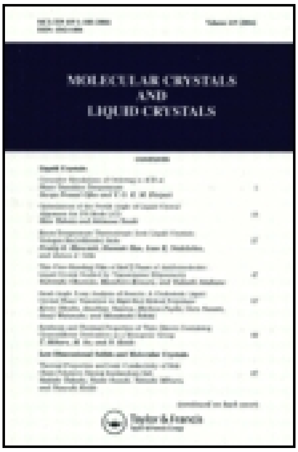

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Soluble Octasubstituted (Phthalocyaninato) Metal Complexes

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Soluble Octasubstituted (Phthalocyaninato) Metal Complexes

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Long chain substituted phthalocyanines are increasingly of interest because of their high solubility in common organic solvents and their liquid crystalline properties. 2,3,9,10,16,17,23, 24-Octakis(decyloxy)phthalocyaninatonickel(II) (**1**), -palladium(II) (**2**) and -platinum(II) (**3**) were synthesized by reacting 1,2-dicyano-4,5-bis(decyloxy)benzene with the corresponding metal(II) salts and their liquid crystalline properties were investigated. Similarly, 1,4,8,11,15,18,22,25- (**4**) and 2,3,9,10,16,17,23,24-octakis(heptyl)phthalocyaninatonickel(II) (**5**) were prepared and their properties were compared. Compound **4** was investigated in detail with respect to its electrochemical properties.

Keywords: Phthalocyanines, DSC, cyclovoltammetry, spectroelectrochemistry.

INTRODUCTION

Transition metalphthalocyanines (PcM), their bisaxially coordinated complexes $PcM(L)_2$ and bridged systems $[PcM(L)]_n$ (L = *e.g.*, diisocyanobenzene, pyrazine, tetrazine) have been investigated intensively by us with respect to their electrical properties.[1] The isotype of bridged macrocyclic metal complexes, either with or without doping, exhibit good semiconducting properties. By appropriate substitution in the peripheral positions of the macrocycle these compounds can be made soluble in common organic solvents.[2–4] They are then suitable for producing LB-films[5] and non-linear optical materials.[6] Long chain substituted phthalocyanines are increasingly of interest because of their high solubility in organic solvents and their liquid crystalline properties,[7] i.e. formation of discotic mesophases.

In this paper we report the synthesis and characterization of 2,3,9,10,16,17,23,24-octakis(decyloxy)phthalocyaninatonickel(II) (1), -palladium(II) (**2**) and -platinum(II) (**3**). Furthermore the synthesis of 1,4,8,11,15,18,22,25- (**4**) and 2,3,9,10,16,17,23,24-octakis(heptyl)phthalocyaninatonickel (5) is described. Compound **4** was investigated in detail with respect to its electrochemical properties.

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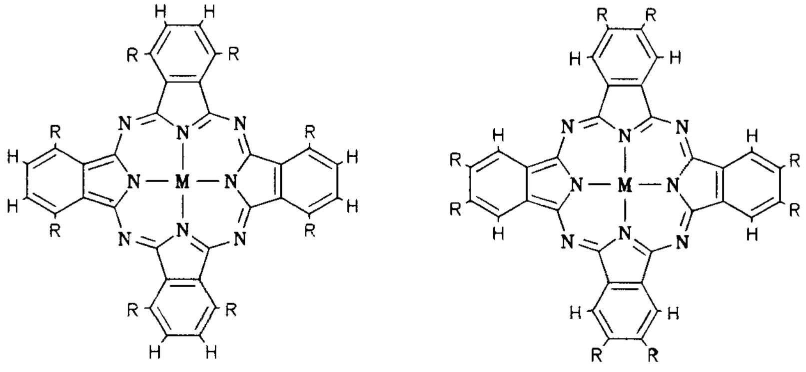
[1] To whom correspondence should be addressed.



(a) (b)

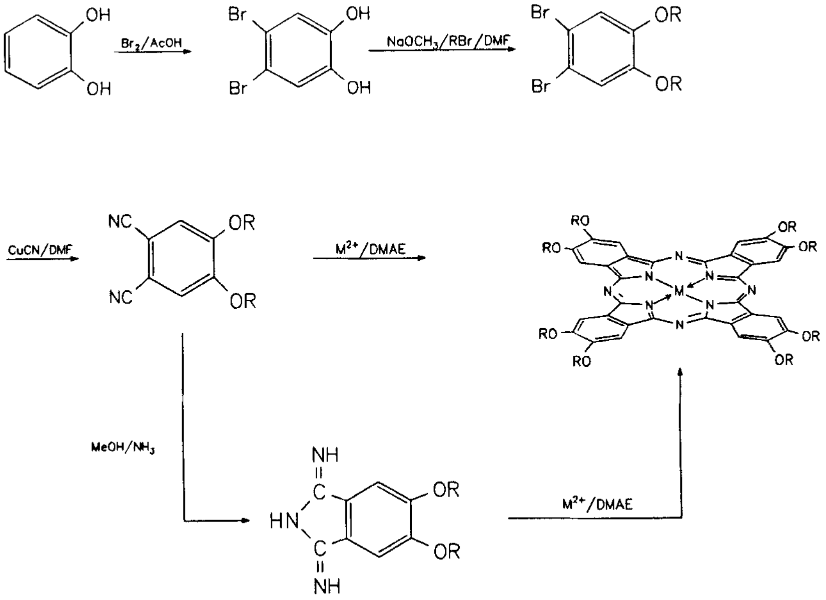
FIGURE 1 a) 1,4,8,11,15,18,22,25-octasubstituted metalphthalocyanine, b) 2,3,9,10,16,17,23,24-octasubstituted metalphthalocyanine.

RESULTS AND DISCUSSION

Syntheses

1–**3** were synthesized by reacting 1,2-dicyano-4,5-bis(decyloxy)benzene[4] with nickel(II)acetate-tetrahydrate, palladium(II)acetylacetonate (Pd(acac)$_2$) and platinum(II)chloride, respectively in N,N-dimethylaminoethanol (DMAE) (Scheme 1). Compounds **4** and **5** were prepared by refluxing a solution of nickel(II)acetate-tetrahydrate with the appropriate dinitrile[8–10] in *n*-pentanol in the presence of DBU (Scheme 2 + 3) adapting the procedure used for preparing phthalocyanines.[11] Compounds **1**–**5** were characterized by NMR-, IR- and UV/Vis-spectroscopy and by elemental analyses (see Experimental). The absorption spectra of **1**–**5** in $CHCl_3$ are typical for divalent metal complexes of phthalocyanines. They are dominated by the π-π^*-transitions within the heteroaromatic 18-π-electron system. The data are given in Table 1. In comparison to compound **5**, a bathochromic shift of the UV/Vis spectrum of **4** is observed.

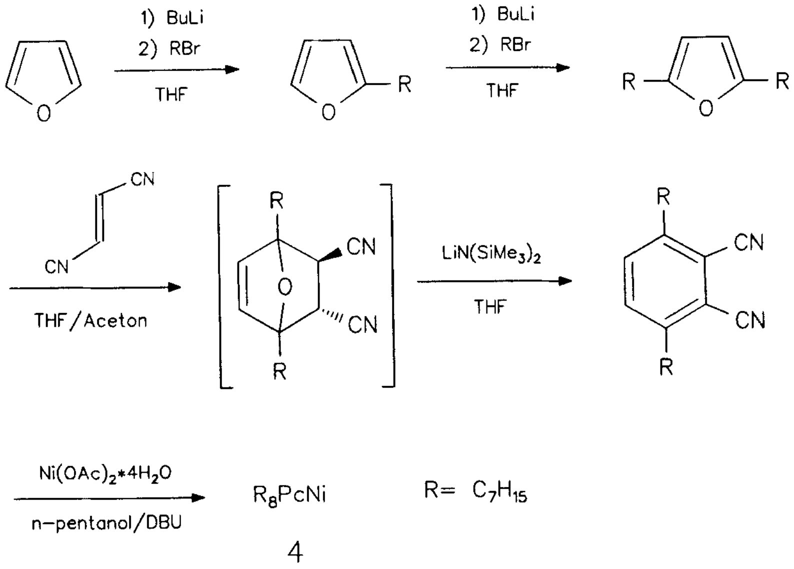
Compounds **1**–**5** are soluble in common organic solvents, *e.g.*, chloroform and toluene. In comparison to alkoxy substituted phthalocyanines, the solubility of *n*-alkyl substituted ones is lower. One reason for this is the better interaction of solvent molecules and the oxygen atom in the side chain of the former. Accordingly, the solubility of **5** is too low to obtain a NMR spectrum in solution. In comparison to this, compound **4** is highly soluble in nonpolar organic solvents, even in petroleum ether (bp 30–50 °C). The reason is the molecular structure of **4**. X-ray diffraction studies of $(C_6H_{13})_8PcH_2$[12] showed that six of the alkyl chains are approximately in the plane of the ring, whereas the remaining two alkyl chains are out of plane and act as spacers between molecules in the packing (stack). The distance between the macrocycles is increased and the solubility in organic solvents raises drastically.



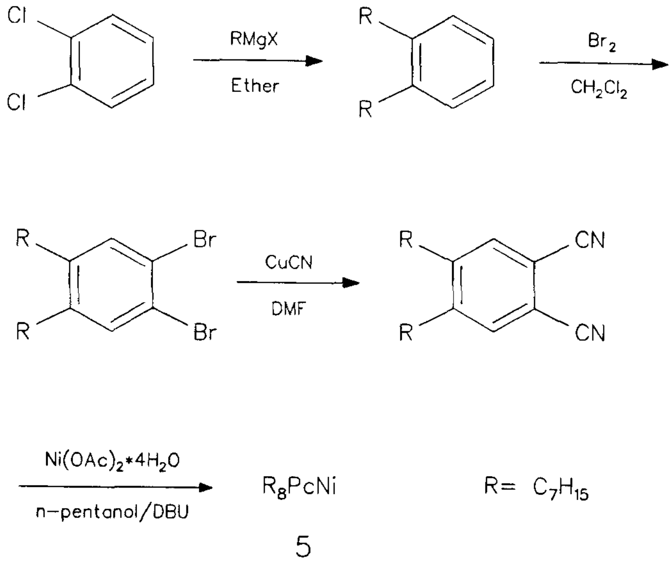
M= Ni, Pd, Pt
1 2 3

R= $C_{10}H_{21}$

SCHEME 1



SCHEME 2



SCHEME 3

TABLE 1

UV/Vis-spectra ($CHCl_3$) of **1**–**5**

Compound	λ [nm]						
1	673	644	607	412	314	293	
2	664	637	602	414	327sh	296	
3	655	631	592	412	314sh	295	
4	707	672	638	386sh	346	305	
5	684	651	616	374	337	300	279

DSC-Measurements

2, 3, 9, 10, 16, 17, 23, 24-Octasubstituted phthalocyanine derivatives are well known to exhibit thermotropic liquid crystalline behaviour.[13] Above the solid-mesophase transition temperature the rigid planar phthalocyanines stack into hexagonally arranged columns (discotic mesophase).[14,15] Cook *et al.*,[16,17] reported that 1, 4, 8, 11, 15, 18, 22, 25-octaalkylated phthalocyanines also exhibit mesomorphic behaviour although the occurrence of the columnar mesophases in these compounds is unexpected in view of the position and nature of the substituents.

The transition temperatures of compounds **1**–**5** from the crystalline to the discotic mesophase are given in Table 2. Although a transition temperature of 118 °C has been reported for **4**,[17] to our knowledge the synthesis and characterization have not been published yet. The transition temperatures of **4** and **5** show that these temperatures are strongly dependent on the position of the substituents. They increase from 1, 4, 8, 11, 15, 18, 22, 25,- to 2, 3, 9, 10, 16, 17, 23, 24-substitution.

TABLE 2

Transition temperatures from the crystalline (K) to the discotic mesophase (M) [°C]

compound	K→M	compound	K→M
1	87	**4**	111
2	90	**5**	203
3	64		

TABLE 3

Redox potentials (halfstep potentials) of 4 in $CH_2Cl_2/(Bu)_4NPF_6$ vs. SCE [V].

$E_{1/2}$(O1)	$E_{1/2}$(O2)	$E_{1/2}$(R1)	$E_{1/2}$(R2)
0.59 V	1.27 V	− 1.05 V	− 1.47 V

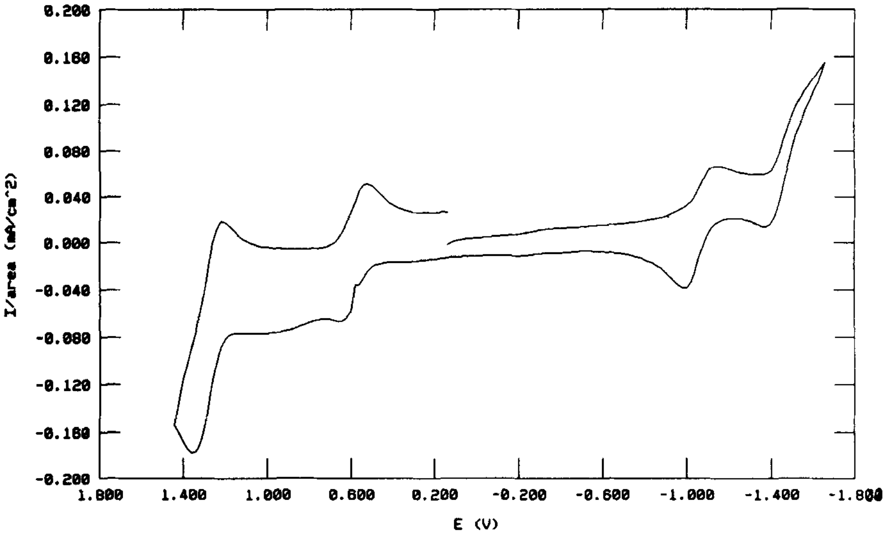


FIGURE 2 Cyclovoltammogram of **4** in $CH_2Cl_2/(Bu)_4NPF_6$ (scan rate: 100 mV/s).

Electrochemical Investigations of $(C_7H_{15})_8$PcNi(4)

The redox potentials obtained and shown in Table 3 were interpreted by spectroelectrochemical investigations.

As shown in Figure 2 the first and the second oxidation of **4** is quasireversible electron-transfer, with $\Delta E = 105$ mV.

Similar to the oxidations of ZnPc[18] the first and second oxidation of **4** at 0.59 V and 1.27 V were ascribed to the oxidation of the macrocycle. As shown in Figure 3 for the first oxidation we observed bands in the UV/Vis-spectrum at 970, 885, 760, 650, 482 nm and for the second oxidation at 670, 630, 475 nm.

For the first reduction of **4** we obtained a UV/Vis-spectrum similar to the spectrum of $[(SO_3^-)_4PcNi]$:[5-19] bands at 970, 890, 690, 650, 603, 475 and 414 nm, (see Fig. 4). It

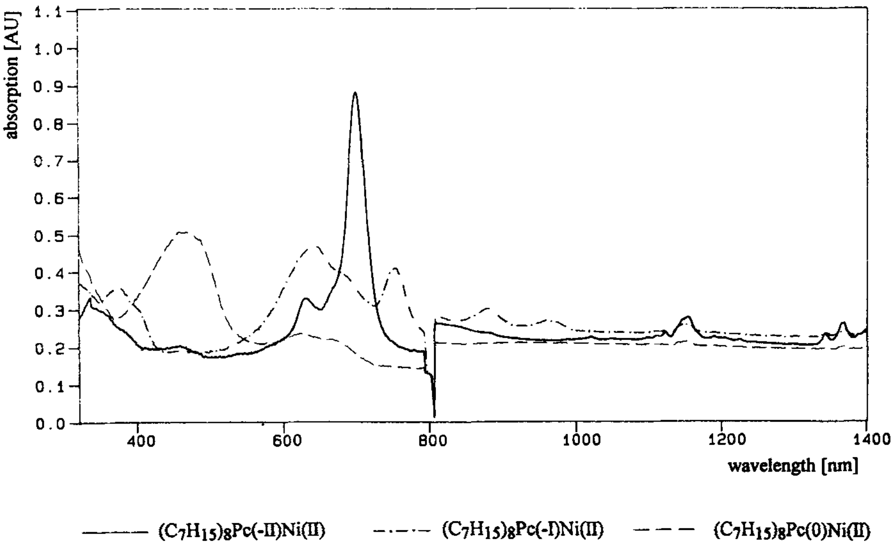


FIGURE 3 UV/Vis-spectrum of **4** in CH_2Cl_2 (1st and 2nd oxidation).

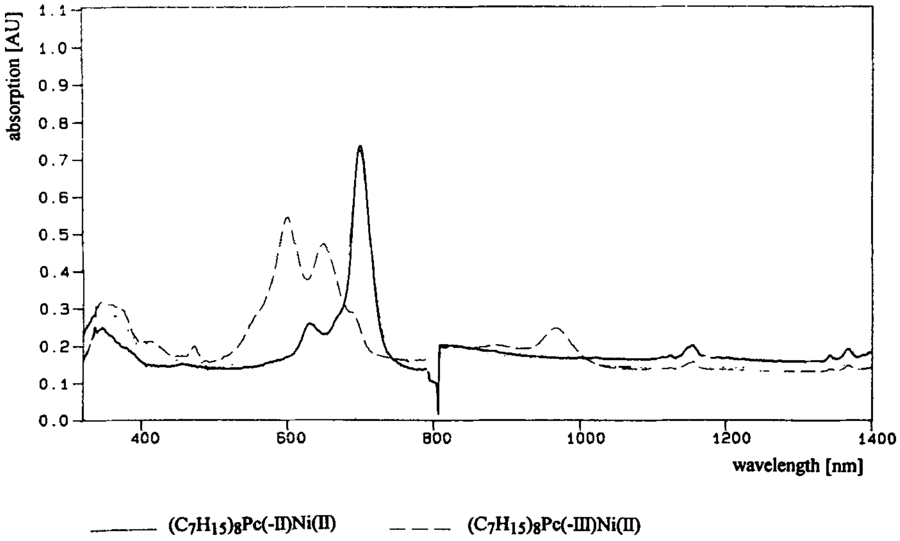


FIGURE 4 UV/Vis-spectrum of **4** in CH_2Cl_2 (1st reduction).

was not possible to obtain an UV/Vis-spectrum for the second reduction of **4**, because of the experimental limitations of the potentiostate used and in CV the second reduction appears at the solvent limit so that only the anodic signal of the reduction is seen.

According to[19] both reductions are ascribed to the reduction of the macrocycle. Because of the fact that the reduction and the oxidation is an electron-transfer reaction within the macrocycle the difference of anodic- and cathodic potentials should correlate with the *Q*-band of **4** ($707\,\text{nm} = 1.75\,\text{eV} = \Delta E_{\text{HOMO-LUMO}}$). We obtained $\Delta E = \Delta E_{\text{Ox/An.}} + |\Delta E_{\text{Red/Cat.}}| = 1.75\,\text{V}$ at a scan rate of 20 mV/s in $CH_2Cl_2/(Bu)_4NPF_6$.

EXPERIMENTAL

The IR spectra were recorded on a Bruker FT-IR, the ^1H and ^{13}C NMR spectra on a Bruker AC 250, the ^{13}C NMR CP/MAS spctrum on a Bruker MSL 200 and the UV/Vis spectra on a Shimadzu 365. Elemental analyses were carried out with Carlo Erba Elemental Analyzers 1104 and 1106. Detection of phase transitions and measurement of transition temperature were made using a Mettler DSC 30, with a heating rate of 10°C/min.

Electrochemical measurements were carried out under argon by using a three-electrode cell. They were performed with a EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273. A platinumdisc-electrode and a platinum sheet were used as working- and counterelectrode. A silver wire and the ferricenium/ferrocene couple as internal references was used as reference electrode. The measurements were correlated versus SCE. The solvent was stirred over P_2O_5 for several hours and then destilled two times under argon.

Spectroelectrochemical measurements were carried out under argon by using a three-electrode cell with cooling of the solvent. They were performed with a Jaissle potentiostat model 1001 T-NC and an Shimadzu UV-Vis-NIR-spectrophotometer model UV-365. An ITO-glas, a platinum sheet and a silver-wire were used as working-, counter- and reference-electrode. The purification of the solvent was carried out in the same way as above.

1,2-Dicyano-4,5-bis(decyloxy)benzene,[4] 1,2-dicyano-3,6-bis(heptyl)benzene[8] and 1,2-dicyano-4,5-bis(heptyl)benzene[9,10] were prepared as described in the literature.

2,3,9,10,16,17,23,24-Octakis(decyloxy)phthalocyaninatonickel(II) (1)

A mixture of 1,2-dicyano-4,5-bis(decyloxy)benzene (880 mg, 0.2 mmol), $Ni(OAc)_2$ $4H_2O$ (248 mg, 0.1 mmol) and a catalytic amount of DBU was heated under nitrogen in DMAE (8 ml) for 18 h under reflux. After cooling the solution was poured into methanol/water 1:1 (50 ml). The precipitate was centrifuged, washed several times with acetone and dried. Further purification was done by column chromatography ($Al_2O_3/CHCl_3$). Yield: 256 mg (28%).

$C_{112}H_{176}N_8O_8Ni$	calc.	C 73.86	H 9.74	N 6.15
(1821.4)	found	C 72.43	H 9.26	N 5.82

^1H NMR ($CDCL_3$): 8.05 (*s*, 8H), 4.43 (*t*, 16H), 2.13 (*m*, 6H), 1.75 (*m*, 16H), 1.42-1.25 (*m*, 96H), 0.87 (*t*, 24H) ppm.
IR (KBr): 750*w*, 852*w*, 1074*w*, 1107*s*, 1164*w*, 1204*m*, 1279*s*, 1362*w*, 1389*m*, 1429*m*, 1466*s*, 1501*m*, 1533*w*, 1609*w*, 2851*s*, 2922*s* cm^{-1}.
UV/Vis ($CHCl_3$): see Table 1

2,3,9,10,16,17,23,24-Octakis(decyloxy)phthalocyaninatopalladium(II) (2)

A mixture of 1,2-dicyano-4,5-bis(decyloxy)benzene (1.22 g, 3 mmol), $Pd(acac)_2$ (228 mg, 0.75 mmol) and a catalytic amount of DBU was heated under nitrogen in DMAE (7 ml) for 12 h under reflux. After cooling the solution was poured into methanol/water 1:1 (50 ml), the precipitate was centrifuged and washed several times with acetone. Further purification was done by column chromatography ($Al_2O_3/CHCl_3$). Yield: 420 mg (30%).

$C_{112}H_{176}N_8O_8Pd$	calc.	C 71.98	H 9.49	N 6.00
(1869.02)	found	C 71.37	H 10.04	N 5.49

^1H NMR ($CDCl_3$): 8.2 (*s*, 8H), 4.49 (*t*, 16H), 2.16 (*m*, 16H), 1.77 (*m*, 16H), 1.45-1.25 (m, 96H), 0.87-0.81 (*t*, 24H) ppm.
IR (KBr): 746*w*, 852*w*, 1074*m*, 1116*m*, 1164*w*, 1203*m*, 1280*S*, 1357*w*, 1384*s*, 1419*m*, 1465*s*, 1510*m*, 1608*w*, 2850*s*, 2920*s* cm^{-1}.
UV/Vis ($CHCl_3$): see Table 1.

2,3,9,10,16,17,23,24-Octakis(decyloxy)phthalocyaninatoplatinum(II) (3)

1,2-Dicyano-4,5-bis(decyloxy)benzene (880 mg, 2 mmol), $PtCl_2$ (142 mg, 0.53 mmol) and a catalytic amount of DBU were added to DMAE (8 ml) and refluxed under nitrogen for 24 h. The cooled solution was poured into a mixture of methanol/water 1:1 (50 ml) and the precipitate was centrifuged, washed with acetone and dried. The crude product was purified by column chromatography b ($Al_2O_3/CHCl_3$). Yield: 120 mg (11%).

$C_{112}H_{176}N_8O_8Pt$	calc.	C 68.71	H 9.06	N 5.72
(1957.8)	found	C 68.92	H 9.29	N 5.25

^1H NMR ($CDCl_3$): 8.11 (*s*, 8H), 4.49 (*t*, 16H), 2.17 (*m*, 6H), 1.78 (*m*, 16H), 1.40-1.28 (*m*, 96H), 0.87 (*t*, 24H) ppm.
IR (KBr): 748*w*, 851*w*, 1074*m*, 1121*m*, 1173*w*, 1204*m*, 1283*s*, 1358*w*, 1387*m*, 1423*s*, 1464*s*, 1512*m*, 1610*w*, 2851*s*, 2922*s* cm^{-1}.
UV/Vis ($CHCl_3$): see Table 1.

1,4,8,11,15,18,22,25-Octakis(heptyl)phthalocyaninatonickel(II) (4)

A mixture of 1,2-dicyano-3,6-bis(heptyl)benzene (324 mg, 1 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (75 mg, 0.3 mmol) and DBU (152 mg, 1 mmol) was heated under nitrogen in *n*-pentanol (15 ml) for 48 h under reflux. The cooled solution was poured into methanol (50 ml) and the precipitate was centrifuged, washed with ethyl acetate and ethanol and dried.

Further purification was done by column chromatography (silica/toluene) and recrystallisation from ethyl acetate, yielding 68 mg (20%) **4** as a green powder.

$C_{88}H_{128}N_8O_8Ni$	calc.	C 77.91	H 9.51	N 8.26
(1356.7)	found	C 78.42	H 9.79	N 8.18

^1H NMR ($CDCl_3$): 7.63 (*s*, 8H), 4.21 (*t*, 16H), 1.94 (*m*, 16H), 1.47 (*m*, 16H), 1.35-1.05 (*m*, 48H), 0.78 (*t*, 24H) ppm.
^{13}C NMR ($CDCl_3$): 146.6 (C-1), 137.5 (C-3), 134.4 (C-2), 129.7 (C-4), 32.6, 31.8, 30.3, 29.5, 29.4, 22.6 (CH_2), 13.9 (CH_3) ppm.
IR (KBr): 723*w*, 760*w*, 802*m*, 926*w*, 1024*m*, 1099*s*, 1180*m*, 1261*s*, 1325*m*, 1377*w*, 1421*w*, 1466*m*, 1514*m*, 1574*w*, 1607*w*, 2854*vs*, 2924*vs*, 2957*vs* cm^{-1}.
UV/Vis ($CHCl_3$): see Table 1.

2,3,9,10,16,17,23,24-Octakis(heptyl)phthalocyaninatonickel(II) (5)

A mixture of 1,2-dicyano-4,5-bis(heptyl)benzene (1.25 g, 3.86 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (288 mg, 1.15 mmol) and DBU (608 mg, 4 mmol) was heated under nitrogen *n*-pentanol (50 ml) for 48 h under reflux. After cooling, to this mixture ethanol (150 ml) was added and the refluxing continued for 1 h. The mixture was filtered and the residue was washed with water, ethanol, acetone and ether to afford **5** (288 mg, 22%) as a blue powder.

$C_{88}H_{128}N_8O_8Ni$	calc.	C 77.91	H 9.51	N 8.26
(1356.7)	found	C 78.06	H 9.86	N 8.14

^{13}C (CP/MAS): 143.86 (C-1), 140.18 (C-4), 136.57 (C-2), 131.57 (C-3), 32.54-14.17 (heptyl-groups) ppm.
IR (KBr): 731*w*, 752*w*, 893*m*, 1084*m*, 1109*s*, 1333*m*, 1377*w*, 1420*m*, 1466*m*, 1535*m*, 1622*w*, 2853*s*, 2922*s*, 2955*s* cm^{-1}.
UV/Vis ($CHCl_3$): see Table 1.

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