Synthesis of Alkyl- and Alkyloxy-Substituted 2,3-Naphthalocyanines

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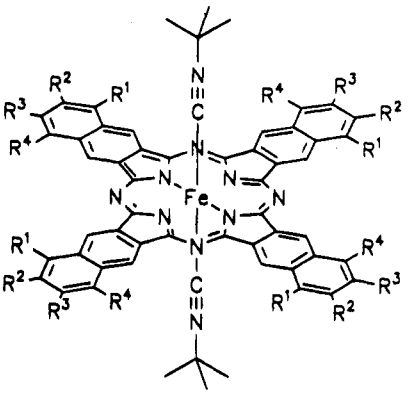
Four novel differently substituted 2,3-dicyanonaphthalenes (6-(hexyloxy)-2,3-dicyanonaphthalene (**5**), 5-(hexyloxy)-2,3-dicyanonaphthalene (**11**), 6,7-bis(hexyloxy)-2,3-dicyanonaphthalene (**17**), and 5,8-diheptyl-2,3-dicyanonaphthalene (**22**)) and the respective peripherally substituted (bis(*tert*-butylisocyano)-2,3-naphthalocyaninato)iron(II) compounds **23**–**26** were synthesized and characterized.

2,3-Naphthalocyanines have attracted much attention because of their potential use as semiconducting materials,[1,2] in nonlinear optics,[3] as laser dyes,[4] and in photodynamic therapy.[5] Due to intermolecular interactions between the macrocycles, peripherally unsubstituted metallophthalocyanines and also metallo-2,3-naphthalocyanines are practically insoluble in common organic solvents such as chloroform or toluene. Solubility, however, is necessary for many applications, e.g., thin film preparation by spin-coating and for the Langmuir–Blodgett technique. Although it has been shown that soluble compounds are formed by inserting side chains in the periphery of (phthalocyaninato)metal complexes,[1] very little is known about the syntheses and properties of peripherally substituted 2,3-naphthalocyanines.[4,6]

2,3-Naphthalocyanines can be prepared by heating a mixture of 2,3-dicyanonaphthalene with the metal or the corresponding metal salt in an inert solvent.[1] To obtain information on the influence of alkyl and alkoxy chains on the solubility of 2,3-naphthalocyanines, we report here on the syntheses and characterization of four different heptyl- and hexyloxy-substituted 2,3-dicyanonaphthalenes, which were converted into the respective substituted (2,3-naphthalocyaninato)nickel complexes. Although these complexes were relatively soluble in organic solvents, their tendency to aggregate made the characterization by UV/vis and especially by NMR spectroscopy difficult, and they are not included in this paper. To prevent an aggregation we decided to synthesize the corresponding axially coordinated (bis(*tert*-butylisocyano)-2,3-naphthalocyaninato)iron compounds (R_x2,3-NcFe(*t*-BuNC)$_2$) **23**–**26** (Scheme 1), which were characterized by IR, UV/vis, Mössbauer, mass, and ^{1}H NMR spectroscopy.

Scheme 1



compound	R^1	R^2	R^3	R^4
23	H	OC_6H_{13}	H	H
24	OC_6H_{13}	H	H	H
25	H	OC_6H_{13}	OC_6H_{13}	H
26	C_7H_{15}	H	H	C_7H_{15}

In contrast to some already known 1,4-dialkoxy-2,3-dicyanonaphthalenes,[4] the 2,3-dicyanonaphthalenes described in this paper, 6-(hexyloxy)-2,3-dicyanonaphthalene (**5**), 5-(hexyloxy)-2,3-dicyanonaphthalene (**11**), 6,7-bis(hexyloxy)-2,3-dicyanonaphthalene (**17**), and 5,8-diheptyl-2,3-dicyanonaphthalene (**22**), are substituted in the peripheric benzene rings. 6-(Hexyloxy)-2,3-dicyanonaphthalene (**5**) was prepared by boiling a mixture of 6-hydroxy-2,3-dicyanonaphthalene (**4**), hexyl iodide, and potassium carbonate in acetone. **4** was synthesized starting from commercially available 4-hydroxy-1,2-dimethylbenzene in a four-step reaction given in the literature[7] (Scheme 2). For the side-chain bromination with *N*-bromosuccinimide and the analogous Diels–Alder reaction with fumarodinitrile, the hydroxyl group has to be protected by formation of the benzoyl ester **1**.

For the preparation of 5-(hexyloxy)-2,3-dicyanonaphthalene (**11**) a comparable reaction path was followed (Scheme 3). However, bromination of the benzoyl ester of 2,3-dimethylphenol (**6**) only forms the tribromide **7**

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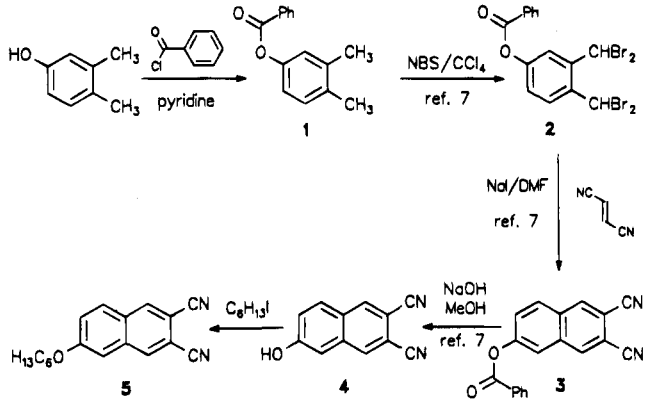
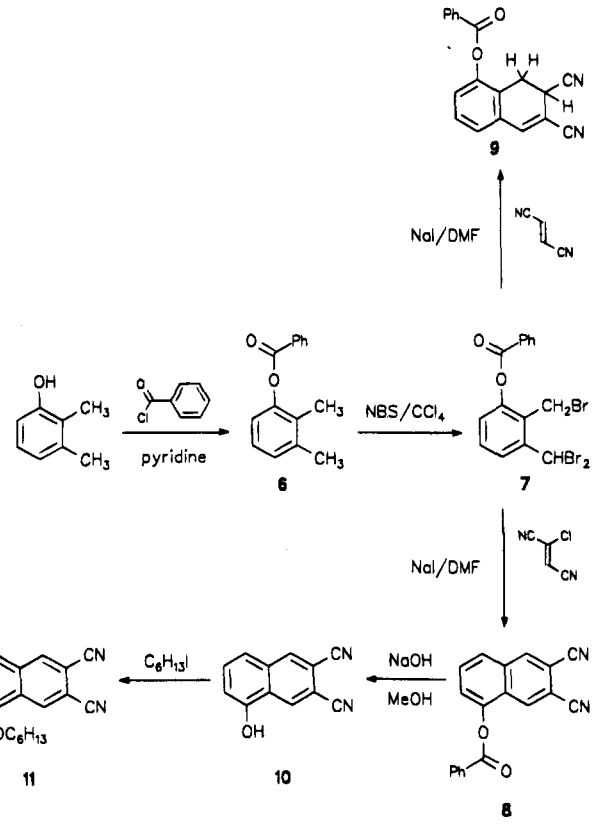
Scheme 2



Scheme 3



contrary to the reaction of **1** → **2** (Scheme 2). The reaction of tribromide **7** and fumarodinitrile gave the dihydronaphthalene derivative **9**, which did not form the naphthalene system under the reaction conditions. Therefore **8** was prepared by the reaction of **7** with a mixture of chlorofumarodinitrile and chloromaleodinitrile which was obtained from succinonitrile and phosphorus pentachloride.[8] During this reaction a chlorinated dihydronaphthalene was formed which eliminated hydrogen chloride under the basic reaction conditions with formation of **8**. The subsequent reactions (**8** → **10** → **11**) were analogously performed as described above for the preparation of **5**. The hydroxy dinitrile **10** could not be obtained completely pure (see Experimental Section); however, its derivatives **8** and **11** (see Experimental Section) were well characterized, confirming the structure of **10**.

6,7-Bis(hexyloxy)-2,3-dicyanonaphthalene (**17**) was synthesized by the reaction path shown in Scheme 4.

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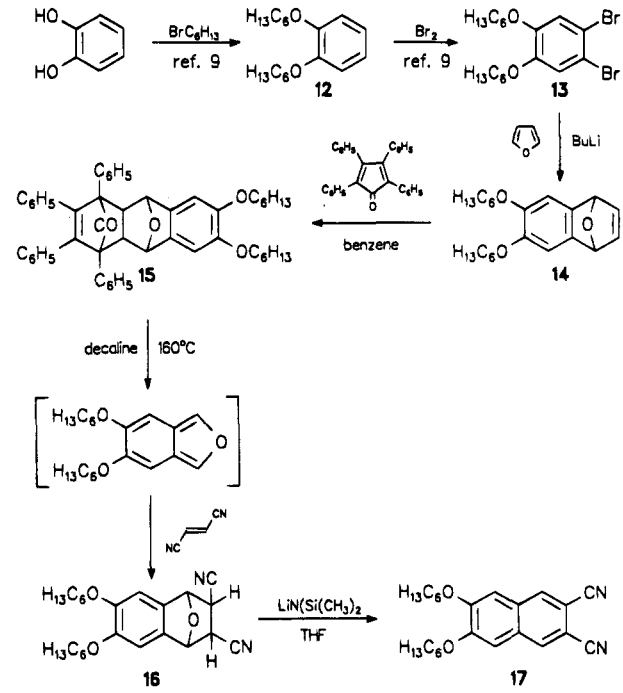
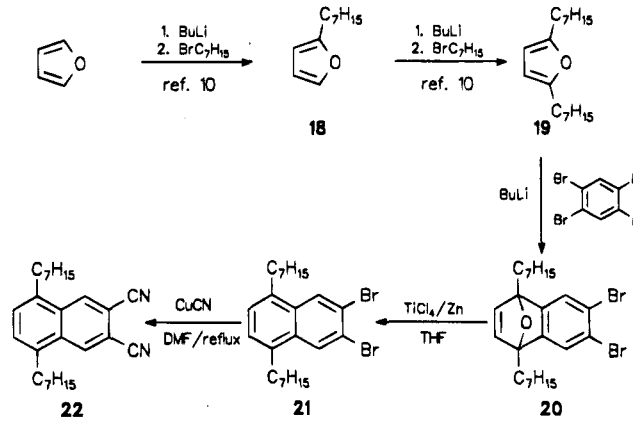
Scheme 4



Scheme 5



Catechol was converted into the bis(hexyl ether) **12** and brominated to yield **13**.[9] With butyllithium, the intermediate dehydrobenzene was generated, which reacted with furan in a Diels–Alder reaction to give **14**. In a second Diels–Alder reaction, **14** with tetraphenylcyclopentadienone affords **15**, which is decomposed in boiling decalin with formation of intermediate dialkoxyisobenzofuran, which is trapped with fumarodinitrile to give **16**. By using lithium bis(trimethylsilyl)amide as base[10,11] **16** was dehydrated to form **17**.

5,8-Diheptyl-2,3-dicyanonaphthalene (**22**) was prepared from furan as shown in Scheme 5. 2,5-Diheptylfuran (**19**)[10] was reacted in a Diels–Alder reaction with dibromodehydrobenzene, which is intermediately formed by reaction of 1,2,4,5-tetrabromobenzene and butyllithium, to yield **20**. Reductive deoxygenation was carried out by treatment of **20** with zinc/titanium tetrachloride.[12] The dinitrile **22** was obtained from **21** by a

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Table 1. ^{1}H NMR Data of the Axial *tert*-Butyl Group of (R)$_x$MacFe(*t*-BuNC)$_2$ ($CDCl_3$)

compound	δ [ppm]
PcFe(*t*-BuNC)$_2$[16]	−0.51
2,3,9,20,26,27,23,24-(C_7H_{15})$_8$PcFe(*t*-BuNC)$_2$[17,18]	−0.50
2,3-NcFe(*t*-BuNC)$_2$[19,20]	−0.38
3,12,21,30-($C_6H_{13}O$)$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**23**)	−0.37
2,11,20,29-($C_6H_{13}O$)$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**24**)	−0.39
3,4,12,13,21,22,30,31-($C_6H_{13}O$)$_8$-2,3-NcFe(*t*-BuNC)$_2$ (**25**)	−0.40
2,4,11,14,20,23,29,32-(C_7H_{15})$_8$-2,3-NcFe(*t*-BuNC)$_2$ (**26**)	−0.35

Rosenmund van Braun reaction[1] with copper cyanide in dimethylformamide.

For the synthesis of the alkyl- and alkyloxy-substituted (2,3-naphthalocyaninato)iron compounds **23**−**26**, the substituted 2,3-dicyanonaphthalenes **5**, **11**, **17**, and **22** were heated under reflux with iron acetate and a catalytical amount of DBU in anhydrous hexanol.[1] The crude products obtained were treated with *tert*-butyl isocyanide and the formed (bis(*tert*-butylisocyano)-2,3-naphthalocyaninato)iron complexes **23**−**26** (Scheme 1) purified by column chromatography. The compounds **23**−**26** were characterized by mass spectrometry, IR, UV/vis, ^{1}H NMR, and ^{57}Fe Mössbauer spectroscopy, and elemental analyses. Due to the bulky axial ligand, no aggregation effects in the UV/vis or ^{1}H NMR spectra were observed. The ^{1}H NMR spectra of phthalocyanines[13] and 2,3-naphthalocyanines[14] are known to show large diamagnetic ring-current shifts. The spectra obtained for the complexes **23**−**26** are in agreement with the proposed structures. The signals of the macrocyclic protons appear at low field, while the protons of the axial *tert*-butyl isocyanide ligands are shifted to higher field. The shift of the protons of the side chains to lower field depends on their distance to the heteroaromatic system. The shorter the distance between them and the center of the macrocycle, the larger the shift of the ^{1}H resonances to lower field. The protons of the axial ligands of **23**−**26** are less shifted to higher field than those of comparable phthalocyanine compounds (Table 1). This observation is in accordance with earlier reported results.[14]

By using monosubstituted dinitriles such as the 5- and 6-(hexyloxy)-2,3-dicyanonaphthalenes **5** and **11**, respectively, as starting material, a mixture of four constitutional isomers (C_{4h}, D_{2h}, C_{2v}, C_s) is formed.[15] This could be confirmed by ^{1}H NMR spectroscopy in the case of 2,-11,20,29-($C_6H_{13}O$)$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**24**). The methyl protons of the alkoxy side chains in **24** show two triplet signals in an intensity ratio of 1:1. This is due to the steric hindrance of the side chains if two of them are on adjacent carbons. In this case they shift out of the plane of the 2,3-naphthalocyanine ring and a different chemical shift is observed as in the case of nonhindered side chains. For 3,12,21,30-(OC_6H_{13})$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**23**) no hindrance of the side chains occurs and therefore the formation of different isomers cannot be proved by ^{1}H NMR.

The data of the Q-bands in UV/vis spectra of the 2,3-naphthalocyanines **23**−**26** are given in Table 2. All peripherally substituted 2,3-naphthalocyanines show a small red shift of their Q-bands compared with the unsubstituted 2,3-NcFe(*t*-BuNC)$_2$. In the case of a substitution in position 2 of the 2,3-Nc ring, the bathochromic shift is somewhat larger as in the case of position 3. The same effect is observed for alkoxy phthalocyanines substituted in positions 1 and 2, respectively (Table 2).[18]

Table 2. λ_{max} of the Q-Band of (R)$_x$MacFe(*t*-BuNC)$_2$ ($CHCl_3$)

compound	Q-band λ_{max} [nm]
PcFe(*t*-BuNC)$_2$[16]	658
1,4,8,11,15,18,22,25-(C_7H_{15})$_8$PcFe(*t*-BuNC)$_2$[17,18]	683
2,3,9,10,16,17,23,24-(C_7H_{15})$_8$PcFe(*t*-BuNC)$_2$[17,18]	675
2,3-NcFe(*t*-BuNC)$_2$[19,20]	750
3,12,21,30-($C_6H_{13}O$)$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**23**)	755
2,11,20,29-($C_6H_{13}O$)$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**24**)	758
3,4,12,13,21,22,30,31-($C_6H_{13}O$)$_8$-2,3-NcFe(*t*-BuNC)$_2$ (**25**)	752
2,5,11,14,20,23,29,32-(C_7H_{15})$_8$-2,3-NcFe(*t*-BuNC)$_2$ (**26**)	760

Table 3. ν_{NC} Valence Frequency of (R)$_x$-2,3-NcFe(*t*-BuNC)$_2$

compound	ν_{NC} valence frequency
2,3-NcFe(*t*-BuNC)$_2$[19,20]	2147
3,12,21,30-($C_6H_{13}O$)$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**23**)	2143
2,11,20,29-($C_6H_{13}O$)$_4$-2,3-NcFe(*t*-BuNC)$_2$ (**24**)	2145
3,4,12,13,21,22,30,31-($C_6H_{13}O$)$_8$-2,3-NcFe(*t*-BuNC)$_2$ (**25**)	2137
2,5,11,14,20,23,29,32-(C_7H_{15})$_8$-2,3-NcFe(*t*-BuNC)$_2$ (**26**)	2147

The IR spectra of **23**−**26** show the characteristic ν_{NC} valence frequency of the axial ligand (Table 3). Compared to the frequency of the unsubstituted 2,3-NcFe(*t*-BuNC)$_2$, all alkoxy-substituted (RO)$_x$-2,3-NcFe(*t*-BuNC)$_2$ show a lower ν_{NC} valence frequency of the axial *tert*-butylisocyano group. This is due to the electron-donating effect of the alkoxy side chains.

The Mössbauer parameters of the complexes **23**−**26** show the typical values of bisaxially coordinated phthalocyaninato iron(II) compounds (Table 4).[21] The isomer shift and the quadrupole splitting is lowered with respect to PcFe and 2,3-NcFe. The decrease of the quadropole splitting is due to the transition of a tetracoordinated to a hexacoordinated iron species, which is accompanied by an equalization of the electron density in the d orbitals.

Experimental Section

6-Hydroxy-2,3-dicyanonaphthalene (**4**),[7] 1,2-dibromo-4,5-bis(hexyloxy)benzene (**13**),[9] and 2,5-diheptylfuran (**19**)[10] were prepared according to literature methods.

1-(Benzoyloxy)-2-(bromomethyl)-3-(dibromomethyl)benzene (7). 1-(Benzoyloxy)-2,3-dimethylbenzene (**6**) (22.6 g, 0.1 mol), 58.7 g (0.33 mol) of *N*-bromosuccinimide (NBS), and 0.1 g of azobis(isobutyronitrile) dissolved in 120 mL of CCl_4 were boiled under reflux for 24 h. The solution was filtered while still hot and washed with CCl_4. The solvent was evaporated and the residue recrystallized from *n*-hexane to yield **7**: 25.9 g (55.9%), white needles, mp 148−150 °C. IR (KBr): ν = 3074 m, 1738 vs, 1599 w, 1464 s, 1450 s, 1271 vs, 1263 vs, 1238 vs, 1213 s, 1175 s, 1159 s, 1082 s, 1065 vs, 1024 m, 756 m, 712 vs, 684 m, 658 m cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.26 (d, *J* = 5.1 Hz, 2H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.73−7.46 (m, 4H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.04 (s, 1H), 4.60 (s, 2H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 164.2, 148.6, 141.5, 134.1, 130.2, 130.0, 128.8, 128.6, 127.5, 125.4, 124.2, 35.8, 29.5 ppm. MS (70 eV): *m/z* = 463 (M^+), 383 (M^+ − Br).

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Table 4. Mössbauer Data of MacFe and MacFe(t-BuNC)$_2$

compound	T [K]	δ [mm/s]	ΔE_Q [mm/s]
PcFe[21]	293	0.38	2.58
PcFe(t-BuNC)$_2$[21]	293	0.16	0.80
2,3-NcFe[21]	293	0.36	2.21
3,12,21,30-($C_6H_{13}O$)$_4$-2,3-NcFe(t-BuNC)$_2$ (**23**)	82	0.21	0.61
2,11,20,29-($C_6H_{13}O$)$_4$-2,3-NcFe(t-BuNC)$_2$ (**24**)	82	0.21	0.61
3,4,12,13,21,22,30,31-($C_6H_{13}O$)$_8$-2,3-NcFe(t-BuNC)$_2$ (**25**)	82	0.21	0.58

Anal. Calcd for $C_{15}H_{11}O_2Br_3$: C, 38.93; H, 2.39; Br, 51.78; Found: C, 39.03; H, 2.35; Br, 51.93.

5-(Benzoyloxy)-2,3-dicyanonaphthalene (8) and 8-(Benzoyloxy)-2,3-dicyano-1,2-dihydronaphthalene (9). 1-(Benzoyloxy)-2-(bromomethyl)-3-(dibromomethyl)benzene (**7**) (23.2 g, 0.05 mol), 5.6 g (0.05 mol) of chlorofumarodinitrile and 3.9 g (0.05 mol) of fumarodinitrile, respectively, and 50 g of sodium iodide were stirred at 70 °C in 150 mL of dry DMF for 18 h. The brown mixture was poured into a solution of 32 g of Na_2SO_3 in 1 L of H_2O. The precipitate was filtered, washed with water, dried and recrystallized from acetone to yield **8** and **9**.

8: 3.0 g (20.1%), white solid, mp 248–251 °C. IR (KBr): ν = 3080 w, 3026 w, 2235 m, 1742 vs, 1599 w, 1585 w, 1569 w, 1450 m, 1358 m, 1259 s, 1232 vs, 1188 m, 1178 m, 1055 s, 1024 w, 1003 w, 928 w, 895 w, 789 w, 750 w, 700 s cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.41 (s, 1H), 8.29 (d, J = 7.1 Hz, 2H), 7.94–7.65 (m, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 164.5, 147.1, 136.0, 134.6, 134.1, 131.0, 130.5, 130.1, 129.1, 128.1, 127.3, 126.4, 123.4, 115.5, 115.4, 110.9, 110.7 ppm. MS (70 eV): m/z = 298 (M^+), 105 (C_6H_5CO). Anal. Calcd for $C_{19}H_{10}O_2N_2$: C, 76.50; H, 3.38; N, 9.39. Found: C, 76.65; H, 2.66; N, 9.10.

9: 7.9 g (52.5%), pale solid, mp 197–198 °C. IR (KBr): ν = 3061 vw, 2210 s, 1734 vs, 1618 w, 1599 w, 1462 s, 1448 m, 1317 w, 1261 s, 1246 vs, 1227 vs, 1175 m, 1092 s, 1061 vs, 1024 m, 932 w, 903 w, 795 m, 706 vs, 685 w cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.21 (d, J = 5.7 Hz, 2H), 7.69 (m, 1H), 7.58 (m, 2H), 7.45 (m, 2H), 7.42 (m, 1H), 7.23 (m, 1H), 3.75 (t, J = 7.1 Hz, 1H), 3.17 (m, 2H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 164.4, 148.6, 143.7, 134.3, 130.8, 130.3, 129.0, 128.8, 128.3, 126.9, 126.1, 124.1, 117.0, 116.6, 104.7, 26.6, 25.0 ppm. MS (70 eV): m/z = 300 (M^+), 105 (C_6H_5CO). Anal. Calcd for $C_{19}H_{12}O_2N_2$: C, 75.99; H, 4.03; N, 9.33. Found: C, 76.45; H, 4.24; N, 8.58.

5-Hydroxy-2,3-dicyanonaphthalene (10). 5-(Benzoyloxy)-2,3-dicyanonaphthalene (**8**) (3 g, 10 mmol) was stirred at room temperature with a solution of 2.2 g of sodium hydroxide in 30 mL of methanol for 0.5 h. The solution was acidified with 2 N HCl to pH 2. The yellow precipitate was filtered and washed with $CHCl_3$ to yield **9**: 1.9 g (97.2%), yellow solid, mp 272–275 °C. IR (KBr): ν = 3306 s, 3057 w, 2239 s, 1618 m, 1574 s, 1454 w, 1387 w, 1367 vs, 1285 vs, 1182 w, 1169 m, 797 s, 750 s cm^{-1}. ^{1}H NMR (250 MHz, DMSO-d_6): δ 11.29 (s, 1H), 8.72 (s, 2H), 7.67 (m, 1H), 7.57 (d, J = 8.1, 1H), 7.25 (d, J = 7.4, 1H) ppm. MS (70 eV): m/z = 194 (M^+). Anal. Calcd for $C_{12}H_6ON_2$: C, 74.22; H, 3.11; N, 14.43. Found: C, 69.90; H, 3.31; N, 13.06.

5- and 6-(hexyloxy)-2,3-dicyanonaphthalenes (11 and 5). 5- or 6-hydroxy-2,3-dicyanonaphthalene (**10** or **4**) (1 g, 5 mmol), 2.6 g (12 mmol) of hexyl iodide, and 3 g (22 mmol) of potassium carbonate were heated in 80 mL of anhydrous acetone for 80 h under reflux. The mixture was filtered and the solvent evaporated. The excess of hexyl iodide was removed in vacuum, the residue was purified by column chromatography (silica gel/$CHCl_3$) and recrystallized from ethanol to yield **11**: 0.4 g (27.9%), white needles, mp 178–179 °C. IR (KBr): ν = 3086 w, 3022 w, 2953 s, 2930 s, 2870 m, 2232 s, 1618 w, 1572 m, 1458 s, 1382 m, 1364 vs, 1279 vs, 1250 w, 1134 s, 1051 m, 962 m, 916 m, 793 m, 743 m cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.25 (s, 1H), 7.67 (dd, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 4.18 (t, J = 6.4 Hz, 2H), 1.95 (m, 2H), 1.55 (m, 2H), 1.41 (m, 4H), 0.93 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 155.0, 135.3, 134.1, 131.6, 131.0, 125.5, 120.0, 116.4, 116.0, 110.5, 109.2, 108.8, 69.0, 31.5, 29.0, 25.9, 22.6, 14.0 ppm. MS (70 eV): m/z = 278 (M^+), 194 ($M^+ - C_6H_{12}$). Anal. Calcd for $C_{18}H_{18}ON_2$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.25; H, 7.00; N, 10.15.

5: 0.8 g (55.8%), buff-colored needles, mp 123–124 °C. IR (KBr): ν = 3065 w, 3030 w, 2943 s, 2910 m, 2855 m, 2232 vs, 1618 vs, 1595 m, 1499 s, 1464 s, 1394 vs, 1276 w, 1258 s, 1238 w, 1205 vs, 1177 w, 1136 m, 1016 s, 930 m, 895 m, 837 m cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.16 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 7.17 (s, 1H), 4.11 (t, J = 6.5 Hz, 2H), 1.86 (m, 2H), 1.52 (m, 2H), 1.36 (m, 4H), 0.90 (t, J = 6.5 Hz, 3H), ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 160.8, 135.2, 135.1, 134.0, 130.0, 128.4, 124.0, 116.2, 116.1, 110.4, 107.0, 68.7, 31.4, 28.8, 25.5, 22.4, 13.9 ppm. MS (70 eV): m/z = 278 (M^+), 194 ($M^+ - C_6H_{12}$). Anal. Calcd for $C_{18}H_{18}ON_2$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.93; H, 7.18; N, 10.11.

2,3-Bis(hexyloxy)-5,6-epoxy-5,6-dihydronaphthalene (14). To a stirred solution of 21.8 g (0.05 mol) of 1,2-dibromo-4,5-bis(hexyloxy)benzene (**13**) and 34 g (0.5 mol) of furan in 1 L of toluene was added slowly a solution of 3.2 g (0.05 mol) of t-BuLi in 500 mL of hexane over 4 h at −50 °C. After 1 h, the cooling was stopped and 3 mL of methanol was added at −30 °C. The solution was washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue purified by column chromatography (silica gel/toluene) to yield **14**: 11.8 g (68.6%), white powder, mp 58–60 °C. IR (KBr): ν = 3026 vw, 3007 vw, 2955 vs, 2932 vs, 2860 vs, 1603 w, 1506 m, 1497 m, 1466 s, 1423 w, 1379 w, 1324 m, 1281 m, 1261 m, 1196 m, 1124 w, 1069 m, 1015 w, 928 w, 851 m, 802 w, 729 m, 694 m, 638 m cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.05 (s, 2H), 6.94 (s, 2H), 5.64 (s, 2H), 3.94 (t, J = 6.6 Hz, 4H), 1.76 (m, 4H), 1.44 (m, 4H), 1.31 (m, 8H), 0.89 (t, J = 6.4, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 146.2, 143.2, 141.9, 109.8, 82.5, 70.2, 31.6, 29.4, 25.7, 22.6, 14.0 ppm. MS (70 eV): m/z = 344 (M^+), 260 ($M^+ - C_6H_{12}$), 176 (260 − C_6H_{12}), 148 (176 − C_2H_4). Anal. Calcd for $C_{22}H_{32}O_3$: C, 76,70; H, 9.36. Found: C, 75.85; H, 9.77.

2,3-Bis(hexyloxy)-5,10-epoxy-6,9-carbonyl-6,7,8,9-tetraphenyl-5,5a,6,9,9a,10-hexahydroanthracene (15). 2,3-Bis(hexyloxy)-5,6-epoxy-5,6-dihydronaphthalene (**14**) (10.3 g, 0.03 mol) and 11.5 g (0.03 mol) of tetraphenylcyclopentadienone were heated in 200 mL of benzene under reflux for 3 d. The solvent was evaporated and the residue purified by column chromatography (silica gel/toluene) to yield **15**: 10 g (45.8%), white powder, mp 166 °C dec. IR (KBr): ν = 3061 w, 3032 w, 2999 w, 2932 s, 2856 s, 1771 vs, 1605 m, 1490 s, 1466 s, 1447 m, 1431 m, 1306 vs, 1219 s, 1169 w, 1090 s, 1074 s, 1026 w, 1007 w, 980 w, 924 w, 908 w, 895 w, 858 w, 841 m, 770 w, 746 m, 696 vs, 660 m cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.37–6.78 (m, 22H), 5.65 (s, 2H), 3.95 (t, J = 6.5 Hz, 4H), 2.95 (s, 2H), 1.75 (m, 4H), 1.42 (m, 4H), 1.28 (m, 8H), 0.83 (t, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 196.7, 148.5, 139.1, 138.4, 135.5, 135.1, 129.8, 129.5, 128.1, 127.4, 127.3, 126.5, 106.6, 81.3, 69.9, 64.3, 47.0, 31.5, 29.3, 25.7, 22.5, 14.0 ppm. MS (FD): m/z = 728 (M^+). Anal. Calcd for $C_{51}H_{52}O_4$: C, 84.03; H, 7.19. Found: C, 83.91; H, 7.68.

2,3-Bis(hexyloxy)-5,8-epoxy-6,7-dicyano-5,6,7,8-tetrahydronaphthalene (16). Fumarodinitrile (19.5 g, 0.25 mol) was heated in 260 mL of decalin to 160 °C. Over 2 h a suspension of 7.3 g (10 mmol) of 2,3-bis(hexyloxy)-5,10-epoxy-6,9-carbonyl-6,7,8,9-tetraphenyl-5,5a,6,9,9a,10-hexahydroanthracene (**15**) in 65 mL of decalin was added and the temperature kept for 0.5 h. The solvent and the excess of fumarodinitrile were distilled off in vacuum. Further purification by column chromatography using 1:1 toluene/hexane (to elute the byproduct tetraphenylbenzene) and later $CHCl_3$ as eluent gave **16**: 2.7 g (68.0%), white powder, mp 71–76 °C. IR(KBr): ν = 2957 s, 2932 vs, 2872 s, 2858 s, 2245 m, 1610 m, 1497 s, 1470 s, 1441 m, 1379 w, 1335 s, 1321 s, 1286 m, 1217 s, 1148 w, 1090 vs, 1005 w, 957 w, 928 w, 850 s, 804 w, 675 m, 627 m cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.01 (s, 1H), 6.92 (s, 1H), 5.65 (m,

2H), 3.97 (m, 4H), 3.47 (m, 1H), 2.73 (d, J = 4.3 Hz, 1H), 1.79 (m, 4H), 1.46 (m, 4H), 1.32 (m, 8H), 0.88 (m, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 149.8, 149.7, 133.6, 132.1, 118.5, 116.3, 107.7, 105.8, 83.2, 80.7, 69.5, 37.4, 36.4, 31.4, 29.1, 29.0, 25.5, 25.5, 22.5, 13.9 ppm. MS (70 eV): m/z = 396 (M^+), 318 ($M^+ - N_2H_2C_4$), 234 (318 − C_6H_{12}), 150 (234 − C_6H_{12}). Anal. Calcd for $C_{24}H_{32}O_3N_2$: C, 72.70; H, 8.13; N, 7.06. Found: C, 73.02; H, 9.14; N, 6.90.

2,3-Bis(hexyloxy)-6,7-dicyanonaphthalene (17). A solution of 2 g (5 mmol) of 2,3-bis(hexyloxy)-5,8-epoxy-6,7-dicyano-5,6,7,8-tetrahydronaphthalene (**16**) was dissolved in 20 mL of THF and cooled to −55 °C. During 30 min 5 mL of a 1 M solution of lithium bis(trimethylsilyl)amide in THF was added. After 15 min 10 mL of a saturated NH_4Cl solution was added. The product was extracted with Et_2O and washed with a solution of NH_4Cl until neutral. The Et_2O phase was dried ($MgSO_4$) and evaporated. The product was purified by column chromatography (silica gel/$CHCl_3$) and recrystallized from ethanol to yield **17**: 0.9 g (47.1%), white powder, mp 147–149 °C. IR (KBr): ν = 2955 vs, 2932 vs, 2224 s, 1612 s, 1510 vs, 1477 s, 1464 s, 1423 s, 1398 w, 1283 vs, 1248 w, 1225 m, 1217 w, 1182 vs, 991 w, 926 w, 908 m cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.07 (s, 2H), 7.14 (s, 2H), 4.13 (t, J = 6.5 Hz, 4H), 1.91 (m, 4H), 1.51 (m, 4H), 1.32 (m, 8H), 0.88 (t, J = 7.0, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 153.0, 133.2, 129.7; 116.5, 107.6, 107.2, 69.2, 31.4, 28.7, 25.6, 22.5, 13.9 ppm. MS (70 eV): m/z = 378 (M^+), 294 ($M^+ - C_6H_{12}$), 210 ($M^+ - 2 \times C_6H_{12}$). Anal. Calcd for $C_{24}H_{30}N_2O_2$: C, 76.16; H, 7.99; N, 7.40. Found: C, 75.69; H, 8.43; N, 6.82.

6,7-Dibromo-1,4-diheptyl-1,4-epoxy-1,4-dihydronaphthalene (20). To a stirred solution of 1,2,4,5-tetrabromobenzene (16 g, 0.04 mol) and 10.6 g (0.04 mol) of 2,5-diheptylfuran (**19**) in 600 mL of toluene was added slowly a solution of 3.2 g (0.044 mol) of t-BuLi in 500 mL of hexane over 4 h at −20 °C. After 1 h, the cooling was stopped and 10 mL of methanol was added. The solution was washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue purified by column chromatography (silica gel/toluene) to yield **20**: 15.4 g (77.4%), pale oil. IR (KBr): ν = 3074 vw, 2955 vs, 2928 vs, 2854 s, 1578 m, 1462 s, 1435 m, 1377 m, 1339 s, 1319 m, 1296 m, 1207 w, 1126 w, 1080 m, 957 s, 876 s, 829 s, 767 w, 702 s, 667 w cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.31 (s, 2H), 6.72 (s, 2H), 2.18 (m, 4H), 1.42 (m, 10H), 0.89 (t, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 154.1, 145.5, 124.1, 120.3, 91.7, 31.8, 30.0, 29.2, 29.2, 24.7, 22.7, 14.1 ppm. MS (FAB): m/z = 499 (M^+). Anal. Calcd for $C_{24}H_{34}Br_2O$: C, 57.8; H, 6.9. Found: C, 57.9; H, 7.3.

2,3-Dibromo-5,8-diheptylnaphthalene (21). To a suspension of 6 g (92 mmol) of zinc in 30 mL of THF was added carefully 21.6 g (12.6 mL, 104 mmol) of $TiCl_4$ at −20 °C. The mixture was heated under reflux for 15 min and cooled to −10 °C, and a solution of 10 g (20 mmol) of **20** in 60 mL of THF was added dropwise. The mixture was refluxed for 12 h, cooled, and poured into a mixture of 120 g of ice and 60 mL of concd HCl. The mixture was extracted with CH_2Cl_2, and the extract was washed with water, dried ($CaCl_2$), and evaporated. The product was purified by column chromatography (silica gel/hexane) to yield **21**: 3.2 g (31.0%), white powder, mp 52–55 °C. IR (KBr): ν = 3026 vw, 2955 vs, 2928 vs, 2856 vs, 1578 m, 1495 vw, 1466 s, 1414 m, 1377 w, 1308 w, 1257 w, 1209 w, 1115 m, 1047 w, 876 s, 841 w, 727 m, 694 w cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.18 (s, 2H), 7.12 (s, 2H), 2.85 (t, J = 7.2 Hz, 4H), 1.59 (m, 4H), 1.34 (m, 4H), 1.27 (m, 12H), 0.79 (t, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 136.2, 132.3, 129.3, 126.8, 121.4, 32.7, 31.8, 30.6, 29.6, 29.1, 22.7, 14.1 ppm. MS (70 eV): m/z = 482 (M^+), 397 ($M^+ - C_6H_{13}$), 317 (397 − Br), 299 (397 − C_7H_{14}). Anal. Calcd for $C_{24}H_{34}Br_2$: C, 59.76; H, 7.10; Br, 33.13. Found: C, 60.88; H, 7.92; Br, 31.56.

2,3-Dicyano-5,8-diheptylnaphthalene (22). 5,8-Diheptyl-2,3-dibromonaphthalene (**21**) (3.2 g, 7.5 mmol) and 4 g of (44 mmol) CuCN were heated in 20 mL of DMF under reflux for 6 h. Concentrated NH_3 (80 mL) was added, and air was bubbled through the suspension for 10 h. The precipitate was filtered and extracted with $CHCl_3$. The solvent was evaporated and the residue recrystallized from n-hexane to yield **22**: 800 mg (32.2%), white powder, mp 74–76 °C. IR (KBr): ν = 2951 s, 2920 vs, 2868 s, 2853 s, 2228 s, 1585 m, 1470 s, 1456 m, 1371 s, 1346 w, 1327 w, 1271 w, 1151 w, 1119 w, 1105 w, 1055 w, 1030 w, 1007 w, 978 w, 901 s, 864 w, 851 w, 814 w, 777 w, 752 w, 719 m, 665 w, 636 w cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.51 (s, 2H), 7.51 (s, 2H), 3.02 (t, J = 7.8 Hz, 4H), 1.69 (m, 4H), 1.34 (m, 4H), 1.29 (m, 12H), 0.87 (t, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 138.5, 132.8, 132.5, 130.5, 116.3, 109.1, 32.6, 31.4, 30.7, 29.7, 29.1, 22.6, 14.0 ppm. MS (70 eV): m/z = 374 (M^+), 289 ($M^+ - C_6H_{13}$), 205 (289 − C_6H_{13}). Anal. Calcd for $C_{26}H_{34}N_2$: C, 83.37; H, 9.15; N, 7.48. Found: C, 81.15; H, 9.04; N, 7.09.

Bis(*tert*-butylisocyano)-3,12,21,30-tetrakis(hexyloxy)- (23), (Bis(*tert*-butylisocyano)-2,11,20,29-tetrakis(hexyloxy)- (24), (Bis(*tert*-butylisocyano)-3,4,12,13,21,22,-30,31-octakishexyloxy)-(25), and (Bis(*tert*-butylisocyano)-2,5,11,14,20,23,29,32-octaheptyl-2,3-naphthalocyaninato)iron(II) (26). **5** or **11** (556 mg) or 756 mg of **17** or 748 mg of **22** (2 mmol), 174 mg (1 mmol) of iron acetate, and 1.5 mL of DBU were heated in 25 mL of hexanol for 3 h under reflux. The mixture was poured into 150 mL of methanol/water (1:1). The black-brown precipitate was filtered and extracted with methanol. The residue was stirred with a mixture of 1 mL of *tert*-butyl isocyanide and 5 mL of $CHCl_3$ for 24 h at 60 °C. The solvent and the excess *tert*-butyl isocyanide were removed in vacuum. The residue was purified by column chromatography (Al_2O_3 (activity 5)/$CHCl_3$) and dried in vacuum (0.01 Torr) at 80 °C to yield the following.

3,12,21,30-(OC_6H_{13})$_4$-2,3-NcFe(*t*-BuNC)$_2$ (23): 230 mg (35%), green powder. IR (KBr): ν = 3059 vw, 2951 m, 2930 m, 2856 m, 2143 vs, 1618 vs, 1512 s, 1454 m, 1429 m, 1362 vs, 1315 w, 1236 vs, 1205 m, 1172 w, 1148 s, 1097 vs, 1045 m, 1026 m, 972 w, 889 s, 806 w, 712 m cm^{-1}. UV/vis ($CHCl_3$): λ_{max} 755, 727 sh, 677, 351 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.67 (m, 8H), 8.40 (m, 4H), 7.78 (m, 4H), 7.46 (m, 4H), 4.33 (t, J = 5.7 Hz, 8H), 2.04 (m, 8H), 1.65 (m, 8H), 1.45 (m, 16H), 0.99 (t, J = 6.9 Hz, 12H), −0.37 (s, 18H) ppm. MS (FD): m/e = 1170 ($M^+ - 2 \times t$-BuNC). Mössbauer (82 K): δ = 0.21 mm/s, ΔE_Q = 0.61 mm/s. Anal. Calcd for $C_{82}H_{90}N_{10}O_4Fe$: C, 73.75; H, 6.79; N, 10.49. Found: C, 73.79; H, 6.87; N, 10.20.

2,11,20,29-(OC_6H_{13})$_4$-2,3-NcFe(*t*-BuNC)$_2$ (24): 280 mg (42%), green powder. IR (KBr): ν = 3055 vw, 2951 m, 2930 m, 2868 m, 2145 vs, 1610 vw, 1587 w, 1504 s, 1456 m, 1406 vw, 1362 vs, 1329 vw, 1263 vs, 1207 m, 1148 vw, 1109 vs, 1059 s, 1040 s, 899 w, 791 w, 766 vw, 754 w, 733 w, 717 w cm^{-1}. UV/vis ($CHCl_3$): λ_{max} 758, 725 sh, 677, 360, 310 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.27 (m, 4H), 9.77 (m, 4H), 8.09 (d, J = 8.3 Hz, 4H), 7.67 (t, J = 7.8 Hz, 4H), 7.11 (d, J = 7.1 Hz, 4H), 4.46 (t, J = 6.3 Hz, 8H), 2.30 (m, 8H), 1.86 (m, 8H), 1.63 (m, 16H), 1.15 (t, J = 7.0 Hz, 6H), 1.03 (t, J = 7.0 Hz, 6H), −0.39 (s, 18H). MS (FD): m/z = 1169 ($M^+ - 2 \times t$-BuNC). Mössbauer (82 K): δ = 0.21 mm/s, ΔE_Q = 0.61 mm/s. Anal. Calcd for $C_{82}H_{90}N_{10}O_4Fe$: C, 73.75; H, 6.79; N, 10.49. Found: C, 73.40; H, 7.05; N, 9.58.

3,4,12,13,21,22,30,31-(OC_6H_{13})$_8$-2,3-NcFe(*t*-BuNC)$_2$ (25): 283 mg (33%), green powder. IR (KBr): ν = 3061 vw, 2953 m, 2928 s, 2856 m, 2137 s, 1620 w, 1593 w, 1501 s, 1462 vs, 1391 m, 1364 s, 1250 vs, 1227 m, 1188 vw, 1137 s, 1101 vs, 1051 m, 1020 w, 937 vw, 889 m, 827 vw, 804 vw, 750 w, 696 vw cm^{-1}. UV/vis ($CHCl_3$): λ_{max} 752, 722 sh, 673, 358 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.55 (s, 8H), 7.71 (s, 8H), 4.35 (t, J = 6.6 Hz, 16H), 2.05 (m, 16H), 1.65 (m, 16H), 1.45 (m, 32H), 0.97 (t, J = 7.0 Hz, 24H), −0.40 (s, 18H) ppm. MS (FAB): m/z = 1569 ($M^+ - 2 \times t$-BuNC). Mössbauer (82 K): δ = 0.21 mm/s, ΔE_Q = 0.58 mm/s. Anal. Calcd for $C_{106}H_{138}N_{10}O_8Fe$: C, 73.33; H, 8.01; N, 8.07. Found: C, 72.72; H, 7.64; N, 8.19.

2,5,11,14,20,23,29,32-(C_7H_{15})$_8$-2,3-NcFe(*t*-BuNC)$_2$ (26): 280 mg (42%), green powder. IR (KBr): ν = 2953 s, 2924 vs, 2853 s, 2147 vs, 1526 w, 1464 m, 1389 vs, 1337 s, 1198 w, 1121 vs, 887 m, 723 m cm^{-1}. UV/vis ($CHCl_3$): λ_{max} 760, 724 sh, 679, 414, 370 nm. ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.03 (s, 8H), 7.57 (s, 8H), 3.70 (t, J = 7.5 Hz, 16H), 2.24 (m, 16H), 1.85 (m, 16H), 1.63 (m, 16H), 1.47 (m, 32H), 0.96 (t, J = 7.0 Hz, 24H), −0.35 (s, 18H) ppm. MS (FD): m/z = 1554 ($M^+ - 2 \times t$-BuNC). Anal. Calcd for $C_{114}H_{154}N_{10}Fe$: C, 79.59; H, 9.02; N, 8.14. Found: C, 78.03; H, 8.85; N, 7.45.

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