (m, 12H, CH_3), 1.47–1.73 (m, 16H, CH_2), 2.09 (m, 8H, CH_2), 4.26 (t, 4H, CH_2), 4.44 (t, 4H, CH_2), 6.63–7.70 (m, 22H, arom.), 8.62 (s, 2H, arom.). – IR: $\tilde{\nu}$ = 3057 cm^{-1}, 3026, 2955, 2928, 2856, 1603, 1524, 1483, 1458, 1439, 1364, 1273, 1261, 1111, 1063, 1026, 698. – UV: see Table 2. – FD-MS, *m/z*: 1524.5 [M^+]. – $C_{100}H_{88}N_8NiO_4 \cdot 2\ H_2O$ (1560.6): calcd. C 77.0, H 5.9, N 7.2; found C 76.8, H 5.8, N 7.4. – R_f (toluene): 0.20.

(2,3-Dipentoxy-8,9,10,11,15,16,17,18,22,23,24,25-dodecaphenylphthalocyaninato)nickel(II) (**7a**): Yield 0.5 mg (0.1%). – ^{1}H NMR: δ = 1.02–1.68 (m, 14H, CH_2 and CH_3), 2.01 (m, 8H, CH_2), 4.17 (t, 4H, CH_2), 6.56–7.58 (m, 62H, arom.). – IR: $\tilde{\nu}$ = 3055 cm^{-1}, 3028, 2926, 2856, 1601, 1493, 1452, 1443, 1362, 1275, 1252, 1186, 1115, 1072, 1026, 748, 696. – UV: see Table 2. – FD-MS, *m/z*: 1556.7 [M^+]. – R_f (toluene): 0.39.

Preparation and Separation of Compounds **3b**–**7b**: The syntheses were carried out according to the above procedure; the amounts of the reactants were as follows: tetraphenylphthalonitrile (**1**) (100 mg, 0.23 mmol), 4,5-diheptylphthalonitrile (**2b**) (75 mg, 0.23 mmol), and nickel acetate (35 mg, 0.2 mmol). Eluent: toluene/hexane (1:2). The order of elution was **3b**, **4b**, **5b**, **6b**, and **7b**.

(2,3,9,10,16,17,23,24-Octaheptylphthalocyaninato)nickel(II) (**3b**): Yield 5 mg (0.8%). – ^{1}H NMR: δ = 0.9–1.1 (m, 24H, CH_3), 1.3–1.8 (m, 64H, CH_2), 2.0 (m, 16H, CH_2), 3.1 (t, 16H, CH_2), 8.77 (s, 8H, arom.). – IR: $\tilde{\nu}$ = 2955 cm^{-1}, 2922, 2853, 1535, 1466, 1420, 1377, 1332, 1109, 1084, 893, 752, 731. – UV: see Table 2. – FD-MS, *m/z*: 1356.7 [M^+]. – R_f (toluene/hexane, 1:1): 0.91.

(2,3,9,10,16,17-Hexaheptyl-22,23,24,25-tetraphenylphthalocyaninato)nickel(II) (**4b**): Yield 20 mg (3%). – ^{1}H NMR: δ = 0.99 (m, 18H, CH_3), 1.41–1.46 (m, 36H, CH_2), 1.59 (m, 12H, CH_2), 1.85 (m, 12H, CH_2), 2.94 (m, 12H, CH_2), 7.02–7.12 (m, 10H, arom.), 7.52–7.65 (m, 12H, arom.), 8.56 (d, 4H, arom.). – IR: $\tilde{\nu}$ = 3055 cm^{-1}, 2954, 2923, 2852, 1601, 1452, 1442, 1348, 1317, 1258, 1109, 1076, 756, 743, 696. – UV: see Table 2. – FD-MS; *m/z*: 1464.7 [M^+]. – R_f (toluene/hexane, 1:1): 0.73.

(2,3,16,17-Tetraheptyl-8,9,10,11,22,23,24,25-octaphenylphthalocyaninato)nickel(II) (**5b**): Yield 8 mg (1.1%). – ^{1}H NMR: δ = 0.90–0.95 (m, 20H, CH_2 and CH_3), 1.35–1.39 (br, 24H, CH_2), 1.77 (br, 8H, CH_2), 2.87 (t, 8H, CH_2), 6.94–7.10 (m, 20H, arom.), 7.49–7.65 (m, 20H, arom.), 7.78 (s, 4H, arom.). – IR: $\tilde{\nu}$ = 3082 cm^{-1}, 3053, 3026, 2953, 2924, 2853, 1601, 1524, 1441, 1362, 1254, 1111, 1070, 743, 696. – UV: see Table 2. – FD-MS, *m/z*: 1572.8 [M^+]. – R_f (toluene/hexane 1:1): 0.53.

(2,3,9,10-Tetraheptyl-15,16,17,18,22,23,24,25-octaphenylphthalocyaninato)nickel(II) (**6b**): Yield 3.5 mg (0.5%). – ^{1}H NMR: δ = 0.95–1.48 (br, 44H, CH_2 and CH_3), 1.87 (br, 8H, CH_2), 3.01 (m, 8H, CH_2), 6.94–7.53 (m, 40H, arom.), 7.88 (s, 2H, arom.), 8.94 (s, 2H, arom.). – IR: $\tilde{\nu}$ = 3084 cm^{-1}, 3055, 2951, 2926, 2856, 1601, 1442, 1252, 1186, 1113, 1072, 746, 696. – UV: see Table 2. – FD-MS, *m/z*: 1572.8 [M^+]. – R_f (toluene/hexane, 1:1): 0.47.

(2,3-Diheptyl-8,9,10,11,15,16,17,18,22,23,24,25-dodecaphenyl phthalocyaninato)nickel(II) (**7b**): Yield 2 mg (0.3%). – ^{1}H NMR: δ = 0.86–1.43 (br, 22H, CH_2 and CH_3), 1.59 (br, 4H, CH_2), 2.89 (t, 4H, CH_2), 6.61–7.56 (m, 60H, arom.), 7.76 (s, 2H, arom.). – IR: $\tilde{\nu}$ = 3057 cm^{-1}, 3028, 2955, 2926, 2854, 1601, 1508, 1497, 1443, 1364, 1254, 1186, 1117, 1072, 1026, 748, 696. – UV: see Table 2. – FD-MS, *m/z*: 1680.8 [M^+]. – R_f (toluene/hexane, 1:1): 0.22.

Preparation and Separation of Compounds **3c–7c**: The syntheses were carried out according to the above procedure; the amounts of reactants were as follows: tetraphenylphthalonitrile (**1**) (100 mg, 0.23 mmol), 3,6-dihexoxyphthalonitrile (**2c**) (76 mg, 0.23 mmol), and nickel acetate (35 mg, 0.2 mmol). Eluent: toluene/hexane (2:1). The order of elution was **7c**, **5c**, **6c**, **4c**, and **3c**.

(1,4,8,11,15,18,22,25-Octahexoxyphthalocyaninato)nickel(II) (**3c**): Yield 4 mg (0.6%). – ^{1}H NMR: δ = 0.88 (t, 24H, CH_3), 1.39 (m, 32H, CH_2), 1.58 (m, 16H, CH_2), 2.18 (m, 16H, CH_2), 4.74 (t, 16H, CH_2), 7.45 (s, 8H, arom.). – IR: $\tilde{\nu}$ = 2955 cm^{-1}, 2926, 2856, 1605, 1516, 1501, 1466, 1381, 1312, 1269, 1221, 1096, 1067, 920, 760, 743. – UV: see Table 2. – FD-MS, *m/z*: 1372.5 [M^+].

(1,4,8,11,15,18-Hexahexoxy-22,23,24,25-tetraphenylphthalocyaninato)nickel(II) (**4c**): Yield 12 mg (1.8%). – ^{1}H NMR: δ = 0.87 (m, 18H, CH_3), 1.23–1.47 (br, 36H, CH_2), 1.50–1.65 (m, 4H, CH_2), 2.12 (m, 8H, CH_2), 4.05 (t, 4H, CH_2), 4.67 (m, 8H, CH_2), 6.85–7.85 (m, 26H, arom.). – IR: $\tilde{\nu}$ = 3084 cm^{-1}, 3055, 2952, 2926, 2856, 1601, 1506, 1263, 1213, 1194, 1144, 1109, 1064, 1026, 804, 746, 696. – UV: see Table 2. – FD-MS, *m/z*: 1476.6 [M^+]. – R_f (toluene): 0.06.

(1,4,15,18-Tetrahexoxy-8,9,10,11,22,23,24,25-octaphenyl-phthalocyaninato)nickel(II) (**5c**): Yield 4.5 mg (0.6%). – ^{1}H NMR: δ = 0.77–0.81 (br, 12H, CH_3), 1.15–1.27 (br, 24H, CH_2), 1.56–1.65 (br, 8H, CH_2), 3.97 (t, 4H, CH_2), 6.91–7.41 (m, 44H, arom.). – IR: $\tilde{\nu}$ = 3080 cm^{-1}, 3055, 3026, 2953, 2924, 2854, 1601, 1506, 1283, 1263, 1211, 1188, 1117, 1101, 1084, 1024, 746, 696. – UV: see Table 2. – FD-MS, *m/z*: 1580.7 [M^+]. – R_f (toluene): 0.44.

(1,4,8,11-Tetrahexoxy-15,16,17,18,22,23,24,25-octaphenyl-phthalocyaninato)nickel(II) (**6c**): Yield 4 mg (0.5%). – ^{1}H NMR: δ = 0.75–0.85 (br, 12H, CH_3), 1.18–1.27 (br, 16H, CH_2), 1.29–1.39 (br, 8H, CH_2), 1.45–1.65 (br, 4H, CH_2), 2.09 (m, 4H, CH_2), 3.96 (t, 4H, CH_2), 4.59 (t, 4H, CH_2), 6.63–7.38 (m, 44H, arom.). – IR: $\tilde{\nu}$ = 3082 cm^{-1}, 3057, 3026, 2955, 2924, 2854, 1603, 1506, 1261, 1246, 1190, 1113, 1069, 1026, 800, 748, 696. – UV: see Table 2. – FD-MS, *m/z*: 1580.7 [M^+]. – R_f (toluene): 0.27.

(1,4-Dihexoxy-8,9,10,11,15,16,17,18,22,23,24,25-dodecaphenyl-phthalocyaninato)nickel(II) (**7c**): Yield 1.5 mg (0.2%). – ^{1}H NMR: δ = 0.8–2.0 (br, 22H, CH_2 and CH_3), 3.94 (t, 4H, CH_2), 6.59–7.36 (m, 62H, arom.). – IR: $\tilde{\nu}$ = 3082 cm^{-1}, 3055, 3026, 2959, 2922, 2853, 1601, 1502, 1261, 1186, 1111, 1026, 802, 748, 696. – UV: see Table 2. – FD-MS, *m/z*: 1684.7 [M^+]. – R_f (toluene): 0.63.

Preparation and Separation of Compounds **3d–7d**: The syntheses were carried out according to the above procedure; the amounts of the reactants were as follows: tetraphenylphthalonitrile (**1**) (100 mg, 0.23 mmol), 3,6-diheptylphthalonitrile (**2d**) (75 mg, 0.23 mmol), nickel acetate (35 mg, 0.2 mmol). Eluent: toluene/hexane (1:3). The order of elution were **3d**, **4d**, **6d**, **5d**, and **7d**.

(1,4,8,11,15,18,22,25-Octaheptylphthalocyaninato)nickel(II) (**3d**): Yield 3 mg (0.5%). – ^{1}H NMR: δ = 0.72–0.82 (m, 24H, CH_3), 1.14–1.35 (br, 48H, CH_2), 1.41–1.53 (br, 16H, CH_2), 1.95 (m, 16H, CH_2), 4.26 (t, 16H, CH_2), 7.69 (s, 8H, arom.). – IR: $\tilde{\nu}$ = 2957 cm^{-1}, 2924, 2854, 1514, 1466, 1325, 1261, 1180, 1099, 1024, 802, 760. – UV: see Table 2. – FD-MS, *m/z*: 1356.7 [M^+]. – R_f (toluene/hexane, 1:1): 0.89.

(1,4,8,11,15,18-Hexaheptyl-22,23,24,25-tetraphenyl-phthalocyaninato)nickel(II) (**4d**): Yield 8 mg (1.2%). – ^{1}H NMR: δ = 0.64–1.51 (br, 70H, CH_2 and CH_3), 1.95 (m, 8H, CH_2), 2.74 (t, 4H, CH_2), 4.25 (m, 8H, CH_2), 6.86–7.44 (m, 22H, arom.), 7.60 (d, 2H, arom.), 7.71 (s, 2H, arom.). – IR: $\tilde{\nu}$ = 3082 cm^{-1}, 3057, 3024, 2953, 2924, 2853, 1510, 1462, 1443, 1333, 1312, 1261, 1186, 1101, 1026, 748, 696. – UV: see Table 2. – FD-MS, *m/z*: 1464.7 [M^+]. – R_f (toluene/hexane, 1:1): 0.75.

(1,4,15,18-Tetraheptyl-8,9,10,11,22,23,24,25-octaphenyl-phthalocyaninato)nickel(II) (**5d**): Yield 4 mg (0.6%). – ^{1}H NMR: δ = 0.66 (t, 12H, CH_3), 0.97–1.52 (br, 40H, CH_2), 2.66 (t, 8H, CH_2), 6.86–7.42 (m, 44H, arom.). – IR: $\tilde{\nu}$ = 3080 cm^{-1}, 3055, 3022, 2961, 2922, 2851, 1510, 1441, 1261, 1211, 1186, 1097, 1024, 800, 746, 696. – UV: see Table 2. – FD-MS, *m/z*: 1572.8 [M^+]. – R_f (toluene/hexane, 1:1): 0.43.

(1,4,8,11-Tetraheptyl-15,16,17,18,22,23,24,25-octaphenyl-phthalocyaninato)nickel(II) (**6d**): Yield 4 mg (0.6%). – ^{1}H NMR: δ = 0.67–1.68 (br, 48H, CH_2 and CH_3), 1.93 (m, 4H, CH_2), 2.69 (t, 4H, CH_2), 4.18 (t, 4H, CH_2), 6.71–7.34 (m, 40H, arom.), 7.40 (d, 2H, arom.), 7.55 (d, 2H, arom.). – IR: $\tilde{\nu}$ = 3082 cm^{-1}, 3055, 3024, 2953, 2922, 2851, 1460, 1441, 1261, 1186, 1136, 1101, 1026, 800, 748, 696. – UV: see Table 2. – FD-MS, *m/z*: 1572.8 [M^+]. – R_f (toluene/hexane, 1:1): 0.51.

(1,4-Diheptyl-8,9,10,11,15,16,17,18,22,23,24,25-dodecaphenyl-phthalocyaninato)nickel(II) (**7d**): Yield 2.5 mg (0.3%). – ^{1}H NMR: δ = 0.67–1.53 (br, 26H, CH_2 and CH_3), 2.62 (br, 4H, CH_2), 6.63–7.33 (m, 62H, arom.). – IR: $\tilde{\nu}$ = 3080 cm^{-1}, 3055, 3024, 2953, 2922, 2851, 1601, 1497, 1441, 1256, 1184, 1111, 1070, 1026, 748, 696. – UV: see Table 2. – FD-MS, *m/z*: 1680.8 [M^+]. – R_f (toluene/hexane, 1:1): 0.18.

☆ Dedicated to Professor E. Lindner on the occasion of his 60th birthday.

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