Synthesis of Hexadecaalkyl-Substituted Metal Phthalocyanines

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Abstract: Hexadecaalkyl-substituted nickel phthalocyanines **11** and **12** and a bisaxially coordinated hexadecaalkyl-substituted ruthenium phthalocyanine **13** were synthesized from the corresponding tetraalkylphthalodinitriles **9** and **10**, respectively, and metal chlorides. The obtained phthalocyanines show excellent solubility in aprotic organic solvents. Their spectral and electrochemical properties are discussed.

Key words: hexadecaalkyl-substituted metal phthalocyanines, tetraalkylphthalodinitriles, UV/Vis spectroscopy, electrochemistry

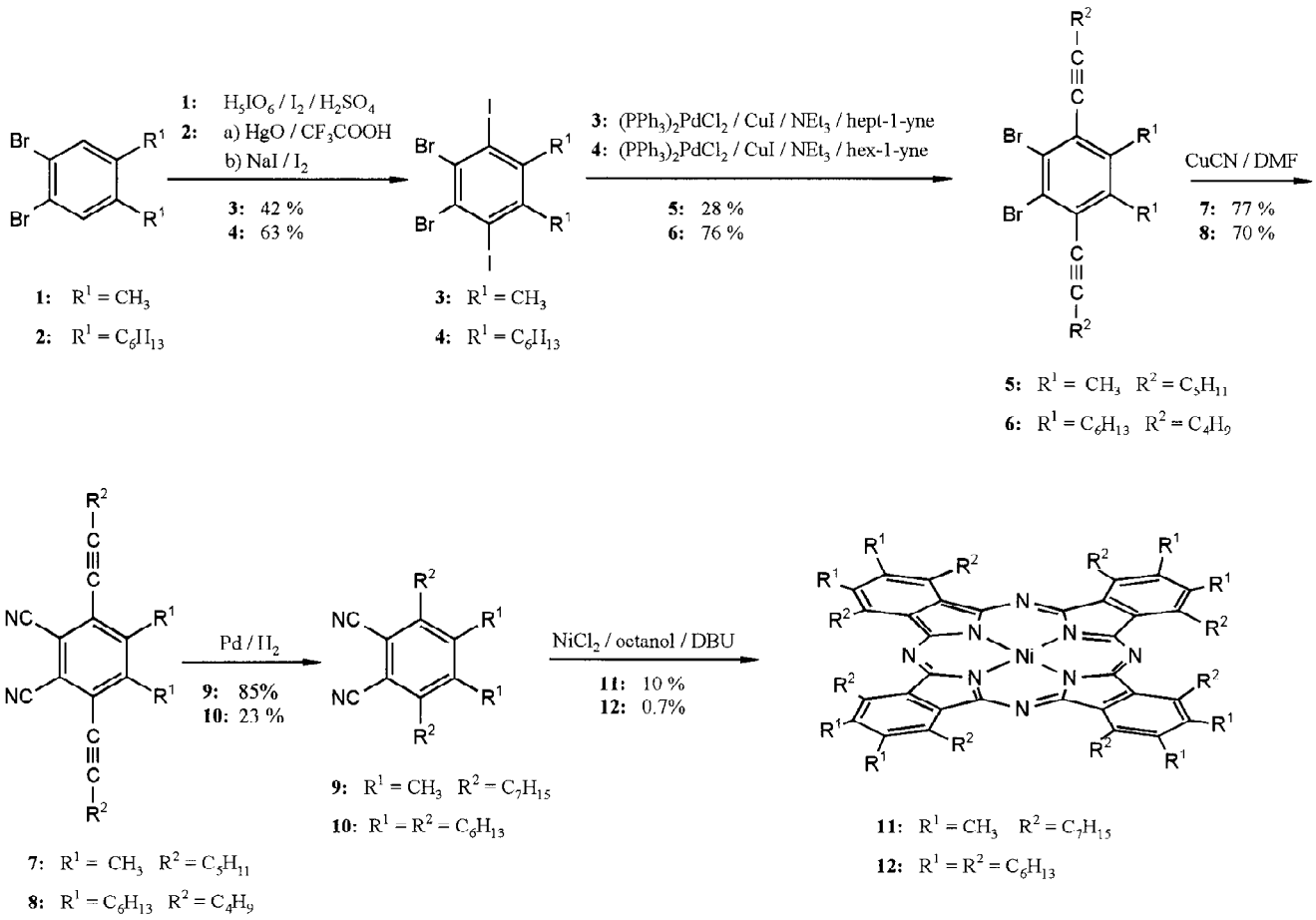
Phthalocyanines are interesting compounds for various applications in material science.[1] Due to intermolecular interactions between the macrocycles, peripherally unsubstituted phthalocyanines are practically insoluble in common organic solvents. The introduction of bulky substituents in the peripheral positions of the macrocycle drastically increases their solubility in organic solvents[1] extending actual and potential fields of their technology. Hence tetra- and octasubstituted phthalocyanines[2] have been intensively studied, among which tetrasubstituted macrocycles exhibit usually a higher solubility than octasubstituted derivatives.

Beside solubility, the spectral and electrochemical properties of phthalocyanines are also strongly influenced by peripheral substituents on the macrocycles. Hence the electronic structure of the phthalocyanine core is most affected in the case of fully substituted, i.e. hexadecasubstituted phthalocyanines. Compared to tetra- and octasubstituted metal phthalocyanines the substituent effects of hexadecasubstituted phthalocyanines are relatively less well-studied. Recently we reported the synthesis and characterization of hexadecaalkoxy-substituted metal phthalocyanines.[3] We found that these fully substituted highly soluble macrocycles show interesting optical and electrochemical properties.[3,4] However, to the best of our knowledge, hexadecaalkyl-substituted metal phthalocyanines $R_{16}PcM$ are unknown in the literature probably due to the difficult accessibility of the tetraalkyl-substituted phthalodinitriles[5] as precursors.

Moreover, starting with tetraalkyl-substituted phthalodinitriles the bulky alkyl substituents make the phthalocyanine formation more difficult, especially when the substituents are located in the 1,4-position of the phthalocyanine core as shown in the case of octasubstituted derivatives.[6,7] Complete peripheral substitution of the phthalocyanine core with alkoxy groups lowers the yield of phthalocyanine formation but, nevertheless, these fully substituted phthalocyanines were still obtained in a yield of up to 20%.[3]

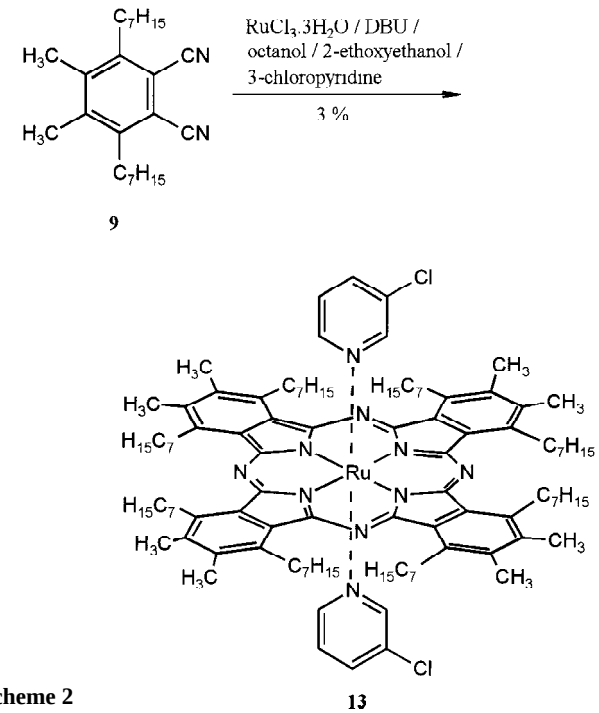
We report here for the first time the synthesis and characterization of tetraalkylphthalodinitriles with different (**9**) and identical **10** alkyl groups and their conversion to the hexadecaalkyl-substituted nickel phthalocyanines $PcNi(C_7H_{15})_8(CH_3)_8$ **11** and $PcNi(C_6H_{13})_{16}$ **12** (Scheme 1). Full substitution of the phthalocyanine with long rather than short chains as in **12** was preferred due to the expected higher solubility of this macrocycle, but due to the bulkiness of the substituents we obtained **12** only in low yield. Assuming that the electronic properties of the phthalocyanines are only little effected by the chain length of the substituents, we synthesized the hexadecaalkyl-substituted phthalocyanine **11** with heptyl substituents in the 1,4-positions and the smaller, methyl substituents in the 2,3-positions, respectively. It was found that the lower steric requirement of the methyl substituents facilitates phthalocyanine formation in the case of phthalocyanine **11**. The synthesis and characterization of the hexadecaalkyl-substituted ruthenium phthalocyanine with bisaxial ligands $PcRu(C_7H_{15})_8(CH_3)_8(3\text{-}ClPy)_2$ **13** is also described.

The synthetic route for the hexadecaalkyl-substituted nickel phthalocyanines **11** and **12** is shown in Scheme 1. 1,2-Dibromo-4,5-dimethylbenzene **(1)** was reacted with iodine and periodic acid in concentrated sulfuric acid[8] to give the diiodo compound **3**. The same procedure with 1,2-dibromo-4,5-dihexylbenzene **(2)** failed and so did other common iodination procedures. Therefore, an unusual iodination method was used to give 1,2-dibromo-3,6-diiodo-4,5-dihexylbenzene **(4)**. 1,2-Dibromo-4,5-dihexylbenzene **(2)** was reacted with HgO in trifluoroacetic acid[9] forming a bis(trifluoroacetatomercury) intermediate which was converted to **4** directly using I_2/NaI as iodinating agent. The alkylbromoiodobenzenes **3** and **4** can be selectively reacted at the iodo groups with alkynes by Heck reaction[10] leading to the dibromobenzenes **5** and **6** which were converted to the substituted phthalodinitriles **7** and **8** in a Rosenmund von Braun reaction with CuCN in dimethylformamide. Catalytic hydrogenation of the phthalodinitriles **7** and **8** with palladium as catalyst gave the tetraalkylated phthalodinitriles **9** and **10**. The hexadecaalkyl-substituted nickel phthalocyanines **11** and **12** were prepared by reaction of the phthalodinitriles **9** and **10** with $NiCl_2$ and a catalytic amount of DBU in octanol at elevated temperature (Scheme 1). The yield of $PcNi(C_6H_{13})_{16}$ **12** was only about 1% even after prolonged reaction times due to the steric hindrance of the long chain alkyl groups making phthalocyanine formation more difficult. The unsymmetrically substituted $PcNi(C_7H_{15})_8(CH_3)_8$ **11** was obtained in moderate yield, ca. 10%, emphasizing the fact that the sterically less demanding phthalodinitrile **9** facilitates phthalocyanine formation compared to the phthalodinitrile **10**.



Scheme 1

The hexadecaalkyl-substituted ruthenium phthalocyanine $PcRu(C_7H_{15})_8(CH_3)_8(3\text{-}ClPy)_2$ **13** with 3-chloropyridine as axial ligands could be obtained by reaction of phthalodinitrile **9** with $RuCl_3 \cdot 3\,H_2O$, a catalytic amount of DBU and 3-chloropyridine in a mixture of octanol and 2-ethoxyethanol (Scheme 2).[11] The preparation of the corresponding iron phthalocyanine $PcFe(C_7H_{15})_8(CH_3)_8$ **14** by reaction of phthalodinitrile **9** with $Fe(OAc)_2$ or $FeSO_4$, respectively, by the same procedure as used for the preparation of the nickel compound **11** was unsuccessful. Attempts to stabilize the fully substituted iron phthalocyanine **14** in the reaction mixture by bisaxial coordination with pyridine failed. All prepared hexadecaalkyl-substituted phthalocyanines **11–13** exhibit a very high solubility in organic aprotic solvents.



Scheme 2

UV/Vis spectra of the phthalocyanines **11–13** (Table 1) in dichloromethane show the typical pattern, mainly the π–π^* transition of the heteroaromatic 18-π electron system: a large intensive Q band in the visible region accompanied by more or less resolved weak satellite bands. In the ultraviolet region the characteristic Soret or B band is also observed. Peripheral substitution of phthalocyanines by alkyl chains gives a bathochromic shift of the Q band compared to the unsubstituted macrocycle. For octasubstituted macrocycles the Q band is more red shifted by substituents at the 1,4-position than by those at the 2,3-position (Table 1).[12] Complete substitution of the macrocycles by alkyl chains gives a distinctly enhanced red shift of the Q band as shown in Table 1. The Q band of the ruthenium phthalocyanine $PcRu(C_7H_{15})_8(CH_3)_8(3\text{-}ClPy)_2$

(13) is less red shifted than those from the corresponding nickel phthalocyanine **11** (Table 1).

Electrochemical studies of $PcNi(C_7H_{15})_8(CH_3)_8$ **11** were carried out to investigate the influence of the fully peripheral substitution on the electronic structure of the phthalocyanine. Two oxidation steps as well as two reduction steps were observed in the cyclic voltammogram of **11** in dichloromethane/Bu_4NPF_6. The half-wave potentials $E_{1/2}$ for the hexadecaalkyl-substituted nickel phthalocyanine $PcNi(C_7H_{15})_8(CH_3)_8$ **11** are slightly more negative than for the 1,4-octasubstituted $PcNi(C_7H_{15})_8$ (Table 2) due to the higher number of electron-donating alkyl substituents in **11**. The peak splittings of all half-wave potentials ($\Delta E_p = E_{pa} - E_{pc}$) were in the range of 100 mV and nearly independent of the scan rate in a range of 20 to 500 mV/s. Therefore quasireversible one-electron transfers can be assumed.

The redox potentials obtained and shown in Table 2 were supported by spectroelectrochemical investigations in CH_2Cl_2/Bu_4NPF_6. As shown in the Figure for the first oxidation step of **11** we observed absorption bands in the UV/Vis spectrum at 662, 783, 900 and 985 nm and for the second oxidation step at 493 nm. According to similar absorption bands during oxidation of the octasubstituted $PcNi(C_7H_{15})_8$[7] both oxidations were ascribed to the oxidation of the macrocycle. Due to the complete peripheral substitution of the macrocycle with electron donating alkyl chains in **11** the absorption bands of the oxidized species of **11** are slightly red shifted compared to the oxidized species of the octasubstituted $PcNi(C_7H_{15})_8$.[7] The UV/Vis spectrum obtained for the first reduction of **11** is characteristic for the reduction of the phthalocyanine core. Absorption bands at 612, 654, 900 and 1002 nm were observed. These bands are also slightly red shifted com-pared to absorption bands of the reduced species of $PcNi(C_7H_{15})_8$.[7] It was not possible to obtain a UV/Vis spectrum of the second reduction of **11** due to experimental limitations of the potentiostate used.

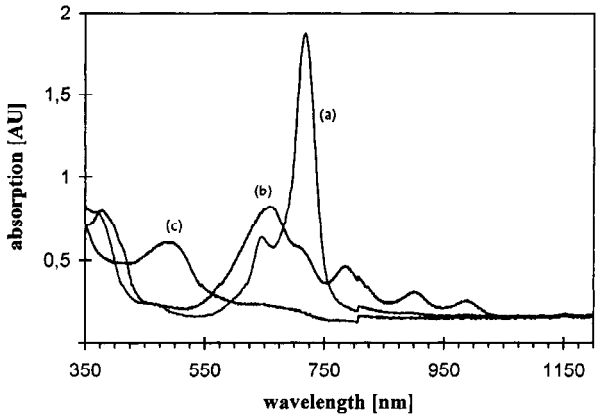


Figure. UV/Vis Spectra of **11**: (a) 1st oxidation, (b) [0.6 V vs Ag/Ag^+] and 2nd oxidation, (c) [1.3 V vs. Ag/Ag^+] in CH_2Cl_2/Bu_4NPF_6.

The ^1H NMR spectra of the hexadecaalkyl-substituted nickel phthalocyanines **11** and **12** (see experimental part) show the resonances of the aliphatic protons at lower field than the corresponding phthalodinitriles **9** and **10** due to the aromatic ring current of the heteroaromatic system.[13] The resonances of the protons close to the phthalocyanine core are distinctly broadened since the mobility of the side chains is reduced. We assume that these broad signals are not caused by aggregation effects since the complete peripheral substitution of the macrocycles diminishes their intermolecular interaction. The ^1H NMR spectra of the bisaxially coordinated ruthenium phthalocyanine $PcRu(C_7H_{15})_8(CH_3)_8(3\text{-ClPy})_2$ **13** differs mainly in the additional signals of the bisaxial 3-chloropyridine ligand. These signals show a diamagnetic ring current shift to higher field compared to the free ligand. The ^{13}C NMR data of the hexadecaalkyl-substituted phthalocyanines **11–13** confirming the proposed structure are given in the experimental part.

In summary, for the first time the synthesis of hexadecaalkyl-substituted metal phthalocyanines is described. The highly soluble macrocycles were characterized by spectroscopic methods. Complete peripheral substitution of the phthalocyanines influences their optical and electrochemical properties compared to less substituted systems.

Table 1. UV/Vis data of Phthalocyanines **11–13** in CH_2Cl_2

Compound	λ_{max} (nm)
$PcNi(C_7H_{15})_8(CH_3)_8$ (**11**)	719 (Q), 647, 375, 342, 304
$PcNi(C_6H_{13})_{16}$ (**12**)	722 (Q),650, 370, 341, 305
1,4-$PcNi(C_7H_{15})_8$[a]	707 (Q), 672sh, 638, 386sh, 346, 305
2,3-$PcNi(C_7H_{15})_8$[a]	684 (Q), 651sh, 616, 374, 337, 300
$PcRu(C_7H_{15})_8(CH_3)_8(3\text{-ClPy})_2$ (**13**)	675 (Q), 608, 430, 318

[a] In $CHCl_3$, ref.[7]

Table 2. Half-Wave Potentials $E_{1/2}$ (V vs. SCE) of **11** in CH_2Cl_2 (Scan Rate 100 mV/s, T = 20°C) in Comparison with 1,4-$PcNi(C_7H_{15})_8$

Compound	$E_{1/2}$ (Ox_1)	$E_{1/2}$ (Ox_2)	$E_{1/2}$ (Red_1)	$E_{1/2}$ (Red_2)
$PcNi(C_7H_{15})_8(CH_3)_8$ (**11**)[a]	0.45	1.15	–1.15	–1.55
1,4-$PcNi(C_7H_{15})_8$[b]	0.59	1.27	–1.05	–1.47

[a] $c = 7.2 \cdot 10^{-4}$ mol/L, 0.1 mol/LBu_4NPF_6.
[b] $c = 3.0 \cdot 10^{-4}$ mol/L, 0.1 mol/L Bu_4NPF_6, ref.[7]

IR spectra: Bruker IFS 48; NMR spectra: Bruker AC 250 (^1H: 250 MHz; ^{13}C: 62.9 MHz); MS: Finnigan MAT ISQ 70 (EI, 70 eV) and Finnigan MAT 711A (FD, FAB); UV/Vis spectra: Shimadzu UV 2102 PC.

Cyclic voltammetric measurements were carried out under argon by using a three-electrode cell. They were performed with a E.G. & G PAR potentiostate model 273. A platinum disc electrode and a platinum sheet were used as the working and counter electrode, a silver wire and the ferrocene/ferrocene$^+$ couple as the internal reference electrode. The measurements were correlated vs. SCE.

Spectroelectrochemical measurements were carried out under argon by using a three-electrode cell. They were performed with a Jaissle potentiostate model 1001 /T-NC and a Shimadzu UV/Vis/NIR spectrometer model UV-365. An ITO-glass, a platinum sheet and a silver wire were used as working, counter and reference electrodes.

1,2-Dibromo-3,6-diiodo-4,5-dimethylbenzene (3):
To a solution of H_5IO_6 (16 g, 0.07 mol) in concd H_2SO_4 (200 mL) was added finely powdered I_2 (53.3 g, 0.21 mol) with vigorous stirring. After 30 min the mixture was cooled to 0°C and 1,2-dibromo-4,5-dimethylbenzene **(1)** (42 g, 0.16 mol) was added in small portions. The mixture was allowed to warm up to r.t. and stirred for another 12 h. Subsequently the mixture was poured onto ice (1 kg). The precipitate was suction filtered, washed with water (500 mL) and MeOH (500 mL) and finally dried; pale beige solid; yield: 35 g (42%).
^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.65 (s, CH_3).
IR (KBr): ν = 1013, 1134, 1163, 1177, 1229, 1283, 1317, 1346, 1377, 1429, 2914, 2951 cm^{-1}.
MS (EI): *m/z* = 515.7 [M$^+$].

$C_8H_6Br_2I_2$	calcd	C	18.63	H	1.17		
(515.8)	found		19.34		1.19		

1,2-Dibromo-3,6-diiodo-4,5-dihexylbenzene (4):
1,2-Dibromo-4,5-dihexylbenzene **(2)** (16.2 g, 0.04 mol) and HgO (26 g, 0.12 mol) were dissolved in CF_3CO_2H (100 mL) and refluxed for 6 h. After cooling, water (300 mL), NaI (24 g, 0.16 mol) and I_2 (40.6 g, 0.16 mol) were added. The mixture was stirred vigorously and heated to 80°C for another 24 h. After cooling, under stirring 10% aq $Na_2S_2O_4$ (300 mL) was added until the solution was pale yellow. The aqueous phase was separated, the residue was washed with water (500 mL) and finally dried (Na_2SO_4). The crude product was dissolved in hexane (100 mL) and filtered through silica gel. Finally the product was recrystallized (EtOH); white crystals; yield: 16.5 g (63%); mp 71°C.
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, 6H, *J* = 6.9 Hz, CH_3), 1.2–1.6 (m, 16H, CH_2), 2.99 (br t, 4H, CH_2).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.05, 22.61, 29.18, 29.50, 31.38, 43.15, 110.90, 130.32, 145.36.
IR (KBr): ν = 723, 986, 1078, 1117, 1139, 1180, 1300, 1331, 1344, 1375, 1466, 2851, 2870, 2918, 2953 cm^{-1}.
MS (EI): *m/z* = 655.8 [M$^+$].

$C_{18}H_{26}Br_2I_2$	calcd	C	32.96	H	3.99		
(656.0)	found		33.18		4.00		

1,2-Dibromo-3,6-dihept-1-ynyl-4,5-dimethylbenzene (5):
A mixture of 1,2-dibromo-3,6-diiodo-4,5-dimethylbenzene **(3)** (28.3 g, 55 mmol), $(PPh_3)_2PdCl_2$ (1.54 g, 2.2 mmol) and CuI (100 mg) in NEt_3 (40 mL), DMF (20 mL) and hept-1-yne (28.8 mL, 0.22 mol) was stirred for 48 h at 40°C under N_2. After cooling, the mixture was poured onto ice (300 g) and acidified with 5% aq HCl (50 mL). The crude product was extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was washed with water (100 mL) and dried (Na_2SO_4). The solvent was evaporated and the dark residue was purified by column chromatography (silica gel, hexane; R_f 0.35); waxy solid; yield: 7.0 g (28%).
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, 6H, *J* = 7.2 Hz, CH_3), 1.3–1.7 (m, 12H, CH_2), 2.37 (s, 6H, CH_3), 2.51 (t, 4H, *J* = 7.0 Hz, CH_2).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.98, 19.21, 19.74, 22.18, 28.26, 31.11, 79.82, 100.79, 125.42, 126.56, 138.73.
IR (NaCl): ν = 646, 669, 737, 899, 920, 999, 1032, 1069, 1113, 1229, 1286, 1325, 1379, 1387, 1410, 1429, 1456, 1466, 2233, 2860, 2870, 2932, 2955 cm^{-1}.
MS (EI): *m/z* = 452.0 [M$^+$].

$C_{22}H_{28}Br_2$	calcd	C	58.43	H	6.24	Br	35.33
(452.3)	found		58.80		6.24		35.25

1,2-Dibromo-4,5-dihexyl-3,6-dihex-1-ynylbenzene (6):
A mixture of 1,2-dibromo-3,6-diiodo-4,5-dihexylbenzene **(4)** (16.4 g, 0.025 mol), $(PPh_3)_2PdCl_2$ (0.7 g, 1 mmol) and CuI (100 mg) in NEt_3 (50 mL) and hex-1-yne (8.2 g, 0.1 mol) was stirred for 24 h at 40°C under N_2. The further preparation is analogous to **5** (column chromatography: silica gel, hexane; R_f 0.45); viscous oil; yield: 10.7 g (76%).
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.0 (m, 12H, CH_3), 1.2–1.7 (m, 24H, CH_2), 2.51 (t, 4H, *J* = 6.7 Hz, CH_2), 2.77 (br t, 4H, CH_2).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.55, 14.04, 19.44, 22.04, 22.61, 29.78, 30.07, 30.65, 31.58, 32.54, 79.53, 99.83, 125.86, 126.55, 143.23.
IR (NaCl): ν = 725, 887, 912, 927, 1008, 1105, 1219, 1249, 1300, 1323, 1379, 1410, 1427, 1466, 2228, 2858, 2928, 2957 cm^{-1}.
MS (FD, CH_2Cl_2): *m/z* = 564.1 [M$^+$].

$C_{30}H_{44}Br_2$	calcd	C	63.83	H	7.86	Br	28.31
(564.5)	found		63.59		7.60		28.53

1,2-Dicyano-3,6-dihept-1-ynyl-4,5-dimethylbenzene (7):
A mixture of 1,2-dibromo-3,6-dihept-1-ynyl-4,5-dimethylbenzene **(5)** (6.8 g, 15 mmol) and CuCN (5.4 g, 60 mmol) was refluxed in DMF (40 mL) under N_2 for 24 h After cooling the mixture was poured into concd aq NH_3 (200 mL) and a strong steam of air was bubbled through the solution for 2 h. The crude product was suction filtered, washed with water (200 mL) and dried (Na_2SO_4). Finally it was purified by column chromatography (silica gel, toluene; R_f 0.6); off-white solid; yield: 4.0 g (77%); mp 45°C.
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, 6H, *J* = 7.2 Hz, CH_3), 1.3–1.7 (m, 12H, CH_2), 2.44 (s, 6H, CH_3), 2.52 (t, 4H, *J* = 7.0 Hz, CH_2).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.87, 18.91, 19.76, 22.11, 27.95, 31.04, 75.85, 104.49, 115.06, 116.17, 127.60, 144.14.
IR (KBr): ν = 663, 729, 837, 908, 1003, 1032, 1065, 1103, 1148, 1200, 1219, 1279, 1323, 1339, 1381, 1414, 1448, 1466, 1537, 1560, 2220, 2232, 2862, 2932, 2953 cm^{-1}.
MS (EI): *m/z* = 344.3 [M$^+$].

$C_{24}H_{28}N_2$	calcd	C	83.68	H	8.19	N	8.13
(344.5)	found		84.04		8.27		7.88

1,2-Dicyano-4,5-dihexyl-3,6-dihex-1-ynylbenzene (8):
This compound was obtained from 1,2-dibromo-4,5-dihexyl-3,6-dihex-1-ynylbenzene **(6)** (8.5 g, 0.015 mol) and CuCN (5.4 g, 0.06 mol) in DMF (40 mL) by the procedure used for the preparation of **7**; pale yellow viscous oil; yield: 4.8 g (70%).
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.0 (m, 12H, CH_3), 1.2–1.7 (m, 24H, CH_2), 2.52 (t, 4H, *J* = 6.9 Hz, CH_2), 2.80 (br t, 4H, CH_2).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.47, 13.97, 19.44, 21.99, 22.49, 29.64, 29.86, 30.29, 31.41, 32.16, 75.71, 103.56, 115.07, 116.46, 127.79, 148.40.
IR (NaCl): ν = 727, 891, 928, 957, 995, 1009, 1115, 1250, 1300, 1323, 1342, 1354, 1366, 1379, 1425, 1466, 1527, 1558, 2230, 2235, 2860, 2930, 2959 cm^{-1}.
MS (EI): *m/z* = 456.2 [M$^+$].

$C_{32}H_{44}N_2$	calcd	C	84.16	H	9.71	N	6.13
(456.7)	found		84.61		9.75		6.13

1,2-Dicyano-3,6-diheptyl-4,5-dimethylbenzene (9):
1,2-Dicyano-3,6-dihept-1-ynyl-4,5-dimethylbenzene **(7)** (3.4 g, 10 mmol) was dissolved in EtOAc (50 mL) and 10% Pd/C (1 g) was added. The mixture was hydrogenated at r.t. for 48 h with a H_2 pressure of 1 bar. Subsequently the catalyst was separated and the solvent evaporated. The crude product was purified by column chromatography (silica gel, toluene; R_f 0.7); white crystals; yield: 3 g (85%); mp 82.5°C.
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, 6H, *J* = 6.8 Hz, CH_3), 1.2–1.6 (m, 20H, CH_2), 2.30 (s, 6H, CH_3), 2.86 (t, 4H, *J* = 7.9 Hz, CH_2).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.99, 16.68, 22.52, 28.90, 29.54, 30.01, 31.63, 32.90, 113.51, 116.05, 141.61, 144.06.
IR (KBr): ν = 729, 1032, 1076, 1119, 1271, 1294, 1342, 1387, 1408, 1460, 1560, 2226, 2853, 2872, 2924, 2951 cm^{-1}.
MS (EI): *m/z* = 352.4 [M$^+$].

$C_{24}H_{36}N_2$	calcd	C	81.76	H	10.29	N	7.95
(352.6)	found		81.76		10.34		7.58

1,2-Dicyano-3,4,5,6-tetrahexylbenzene (10):
1,2-Dicyano-4,5-dihexyl-3,6-dihex-1-ynylbenzene **(8)** (4.6 g, 10 mmol) was dissolved in a mixture of *i*-PrOH (30 mL) and HOAc (3 mL) and Pd black (0.21 g) was added. The mixture was hydrogenated at r.t. for 24 h with a H_2 pressure of 3 bar. The progress of the reaction was monitored by TLC (silica gel, toluene; R_f 0.7). When the reaction was complete, the catalyst was separated and the solvent evaporated. The product was purified by column chromatography (silica gel, toluene); viscous oil; yield: 1.1 g (23%).
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.8–1.0 (m, 12H, CH_3), 1.2–1.6 (m, 32H, CH_2), 2.60 (br t, 4H, CH_2), 2.79 (br t, 4H, CH_2).
^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.97, 22.49, 22.53, 29.56, 29.78, 29.88, 31.02, 31.11, 31.35, 32.29, 114.13, 116.00, 144.53, 145.50.
IR (NaCl): ν = 725, 800, 889, 928, 1015, 1113, 1177, 1219, 1281, 1352, 1379, 1420, 1466, 1558, 2226, 2858, 2928, 2957 cm^{-1}.
MS (EI): *m/z* = 464.2 [M$^+$].

$C_{32}H_{52}N_2$	calcd	C	82.70	H	11.28	N	6.03
(464.8)	found		82.98		10.61		6.09

1,4,8,11,15,18,22,25-Octaheptyl-2,3,9,10,16,17,23,24-octamethylphthalocyaninatonickel (11):
A mixture of 1,2-dicyano-3,6-diheptyl-4,5-dimethylbenzene **(9)** (1.0 g, 2.8 mmol), $NiCl_2$ (0.12 g, 0.9 mmol) and DBU (1 mL) was refluxed in octanol (15 mL) for 7 d under N_2. After cooling the crude product was precipitated by adding MeOH (50 mL), washed and purified by column chromatography (silica gel, hexane/CH_2Cl_2 10:1). For further purification the product was dissolved in CH_2Cl_2 (1 mL) and precipitated by adding MeOH (30 mL). Finally, it was dried for 6 h at 50 °C in vacuo; green solid; yield: 105 mg (10%); mp 222 °C.
^{1}H NMR (250 MHz, C_6D_6): δ = 0.8 (t, 24H, *J* = 6.8 Hz, CH_3), 1.2 (m, 32H, CH_2), 1.4 (m, 16H, CH_2), 1.8 (m, 16H, CH_2), 2.0 (m, 16H, CH_2), 2.67 (s, 24H, CH_3), 4.9 (br, 16H, CH_2).
^{13}C NMR (62.9 MHz, C_6D_6): δ = 14.23, 16.95, 23.00, 29.19, 29.96, 30.33, 31.18, 32.26, 133.13, 136.17, 137.46, 147.34.
IR (KBr): ν = 931, 1101, 1138, 1170, 1223, 1275, 1306, 1331, 1369, 1458, 1506, 2854, 2924, 2955 cm^{-1}.
MS (FD, CH_2Cl_2): *m/z* = 1468.2 [M$^+$].

$C_{96}H_{144}N_8Ni$	calcd	C	78.50	H	9.88	N	7.63
(1468.9)	found		78.45		9.27		7.71

1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecahexylphthalocyaninatonickel (12):
This compound was obtained from 1,2-dicyano-3,4,5,6-tetrahexylbenzene **(10)** (0.6 g, 1.3 mmol), $NiCl_2$ (52 mg, 0.4 mmol) and DBU (0.5 mL) in octanol (5 mL) by the procedure used for the preparation of **11** (column chromatography: silica gel, hexane); green waxy solid; yield: 4.5 mg (0.7%).
^{1}H NMR (250 MHz, C_6D_6): δ = 0.87 (t, 24H, *J* = 7.0 Hz, CH_3), 1.06 (t, 24H, *J* = 7.0 Hz, CH_3), 1.2–1.6 (m, 64H, CH_2), 1.7–2.0 (m, 32H, CH_2), 2.09 (br, 32H, CH_2), 3.39 (br, 16H, CH_2), 4.88 (br, 16H, CH_2).
^{13}C NMR (62.9 MHz, C_6D_6): δ = 14.22, 14.37, 23.16, 23.19, 29.27, 30.18, 30.47, 30.78, 30.85, 32.20, 32.35, 32.77, 133.63, 136.77, 141.60, 147.37.
IR (NaCl): ν = 723, 743, 762, 804, 829, 1015, 1092, 1140, 1175, 1217, 1227, 1283, 1323, 1377, 1466, 1506, 1576, 2855, 2924, 2957 cm^{-1}.
MS (FD, CH_2Cl_2): *m/z* = 1916.2 [M$^+$].

$C_{128}H_{208}N_8Ni$	calcd	C	80.17	H	10.93	N	5.84
(1917.8)	found		80.18		11.05		5.26

Bis(3-chloropyridine)-1,4,8,11,15,18,22,25-octaheptyl-2,3,9,10,16,17,23,24-octamethylphthalocyaninatoruthenium(II) (13):
A mixture of 1,2-dicyano-3,6-diheptyl-4,5-dimethylbenzene **(9)** (1.0 g, 2.8 mmol), $RuCl_3 \cdot 3\,H_2O$ (0.18 g, 0.7 mmol), 3-chloropyridine (0.5 mL) and DBU (0.5 mL) was refluxed in 2-ethoxyethanol (5 mL) and octanol (5 mL) for 7 d under N_2. The further preparation is analogous to compound **11**; blue-green solid; yield: 36 mg (3%).
^{1}H NMR ($CDCl_3$): δ = 0.75 (t, 24H, *J* = 6.8 Hz, CH_3), 1.0–1.5 (m, 48H, CH_2), 1.6 (m, 16H, CH_2), 1.9 (m, 16H, CH_2), 2.4–2.5 (m, 4H, 3-ClPy), 2.74 (s, 24H, CH_3), 4.7 (br, 16H, CH_2), 5.04 (m, 2H, 3-ClPy), 5.96 (m, 2H, 3-ClPy).
^{13}C NMR ($CDCl_3$): δ = 14.05, 16.57, 22.67, 28.36, 29.53, 29.75, 31.31, 31.90, 121.88, 129.37, 132.46, 135.50, 136.02, 148.27, 149.17.
IR (KBr): ν = 690, 727, 745, 758, 798, 1047, 1103, 1121, 1148, 1221, 1302, 1373, 1416, 1466, 2853, 2922, 2953, 3051, 3096 cm^{-1}.
MS (FAB): *m/z* = 1510.5 [M$^+$ – 2 3-ClPy].

$C_{106}H_{152}Cl_2N_{10}Ru$	calcd	C	73.24	H	8.81	N	8.06	Cl	4.08
(1738.4)	found		73.47		8.89		7.82		4.00

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