Reaction of Cyanogen with Cobalt Phthalocyanines

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Received January 26, 1995[⊗]

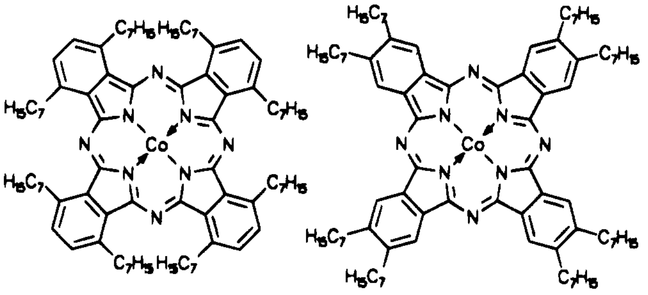
The soluble (phthalocyaninato)- and (2,3-naphthalocyaninato)cobalt(II) complexes ($(t\text{-Bu})_4$PcCo, 2,3,9,10,16,17,23,24-$(C_7H_{15})_8$PcCo, 1,4,8,11,15,18,22,25-$(C_7H_{15})_8$PcCo, and $(t\text{-Bu})_4$2,3-NcCo react with cyanogen with formation of cyano-bridged oligomers of the type ([MacCo(CN)]$_n$). The same products are also prepared via an earlier developed method by reaction of the (phthalocyaninato)cobalt(II) compounds with KCN via K[MacCo(CN)$_2$] complexes and treatment with water. The conductivities of the obtained cyano-bridged systems ([MacCo(CN)]$_n$) are measured, and [$(t\text{-Bu})_4$-2,3-NcCo(CN)]$_n$ shows a remarkable conductivity of 8×10^{-2} S/cm.

Cyanogen is a versatile cyano compound and a molecule of potential interest in organic synthesis.[1] Cyanogen reacts with metal complexes in two different ways, either to form coordination compounds or as an oxidant.[2] Oxidative addition reactions of cyanogen to transition metal complexes (e.g., [Pt(PPh$_3$)$_4$]) lead to cyanometal complexes.[3] Such oxidative addition reactions have been successfully carried out with vanadium, nickel, palladium, and platinum complexes.[2,4] To our knowledge, nothing is known however about the behavior of cyanogen toward transition metal phthalocyanines.

In this paper, we report the reaction of cyanogen with cobalt phthalocyanines and cobalt 2,3-naphthalocyanines. The reactions were carried out with 1,4,8,11,15,18,22,25-$(C_7H_{15})_8$PcCo (**1**), and 2,3,9,10,16,17,23,24-$(C_7H_{15})_8$PcCo (**2**), $(t\text{-Bu})_4$PcCo (**3**), and $(t\text{-Bu})_4$-2,3-NcCo (**4**) (Figure 1). Cyanogen reacts with **1**–**4** as an oxidant with formation of cyano-bridged systems of the type [MacCo(CN)]$_n$ (Mac = $(t\text{-Bu})_4$Pc, $(t\text{-Bu})_4$-2,3-Nc, 1,4,8,11,15,18,22,25-$(C_7H_{15})_8$Pc, and 2,3,9,10,16,17,23,24-$(C_7H_{15})_8$Pc).

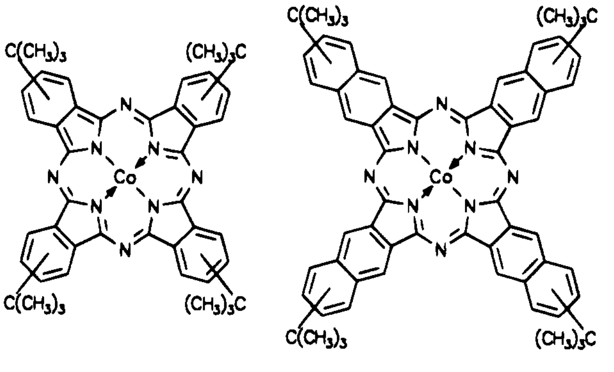
Earlier, we have reported on the synthesis and conductivities of cyano-bridged (phthalocyaninato)-, (naphthalocyaninato)- and (tetrabenzoporphyrinato) metal compounds [MacM(CN)]$_n$ (Mac = Pc, 2,3-Nc, TBP), with the central transition metal atom, e.g., Co, Rh, Fe, Mn, or Cr in the oxidation state III. These compounds show remarkably good semiconducting properties with $\sigma_{RT} = 10^{-3}$–10^{-1} S/cm at room temperature without additional external doping.[5]

A direct route to [PcM(CN)]$_n$ (M = Fe,[5,6] Mn[5,7]) is the displacement of an axial anion X$^-$ by CN$^-$ in coordinatively unsaturated compounds PcMX (X = Cl, OAc, CCl$_3$CO$_2$).[5–8]



1,4,8,11,15,18,22,25-$(C_7H_{15})_8$PcCo (**1**)

2,3,9,10,16,17,23,24-$(C_7H_{15})_8$PcCo (**2**)



$(t\text{-Bu})_4$PcCo (**3**)

$(t\text{-Bu})_4$-2,3-NcCo (**4**)

Figure 1. Structures of the four cobalt-bound macrocycles used in this study.

Another general route also leading to cyano-bridged complexes [MacM(CN)]$_n$ is the elimination of alkali metal cyanide from alkali metal dicyano(phthalocyaninato or 2,3-naphthalocyaninato) transition metalate(III) complexes M′[MacM(CN)$_2$] (M′ = Na, K; M = Co,[9] Rh,[10] Fe,[6] Mn,[7] Cr;[7] Mac = Pc, 2,3-Nc). The synthesis of the complexes M′[MacM(CN)$_2$] is possible by in situ oxidation of PcM (M = Co, Mn) with atmospheric oxygen in the presence of excess of cyanide. The conversion of PcCoCl$_2$[11] or 2,3-NcFeCl$_2$[12] to [PcCo(CN)]$_n$ and [2,3-NcFe-

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

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Table 1. UV/Vis Data (Q-band) of MacCo, M′[MacCo(CN)$_2$], and [MacCo(CN)]$_n$, Recorded in DMF

compound	$\lambda_{\max}$
(t-Bu)$_4$PcCo (**3**)	664
K[(t-Bu)$_4$PcCo(CN)$_2$] (**12**)	676
[(t-Bu)$_4$PcCo(CN)]$_n$ (**8**)	675
1,4-(C$_7$H$_{15}$)$_8$PcCo (**1**)	insoluble in DMF
Na[1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)$_2$] (**10**)	708
[1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**6**)	710
(t-Bu)$_4$-2,3-NcCo (**4**)	748
K[(t-Bu)$_4$-2,3-NcCo(CN)$_2$] (**13**)	765
[(t-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**)	767
(t-Bu)$_4$-2,3-NcCo(py)(CN) (**14**)	768
2,3-(C$_7$H$_{15}$)$_8$PcCo (**2**)	insoluble in DMF
Na(2,3,9,10,16,17,23,24-(C$_7$H$_{15}$)$_8$PcCo(CN)$_2$] (**11**)	683
[2,3,9,10,16,17,23,24-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**7**)	683

(CN)]$_n$, respectively, in an aqueous alkali metal cyanide solution is also possible.[5-7,9,12]

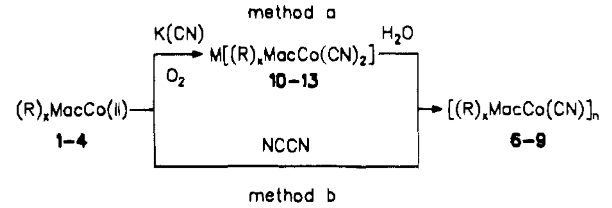
For comparison, all cyano-bridged complexes which were prepared by reaction with cyanogen were also synthesized by the pathway starting from M′[MacCo(CN)$_2$] (vide supra).

Results and Discussion

(1,4,8,11,15,18,22,25-Octaheptylphthalocyaninato)cobalt ((1,4-C$_7$H$_{15}$)$_8$PcCo, **1**), (2,3,9,10,16,17,23,24-octaheptylphthalocyaninato)cobalt ((2,3-C$_7$H$_{15}$)$_8$PcCo, **2**), and (tetra-*tert*-butylphthalocyaninato)cobalt ((t-Bu)$_4$PcCo, **3**) (mixtures of isomers), respectively, were prepared in high yields by refluxing a solution of CoCl$_2$·6H$_2$O with the appropriately substituted phthalodinitrile in ethylene glycol according to ref 13. (Tetra-*tert*-butyl-2,3-naphthalocyaninato)cobalt ((t-Bu)$_4$-2,3-NcCo, **4**) was synthesized by refluxing a mixture of cobalt(III) acetylacetonate, 6-*tert*-butyl-1*H*-benz[*f*]diiminodihydroisoindole (**5**), and DBU in 2-ethoxyethanol. The isoindolenine **5** was prepared by reaction of 6-*tert*-butyl-2,3-dicyanonaphthalene[14] with ammonia in methanol. Compounds **1**, **2** and **4** were characterized by IR and UV/vis spectroscopies as well as by elemental analyses. The UV/vis spectra of **3** and **4** were recorded in DMF. The phthalocyanines **1** and **2** are insoluble in DMF, and therefore the UV/vis spectra were recorded in CHCl$_3$. The Q- and B-bands in the spectra confirmed the formation of the phthalocyanines (Table 1 and Experimental Section). NMR spectroscopic investigations were not possible because of the paramagnetism of Co(II).

The substituted (phthalocyaninato)- and (2,3-naphthalocyaninato)cobalt(II) complexes **1**–**4** (MacCo) were dissolved in chloroform and reacted with an excess of cyanogen (NCCN) at room temperature in an autoclave. A reaction takes place only if the MacCo is in solution, which is achieved by peripheral substitution of the macrocycle with *tert*-butyl or long-chain alkyl or alkyloxy groups.[5] Unsubstituted MacCo, e.g., PcCo or 2,3-NcCo, are insoluble in CHCl$_3$ and do not react with cyanogen by this technique. During the reaction of the soluble MacCo with cyanogen, the color of the chloroform solution changed in the case of the phthalocyanines **1**–**3** from blue to green (**4** changed from dark green to light green), indicating the oxidation of the central metal: Co(II) → Co(III). In this reaction, cyanogen serves as the oxidant and the thereby-formed cyanide (CN$^-$) coordinates the Co^{3+} ion in the macrocycle. The products obtained have the stoichiometry [MacCo(CN)]$_n$ which was confirmed by elemental analyses. The obtained complexes [1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**6**), [2,3,9,10,16,17,23,24-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**7**), [(t-Bu)$_4$PcCo(CN)]$_n$ (**8**), and [(t-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**) are soluble in common organic solvents (e.g., chloroform). They were purified by column chromatography and characterized by IR, UV/vis, and ^{1}H NMR spectroscopies. The IR spectra of **6**–**8** (Table 2) exhibit ν_{CN} valence frequencies of low intensity, which are typical for metal-coordinated cyanides.[5-8,12] For [(t-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**), no ν_{CN} absorption could be found in the spectra. However, the existence of CN$^-$ is confirmed by the mass spectrum (FD technique) of **9**. The signals of the fragments [(t-Bu)$_4$-2,3-NcCo]$^+$, [(t-Bu)$_4$-2,3-NcCo(CN)]$^+$, an [(t-Bu)$_4$-2,3-NcCo(CN)$_2$]$^+$ appear at m/z = 995, 1021, and 1047. Further evidence for the cyano-bridged structure of [(t-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**) is the reaction of **9** with pyridine, forming the monomeric complex (t-Bu)$_4$-2,3-NcCo(py)(CN) (**14**) which was characterized by ^{1}H NMR, UV/vis, and IR spectroscopies. In general, treatment of bridged complexes [MacM(CN)]$_n$ with bases, e.g., pyridine, pyrazine, etc., leads to monomers MacM(L)(CN).[5,7,9,10] The IR spectrum of (t-Bu)$_4$-2,3-NcCo(py)(CN) (**14**) shows the absorption of the CN group at 2141 cm^{-1}, indicative of a nonbridged CN group.

Scheme 1



The UV/vis spectra of **6**–**9** recorded in chloroform or DMF show a bathochromic shift of the Q-band in comparison to **1**–**4** due to the increase of the oxidation state of the cobalt ion form II to III (Table 1). The ^{1}H NMR spectra of **6**–**9**, recorded in pyridine-d_5, show the expected signals of the aromatic and side-chain groups. It must be considered that, in pyridine-d$_5$, not the bridged but the monomeric complexes of the type MacCo(CN)(py-d_5) are recorded. In CDCl$_3$, no ^{1}H NMR spectrum was obtained because of the paramagnetism of the samples. This is due to the fact that, also in noncoordinating solvents like CHCl$_3$, the bridged structures of **6**–**9** dissociate and are converted into pentacoordinated monomers of the type MacCo(CN), which have only 16 electrons at the central Co atom, leading to paramagnetism.[5,15]

For comparison, the cyano-bridged compounds **6**–**9** were also prepared by the earlier described pathway (Scheme 1, method a).[5-8,16] First, the monomeric dicyano complexes Na[1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)$_2$] (**10**), Na[2,3,9,10,16,17,23,24-(C$_7$H$_{15}$)$_8$PcCo(CN)$_2$] (**11**), K[(t-Bu)$_4$PcCo(CN)$_2$] (**12**), and K[(t-Bu)$_4$-2,3-NcCo(CN)$_2$[(**13**) were synthesized by reacting the appropriate MacCo **1**–**4** with NaCN or KCN in ethanol or acetone, respectively. During the reaction, air was bubbled through the solution to oxidize the central metal atom in MacCo. The complexes **10**, **11**, and **13** were characterized by IR, UV/vis, and ^{1}H NMR spectroscopies, as well as by elemental analyses. Compound **12** is described in ref 16. The IR ν_{CN} valence frequencies of **10**–**13** are given in Table 2. The increase in ν_{CN} valence frequency going from the monomeric complexes M′[MacCo(CN)$_2$] **10**–**13** to **6**–**9** is evidence for μ-cyano-bridged structures in the latter.[5,16,17] In the solid state, **6**–**9** form bridged structures, which is confirmed as shown with many other examples earlier by their IR spectra.[5] In general,

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Table 2. IR Data of M′[MacCo(CN)$_2$] and [MacCo(CN)]$_n$

compound	ν_{CN} (cm^{-1})
K[(*t*-Bu)$_4$PcCo(CN)$_2$] (**12**)	2137
Na[1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)$_2$] (**10**)	2131
Na[2,3,9,10,16,17,23,24-(C$_7$H$_{15}$)$_8$PcCo(CN)$_2$] (**11**)	2139
K[(*t*-Bu)$_4$-2,3-NcCo(CN)$_2$] (**13**)	2130
[(*t*-Bu)$_4$PcCo(CN)]$_n$ (**8**)	2197
[2,3,9,10,16,17,23,24-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**7**)	2151
[(*t*-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**)	
[1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**6**)	2212
(*t*-Bu)$_4$-2,3-NcCo(py)(CN) (**14**)	2141

Table 3. Powder Conductivities of [MacCo(CN)]$_n$

compound	σ_{RT} [S/cm]
[PcCo(CN)]$_n$[9]	2×10^{-2}
[1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**6**)	$<10^{-12}$
[(*t*-Bu)$_4$PcCo(CN)]$_n$ (**8**)	9×10^{-8}
[2,3,9,10,16,17,23,24-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**7**)	3×10^{-9}
[(*t*-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**)	8×10^{-2}

the CN valence frequencies of cyano-bridged compounds are shifted to higher energy by about 20 cm^{-1}, as compared with the mononuclear complexes M[MacM(CN)$_2$].[5,17]

The UV/vis spectra of **10**–**13** recorded in chloroform or DMF are similar to those obtained from **6**–**9** (Table 1). The ^{1}H NMR spectra of **10**–**13** recorded in acetone-d_6 show the expected number and intensities of signals which confirm the proposed structures. The resonances of the aromatic protons in the macrocycles **10**–**13** appear at lower δ values, as observed for the bridged complexes **6**–**9** in pyridine-d_5. This fact is good evidence that, in pyridine-d_5, the cyano-bridged compounds **6**–**9** are transformed into monomers MacCo(CN)(py-d_5). If **6**–**9** existed as bridged structures in solution, the signals due to the aromatic protons would be shifted to higher field in comparison to the monomers **10**–**13** as we have shown earlier, e.g., with [*t*-Bu)$_4$PcFe(dib)]$_n$ (dib = 1,4-diisocyanobenzene).[18] Compounds **7**–**9** are formed as described above by treating the monomeric cyano complexes **11**–**13** with boiling water, thereby removing 1 mol of NaCN or KCN. The products obtained by this pathway are identical with those obtained by the cyanogen method. In the case of Na[1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)$_2$] (**10**), this reaction was not successful; **10** did not react with water to form [1,4,8,11,15,18,22,25-(C$_7$H$_{15}$)$_8$PcCo(CN)]$_n$ (**6**). The monomeric complex **10** was obtained as a waxy product, like most 1,4,8,11,15,18,22,25-octasubstituted phthalocyanines.[5] This type of phthalocyanines shows relatively low transition temperatures for the formation of the liquid crystalline state.[5,19] This property of **10** probably hinders an attack of the water molecules to form the cyano-bridged compound.

The powder conductivities of the cyano-bridged compounds **6**–**9** are given in Table 3. Comparing the conductivities of [PcCo(CN)]$_n$ and [(*t*-Bu)$_4$PcCo(CN)]$_n$ (**8**), a decrease of 10^5 is observed. Generally, the conductivities of axially bridged substituted phthalocyanines are lower than those of the unsubstituted systems;[5] steric hindrance of the bulky or long-chain groups in the peripheric positions of the macrocycles prevents an intercalation between the polymeric chains, which is necessary for charge transport by the hopping mechanism.[5] In (*t*-Bu)$_4$-2,3-Nc, the influence of the bulky *tert*-butyl groups seems to be lower. The *tert*-butyl substituent is relatively small compared with the large heteroaromatic π system of the naphthalocyanine ring, hence leading to good semiconducting properties of [(*t*-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**) without losing the advantage of high solubility in common organic solvents.

In summary, we have shown that soluble MacCo react quantitatively with cyanogen to form μ-cyano-bridged (phthalocyaninato)- and (2,3-naphthalocyaninato)cobalt(III) complexes **6**–**9** in a one-step reaction starting from MacCo. The bridged [MacCo(CN)]$_n$ **7**–**9** obtained by this method starting from MacCo **2**–**4** are identical with the bridged complexes **7**–**9** obtained by the method via the monomeric dicyano complexes M′[MacCo(CN)$_2$] **10**–**13**, respectively. With [(*t*-Bu)$_4$-2,3-NcCo(CN)]$_n$ (**9**), a good semiconducting material was found which is easy to manufacture due to its high solubility in common organic solvents.

Experimental Section

General Methods. IR: Bruker IFS 48. UV/vis: Shimadzu UV-365, Shimadzu UV-3102 PC. MS: Varian MAT 711. ^{1}H NMR: Bruker AC 250. Elemental analyses: Carlo Erba elemental analyzer 1104, 1106. 1,2-Dicyano-3,6-diheptylbenzene,[20] 1,2-dicyano-4,5-diheptylbenzene,[21] 2,3-dicyano-6-*tert*-butylnaphthalene,[14] potassium dicyano(tetra-*tert*-butylphthalocyaninato)cobalt(III) (**12**),[16] and cyanogen (NCCN)[22] were prepared according to literature methods. Compound **3** was purified by column chromatography (silica gel/toluene).

6-*tert*-Butyl-1*H*-benz[*f*]diiminodihydroisoindole (5). Anhydrous NH$_3$ was bubbled into a stirred mixture of 6-*tert*-butyl-2,3-dicyanonaphthalene[14] (5.7 g, 20 mmol), 0.5 g of sodium methanolate, and 50 mL of dry methanol for 1 h while the mixture was at room temperature and then for about 20 h while it was at reflux. The product was purified by column chromatography (silica gel/methanol) and evaporated, affording **5**: 5,6 g (92%), white powder, mp 195 °C dec. Analytical data. IR (KBr), ν (cm^{-1}): 3400–2500 vs, b, 2961 vs, 2868 m, 1690 m, 1641 s, 1597 m, 1541 vs, 1510 s, 1456 s, 1393 m, 1366 m, 1325 s, 1288 vs, 1273 m, 1259 m, 1225, vw, 1142 vs, 1099 m, 1070 m, 1041 w, 910 m, 872 s, 816 m, 737 w, 648 m, 606 w. ^{1}H NMR (250 MHz), DMSO-d_6: δ 8.43 (s, 3H), 8.27 (s, 1H), 8.24 (s, 1H), 7.99 (d, J = 8.73 Hz, 1H), 7.94 (s, 1H), 7.75 (d, J = 8.69, 1H), 1.39 (s, 9H). MS (70 eV), m/z (relative intensity): 251 (M$^+$, 50), 236 (M$^+$ − NH, 100), 194 (M$^+$ − *t*-Bu, 60). Anal. Calcd for $C_{16}H_{17}N_3$ (251.33): C, 74.46; H, 6.82; N, 16.72. Found: C, 74.49; H, 7.00; N, 14.51.

(1,4,8,11,15,18,22,25-Octaheptylphthalocyaninato)cobalt(II) (1) and (2,3,9,10,16,17,23,24-Octaheptylphthalocyaninato)cobalt(II) (2). 1,2-Dicyano-3,6-diheptylbenzene (1.5 g, 4.62 mmol) or 1,2-dicyano-4,5-diheptylbenzene (1.5 g, 4.62 mmol) and cobalt trichloride (500 mg, 2.1 mmol), respectively, were refluxed for 24 h in 25 mL of ethylene glycol. The cooled dark blue solution was poured into methanol (100 mL), and the precipitate formed was centrifuged, washed with acetone, and dried. Further purification was performed by column chromatography (silica gel/toluene). The blue fraction was collected, and the solvent was evaporated. **1**: 910 mg (58%) waxy blue powder. **2**: 990 mg (63%), blue powder. Analytical data. **1**. IR (KBr), ν (cm^{-1}): 3084 w, 3055 w, 2955 s, 2922 vs, 2853 s, 1574 w, 1560 w, 1506 m, 1466 m, 1458 m, 1377 w, 1345 w, 1325 m, 1304 w, 1269 w, 1241 w, 1177 m, 1094 m, 1040 w, 920 m, 828 w, 802 w, 762 m, 722 w. UV/vis (CHCl$_3$): λ_{max} 700 nm, 666 (sh), 634, 329, 304. MS (FD) m/z: 1356.8 (M$^+$). Anal. Calcd for $C_{88}H_{128}N_8Co$ (1356.96): C, 77.89; H, 9.50; N, 8.26. Found: C, 77.92; H, 10.25; N, 8.09. **2**. IR (KBr), ν (cm^{-1}): 3090 w, 3060 w, 2955 s, 2922 vs, 2853 s, 1524 m, 1466 m, 1418 m, 1402 w, 1377 m, 1333 m, 1109 s, 895 w, 754 m, 731 w. UV/vis (CHCl$_3$): λ_{max} 679 nm, 651 (sh), 610, 329, 290. MS (FD), m/z: 1357.0 (M$^+$). Anal. Calcd for $C_{88}H_{128}N_8Co$ (1356.96): C, 77.89; H, 9.50; N, 8.26. Found: C, 78.47; H, 9.77; N, 7.34.

(Tetra-*tert*-butyl-2,3-naphthalocyaninato)cobalt(II) (4). A mixture of 1.5 g of 6-*tert*-butyl-1*H*-benz[*f*]diiminodihydroisoindole (**5**), 780 mg

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of cobalt(II) acetylacetonate, and 1 mL of 1,8-diazabicyclo[5.4.0]-undecene (DBU) was refluxed for 7 h in 2-ethoxyethanol. The cooled dark green solution was poured into methanol (100 mL), and the precipitate was filtered and extracted with acetone. The residue was dried and purified by column chromatography (alumina, neutral/toluene: tetrahydrofuran 3:1). The green fraction was collected, the solvent was evaporated, and the residue was dried (80 °C, 0.01 Torr). **4**: 770 mg (51%), green powder. Analytical data. IR (KBr), ν (cm^{-1}): 3053 w, 2953 s, 2905 m, 2867 m, 1616 w, 1528 w, 1502 w, 1477 w, 1462 w, 1377 s, 1361 s, 1346 s, 1317 m, 1271 m, 1258 m, 1205 w, 1163 w, 1144 m, 1103 vs, 1088 s, 1049 m, 1022 w, 947 w, 901 m, 887 m, 808 m, 748 m, 729 m, 642 w. UV/vis (DMF): λ_{max} 748 nm, 717 (sh), 669, 336. MS (FD), *m/z*: 995.6 (M^+). Anal. Calcd for $C_{64}H_{56}N_8Co$ (996.2): C, 77.17; H, 5.67; N, 11.25. Found: C, 77.49; H, 5.80; N, 11.27.

Sodium Dicyano(1,4,8,11,15,18,22,25-octa-*n*-heptylphthalocyaninato)cobalt(III) (10) and Sodium Dicyano(2,3,8,10,16,17,23,24-octa-*n*-heptylphthalocyaninato)cobalt(III) (11). A mixture of NaCN (420 mg, 8.4 mmol) and **1** or **2** (600 mg, 0.44 mmol), respectively, was refluxed at 24 h in ethanol (20 mL) while air was bubbled through the suspension. The cooled green solution was purified by chromatography (silica gel/ethanol). **10**: 530 mg (84%), green waxy powder. **11**: 540 mg (86%), green powder. Analytical data. **10**. IR (KBr), ν (cm^{-1}): 3080 w, 3066 w, 2955 s, 2924 vs, 2854 s, 2131 w, 1605 w, 1575 w, 1504 m, 1458 m, 1377 w, 1323 m, 1229 w, 1184 m, 1099 m, 1038 w, 982 w, 918 w, 831 w, 756 w, 743 w, 721 w. UV/vis (DMF): λ_{max} 708 nm, 637, 440, 349, 289. ^{1}H NMR (acetone-d_6): δ 0.84 (t, 24H, CH_3), 1.29 (m, 32H, CH_2), 1.43 (m, 16H, CH_2), 1.70 (m, 16H, CH_2), 2.20 (m, 16H, CH_2), 4.60 (t, 16H, CH_2), 7.90 (s, 8H, Pc). Anal. Calcd for $C_{90}H_{128}N_{10}NaCo$ (1431.99): C, 75.48; H, 9.01; N, 9.78. Found: C, 76.16; H, 9.94; N, 9.61. **11**. IR (KBr), ν (cm^{-1}): 2955 s, 2924 vs, 2853 s, 2139 w, 1518 m, 1454 s, 1414 m, 1369 m, 1350 m, 1333 m, 1165 w, 1103 s, 1042 w, 1006 w, 921 w, 893 w, 835 w, 750 w, 729 w. UV/vis (DMF): λ_{max} 683 nm, 648 (sh), 615, 435, 363, 344 (sh), 291. ^{1}H NMR (acetone-d_6): δ 0.93 (t, 24H, CH_3), 1.45−1.37 (m, 48H, CH_2), 1.55 (m, 16H, CH_2), 1.68 (m, 16H, CH_2), 3.26 (t, 16H, CH_2), 9.25 (s, 8H, Pc). Anal. Calcd for $C_{90}H_{128}N_{10}NaCo$ (1431.99): C, 75.48; H, 9.01; N, 9.78. Found: C, 76.19; H, 8.94; N, 9.43.

Potassium Dicyano(tetra-*tert*-butyl-2,3-naphthalocyaninato)cobalt(III) (13). A mixture of KCN (400 mg) and **4** (250 mg) was refluxed for 18 h in acetone (50 mL) while air was bubbled through the suspension. The cooled green solution was purified by chromatography (silica gel/acetone). The volume of the solvent was reduced, and the product was precipitated with *n*-hexane. **13**: 110 mg (40%), green powder. Analytical data. IR (KBr), ν (cm^{-1}): 3053 w, 2955 s, 2905 m, 2866 m, 2130 vw, 1701 w, 1616 w, 1522 w, 1462 w, 1360 s, 1319 m, 1271 m, 1259 m, 1205 w, 1142 m, 1103 vs, 1086 s, 1051 m, 903 m, 887 m, 723 m. UV/vis (DMF): λ_{max} 765 nm, 728 (sh), 684, 424, 344, 326. ^{1}H NMR (acetone-d_6): δ 1.69 (s, 36H, *t*-Bu), 8.08 (m, 4H, Nc), 8.65 (m, 8H, Nc), 9.89 (m, 8H, Nc). Anal. Calcd for $C_{66}H_{56}N_{10}CoK$ (1087.27): C, 72.91; H, 5.19; N, 12.88. Found: C, 71.89; H, 6.52; N, 11.00.

(μ-Cyano)(tetra-*tert*-butylphthalocyaninato)cobalt(III) (8), (μ-Cyano)(2,3,9,10,16,17,23,24-octaheptylphthalocyaninato)cobalt(III) (7), (μ-Cyano)(tetra-*tert*-butyl-2,3-naphthalocyaninato)cobalt(III) (9), and (μ-Cyano)(1,4,8,11,15,18,22,25-octaheptylphthalocyaninato)cobalt(III) (6). Method a. The alkali salts **11**, **12**, and **13** (100 mg) were refluxed in water (50 mL) for 2 d. The precipitate was filtered and dried. Further purification was performed by column chromatography: **8** (alumina, neutral Ak 5/$CHCl_3$) 80 mg (85%); **7** (silica gel/$CHCl_3$) 70 mg (72%); **9** (silica gel/$CHCl_3$:tetrahydrofuran 3:1) 50 mg (53%).

Method b. Cyanogen (ca. 2.5 g) was condensed in an autoclave, which was cooled in a bath of liquid nitrogen. Then an open flask filled with a solution of **1**, **2**, **3**, and **4** (100 mg), respectively, in $CHCl_3$ was introduced into the autoclave. The autoclave was shut, and the cooling was stopped. The solution was stirred for 3 d at room temperature. Then the excess of cyanogen was allowed to escape, and the solvent was evaporated. Further purification was done as described above. **8**: 90 mg (87%). **7**: 87 mg (85%). **9**: 90 mg (88%). Compound **6** was purified by column chromatography (silica gel/$CHCl_3$): 92 mg (90%). Analytical data. **8**. IR (Nujol), ν (cm^{-1}) 2197 m, 1616 m, 1519 m, 1404 w, 1394 m, 1377 m, 1364 m, 1323 m, 1281 s, 1202 m, 1155 m, 1094 s, 1057 m, 941 s, 893 w, 827 s, 766 m, 752 s, 690 w, 669 m. UV/vis (DMF): λ_{max} 675 nm, 645 (sh), 609, 358, 286. ^{1}H NMR (pyridine-d_5): δ 1.64 (m, 36H, *t*-Bu), 8.34 (m, 4H, Pc), 9.69 (m, 4H, Pc), 9.85 (m, 4H, Pc). Anal. Calcd for $C_{49}H_{48}N_9Co$ (821.34): C, 71.61; H, 5.89; N, 15.34. Found: C, 70.57; H, 6.14, N, 15.03. **7**. IR (KBr), ν (cm^{-1}): 2955 s, 2926 vs, 2855 s, 2151 vw, 1724 w, 1522 w, 1460 m, 1416 w, 1348 w, 1258 w, 1176 w, 1101 s, 1041 w, 891 w, 750 m, 728 w. UV/vis (DMF): λ_{max} 683 nm, 655 sh, 615, 362, 341 sh, 292. ^{1}H NMR (pyridine-d_5): δ 0.92 (t, 24H, CH_3), 1.34 (m, 32H, CH_2), 1.39 (m, 16H, CH_2), 1.57 (m, 16H, CH_2), 1.98 (m, 16H, CH_2), 3.25 (t, 16H, CH_2), 9.71 (s, 8H, Pc). Anal. Calcd for $C_{89}H_{128}N_9Co$ (1382.99): C, 77.29; H, 9.33; N, 9.12. Found: C, 76.07, H, 9.97; N, 8.46. **9**. IR (KBr), ν (cm^{-1}) 3057 w, 2958 s, 2906 m, 2868 m, 1614 w, 1597 w, 1506 w, 1477 w, 1463 w, 1350 vs, 1319 w, 1273 m, 1259 m, 1101 m, 1086 s, 1051 m, 905 m. UV/vis (DMF): λ_{max} 767 nm, 732 sh, 687, 325. ^{1}H NMR (pyridine-d_6): δ 1.63 (s, 36H, *t*-Bu), 8.07 (m, 4H, Nc), 8.75 (m, 8H, Nc), 10.22 (m, 8H, Nc). Anal. Calcd for $C_{65}H_{56}N_9Co$ (1022.15): C, 76.38; H, 5.52; N, 12.33. Found: C, 74.13; H, 5.58; N, 12.37. **6**. IR (KBr) ν (cm^{-1}): 3086 w, 3059 w, 2955 s, 2926 vs, 2854 s, 2212 w, 1605 m, 1576 w, 1504 m, 1466 s, 1408 m, 1377 m, 1339 s, 1231 w, 1173 s, 1003 m, 920 m, 835 w, 756 w, 744 w, 730 w. UV/vis (DMF): λ_{max} 710, 640, 445, 355, 289. ^{1}H NMR (pyridine-d_5): δ 0.80 (t, 24H, CH_3), 1.20 (m, 32H, CH_2), 1.33 (m, 16H, CH_2), 1.66 (m, 16H, CH_2), 2.22 (m, 16H, CH_2), 4.70 (t, 16H, CH_2), 8.10 (s, 8H, Pc). Anal. Calcd for $C_{89}H_{128}N_9Co$ (1382.99): C, 77.29; H, 9.33; N, 9.12. Found: C, 76.20; H, 9.13; N, 9.25.

Cyano(pyridine)(tetra-*tert*-butyl-2,3-naphthalocyaninato)cobalt(III) (14). A 25 mg sample of $[(t\text{-Bu})_4\text{-2,3-NcCo(CN)}]_n$ (**9**) was stirred in 2 mL of pyridine at 60 °C for 24 h. The solution was poured into 20 mL of methanol/H_2O (3:1), and the precipitate was filtered and washed with methanol. Further purification was performed by column chromatography (silica gel/$CHCl_3$). **14**: 24 mg (88%), green powder. Analytical data. IR (Nujol), ν (cm^{-1}): 3051 vw, 2912 vs, 2858 vs, 2141 vw, 1618 w, 1603 w, 1522 w, 1504 w, 1558 vs, 1375 vs, 1360 vs, 1319 w, 1271 m, 1259 m, 1205 w, 1142 m, 1101 vs, 1088 vs, 1051 m, 949 w, 899 m, 887 m, 810 m, 748 s, 725 s, 704 w. UV/vis (DMF): λ_{max} 768, 686, 325. ^{1}H NMR ($CDCl_3$): δ 1.67 (s, 36H, *t*-Bu), 2.99 (d, *J* = 5.4 Hz, 2H, py); 5.52 (m, 2H, py); 6.30 (t, *J* = 7.7 Hz, 1H, py); 7.99 (m, 4H, Nc); 8.49 (m, 8H, Nc); 9.86 (m, 8H, Nc). Anal. Calcd for $C_{70}H_{61}N_{10}Co$ (1101.25): C, 76.35; H, 5.58; N, 12.72. Found: C, 75.41; H, 5.62; N, 12.03.

IC950088V