Synthesis and Electrochemistry of Diels-Alder Adducts of [60]Fullerene with a Phthalocyanine and a Hemiporphyrazine

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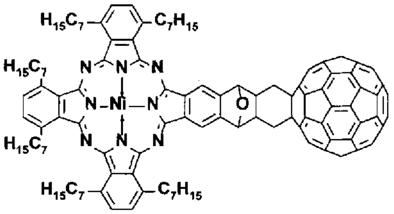
The synthesis of a new Diels-Alder adduct **7** of [60]fullerene and a phthalocyaninenickel compound containing a longer spacer than the originally reported Diels-Alder adduct **1** is described. The bisenophilic hemiporphyrazinenickel compound **11** reacts with [60]fullerene to form a Diels-Alder adduct **12** containing two fullerene units. Spectroelectrochemical investigations of **7** and **12** reveal multiple reductions, which are attributed to the corresponding subunits of the molecules. In contrast to **1**, the electron acceptor properties of the [60]fullerene unit in both molecules have no influence on the electronic properties of the phthalocyanine and hemiporphyrazine, respectively.

Recently, we reported on the synthesis and the electrochemistry of the [60]fullerene derivative **1** which contains a covalently bound phthalocyanine[1] (Figure 1). In this green fullerene the two electroactive species are held in close proximity by a spacer consisting of two six-membered rings. Multiple electron reductions of both electroactive moieties were determined and could be attributed to the corresponding subunits of the molecule. Athough a charge transfer from the phthalocyanine to the fullerene moiety at ambient conditions was not found we have shown that the optical properties of the phthalocyanine substructure of this molecule are characteristically influenced by the fullerene addend, especially after the first reduction of the C_{60} moiety.

Figure 1. Diels-Alder adduct **1**[1] of [60]fullerene with an unsymmetrically substituted phthalocyaninenickel moiety



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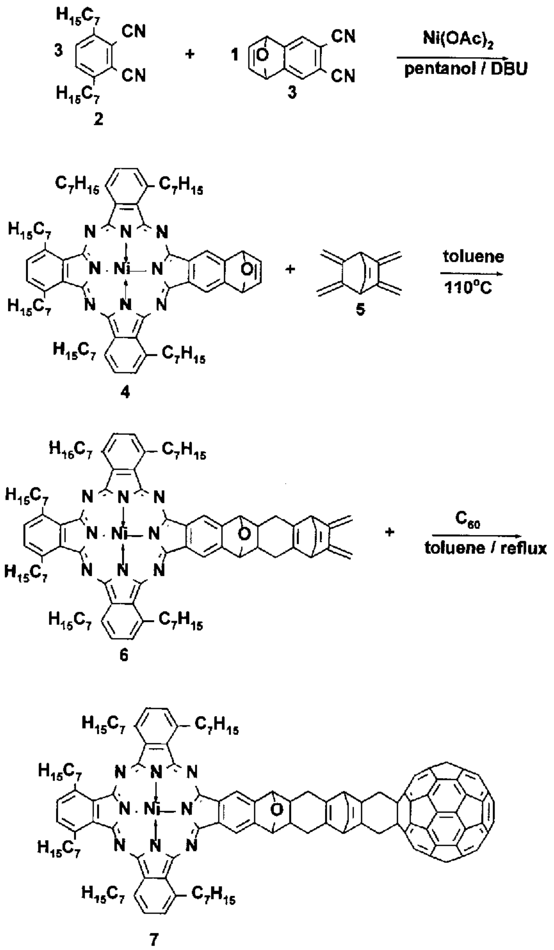
In this paper we report on the synthesis and electrochemical characterization of a new fullerene-phthalocyanine diad **7** and for the first time on a triad **12** containing two fullerenes and a bridging hemiporphyrazine as macrocycle. The construction principle, which we used in this approach is based on the pronounced dienophilic behaviour of [60]fullerene undergoing facile Diels-Alder-reactions with a large variety of dienes. Hence, the synthesis of compounds **7** and **12** was accomplished by allowing [60]fullerene to react with the corresponding macrocycles **6** and **11** containing one or two diene subunits, respectively (Scheme 1 and 2).

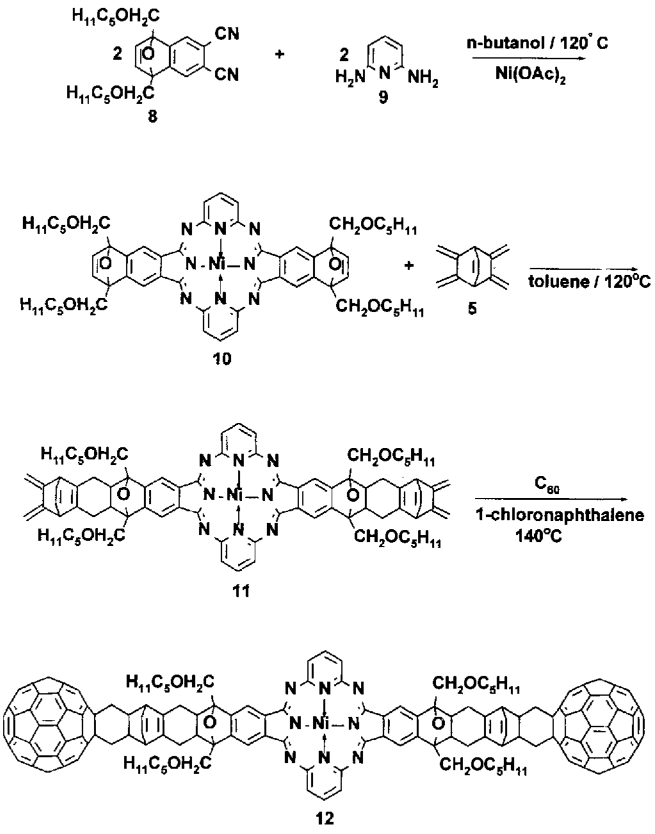
The unsymetrically substituted phthalocyaninenickel compound **4** was synthesized using a statistical method[2]. Three equivalents of 3,6-diheptylphthalodinitrile[3] (**2**) and one equivalent of 6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalene[4] (**3**) were allowed to react with nickel acetate in the presence of a catalytic amount of DBU in pentanol under reflux (Scheme 1). The phthalocyaninenickel compound **4** was separated from other phthalocyanines by column chromatography on silica gel with toluene and then chloroform/ethanol as the mobile phases. Addition of the "tetraene" **5**[5] to the dienophilic phthalocyanine **4** in toluene at 110°C led to the formation of phthalocyanine **6** which was purified by column chromatography on silica gel with chloroform as eluent[2]. In the ^{1}H-NMR spectrum of compound **6** the signal of the O−CH protons appear as a singlet at $\delta = 5.41$. Due to the missing coupling with the neighbouring protons only the *exo* configuration of the spacer is possible[6]. Compound **7** was obtained by the reaction of C_{60} with **6** in toluene (Scheme 1). Purification was carried by column chromatography on silica gel (toluene/hexane, 1:1; $R_f = 0.3$; 62% yield).

The formation of **7** is clearly demonstrated by comparison of the NMR spectra of **4**, **6** and **7**. The ^{1}H-NMR spectrum of **7** shows similar features as that of compound **6** with the exception that the resonances for the protons at the exocyclic double bonds in **6** at $\delta = 4.95$ disappear, whereas in **7** the newly formed methylene protons resonate as a complex multiplet. In most cases a splitted Q-band in the UV/Vis spectra of unsymetrically substituted phthalocyanines is observed, but in contrast to this behaviour and also to our first report[1] on a phthalocyanine-fullerene adduct the UV/Vis spectrum of **7** shows a single Q-band[7].

Scheme 1. Synthesis of the Diels-Alder adduct **7** of [60]fullerene with the unsymmetrically substituted phthalocyanine-nickel compound **6**



Scheme 2. Synthesis of the Diels-Alder adduct **12** of [60]fullerene with the symmetrically substituted hemiporphyrazine-nickel compound **11**



This indicates, that the electron-withdrawing influence of the fullerene moiety of **7** is significantly reduced due to the enlarged spacer (two additional six-membered rings) compared to **1**[1]. In the region between 300 and 500 nm the UV/Vis spectrum of **7** is superimposable with that of **6** and typical fullerene monoaddition products[8]. The M^+ peak of **7** at *m/z* 2103 appears as the only signal in the FD-MS.

The cyclic voltammogram of **7** shows four reversible reduction waves at −0.56, −0.91, −0.96 and −1.34V vs. SCE. The second and third reduction are very close to each other. In the differential pulse voltammogram a further electron transition at −1.6V is observed. The waves were assigned to the corresponding reduction steps by spectroelectrochemistry (UV/Vis/NIR). The first reduction step at −0.56V is due to the fullerene moiety, which is reflected by the appearance of an absorption at 1075 nm, characteristic for singly reduced fullerene[9]. Compared with compound **1**[1] the electron acceptor properties of the fullerene unit have no influence to minimize the splitting Q-band. The second and the third reduction step at −0.91V and −0.96V, which are attributed to the reduction of the phthalocyaninenickel subunit and to the second reduction of the fullerene part respectively, are very close to each other. The corresponding UV/Vis/NIR spectra are characterized by (i) split and a shift of the Q-band from 691 nm to 655 nm and 595 nm, (ii) a further absorption at 945 nm (characteristic for singly reduced phthalocyaninenickel compounds[10]), and (iii) the disappearance of the band at 1075 nm and the development of the absorption at 870 nm and 945 nm (fullerene). The fourth reduction at −1.34V is due to the fullerene, reflected by an absorption at 900 nm (beside 650 and 590 nm which are characteristic absorption bands for singly reduced phthalocyaninenickel compounds). Finally, the fifth reduction step is probably due to the phthalocyanine, formed by the disappearance of the absorptions at 650 and 590 nm. Also a fullerene electron transfer, caused of the potential shift of the fifth reduction compared to the free C_{60} step at −1.37V is possible.

Compared to the reduction steps of free C_{60} (Table 1) the first, the third and perhaps the fifth reduction of **7** are shifted by about 180−250 mV to more negative potentials. These measurements show that the reduction potentials of both, the fullerene and the phthalocyaninenickel moieties in **7** do not change significantly compared to the seperated phthalocyaninenickel compounds and other C_{60} monoaddition products[8]. In contrast to **1**[1], the electron acceptor properties of the fullerene unit in **7** have only a small influence on the electronic properties of the phthalocyanine. This is probably due to the larger spacer linking the two electroactive sites.

Table 1. Redox potenials ($E_{1/2}$ in V vs. SCE) of C_{60}, **7**, **11** and **12** in DMF/toluol (1:1)/n-Bu_4NPF_6 [*number of electrons* which are transfered (the number of electrons signed with * is not available)]; R1 (1st reduction), R2 (2nd reduction), R3 (3rd reduction), R4 (4th reduction), R5 (5th reduction)

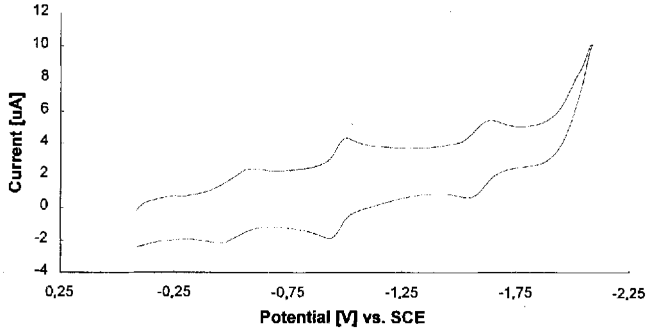
Compound	$E_{1/2}$ (R1)	$E_{1/2}$ (R2)	$E_{1/2}$ (R3)	$E_{1/2}$ (R4)	$E_{1/2}$ (R5)
C_{60}	−0.31 [*1*]	−0.78 [*1*]	−1.37 [*1*]	−1.88 [*1*]	–
7	−0.56 [*1*]	−0.91 [–]*	−0.96 [–]*	−1.34 [–]*	−1.6 [–]*
12	−0.52 [*2*]	−0.97 [*3*]	−1.59 [–]*	−1.96 [–]*	–
11	−0.91 [*2*]	−1.63 [–]*	–	–	–

For the synthesis of bidentate diene **11** (Scheme 2)[11], equivalent amounts of 6,7-dicyano-1,4-dihydro-1,4-bis(2′-methylbutoxymethylene)-1,4-epoxynaphthalene (**8**) and 6,7-diaminopyridine (**9**) were treated with nickel acetate in n-butanol at 120°C. The product **10** was purified by column chromatography on silica gel using toluene/ethyl acetate as the mobile phase. After addition of the "tetraene" **5**[5] to the bifunctional dienophilic hemiporphyrazine **10** in toluene at 120°C, compound **11** was formed, which was isolated by column chromatography (silca gel; toluene/ethyl acetate). The synthesis of compound **12** was accomplished by stirring C_{60} with **11** in 1-chloronaphthalene at 140°C for one day; **12** was obtained as a brown product and was purified by column chromatography (silca gel; toluene/ethyl acetate, 10:1) in 12% yield.

In the ^{1}H-NMR spectrum of **11** the signals for the protons of the exocyclic double bonds appear at δ = 5.00–5.19 and 6.38–6.41. As expected, in the ^{1}H-NMR spectrum of **12** these resonances are missing. Compared with the ^{1}H-NMR spectrum of compound **6**, the signals due to the H atoms of the spacer unit of **11** appear at the same chemical shifts, therefore the *exo* configuration of the spacer is likely. The UV/Vis spectrum of the brown product shows the typical bands for [60]fullerene monoadducts at 463nm[8]. The M^+ peak of **12** at *m/z* 2782 appears as the only signal in the FD-MS.

The cyclic voltammogram of the dumbbell compound **12** shows three reductions (Table 1) at −0.52, −0.97 and −1.59 V vs. SCE (Figure 2). In the differential pulse voltammogram a further electron transition at −1.96 V can be observed. The assignment of the corresponding reduction steps was done by spectroelectrochemistry (UV/Vis/NIR). The number of electrons, which are transferred were determined using chronocoulometry. During the first reduction step two electrons are transferred. The electron transitions are due to the fullerene moiety[8]. This is reflected by an absorption at 980 nm in the UV/Vis/NIR spectrum[1]. The second and the third reduction waves at −0.97 and −1.59 V are due to almost simultaneous one-electron reductions of the two fullerene units as well as of the hemiporphyrazine moieties, respectively (Table 1). The uptake of a third electron at each of the two fullerene sites in **12** is responsible for the fourth reduction wave at −1.96 V, which again was confirmed by spectroelectrochemistry[1] and the comparision of the reduction potential with those of other C_{60} monoaddition products[8]. In contrast to compound **1**[1] no influence of the electron acceptor properties of the C_{60} unit on the electronic properties of the hemiporphyrazine unit within **12** can be detected.

Figure 2. Cyclic voltammogram of **12** measured in toluene/DMF (1:1); n-Bu_4NPF_6 (c = 0.1 M)



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Experimental Section

1,4,8,11,15,18-Hexaheptyltribenzo[b,g,l]-23,26-dihydro-23,26-epoxynaphtho[q]porphyrazinatonickel(II) (**4**): 100 mg (0.5 mmol) of 6,7-dicyano-1,4-dihydro-1,4-epoxynaphthalene (**3**), 480 mg (1.5 mmol) of 3,6-diheptylphthalonitrile (**2**), 90 mg of $Ni(OAc)_2$ and catalytical amounts of DBU were refluxed under nitrogen in 5 ml of n-pentanol for 1 d. The mixture was poured into 50 ml of methanol/water (5:1), the precipitate was filtered, washed several times with cold methanol, dried and seperated from other phthalocyanines by column chromatography on silica gel with toluene and then chloroform/ethanol as the mobile phase. – Yield: 12 mg (2%), R_f ($CHCl_3$) = 0.79. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.75–0.95 (m, 18 H, $-CH_3$), 1.15–1.75 (m, 48 H, $-CH_2-$), 1.83 (br., 12 H, $-CH_2-$), 3.30–3.90 (br., 12 H, $-CH_2-$), 6.08 (s, 2 H, $-O-CH$), 7.10 (s, 4 H, H_{arom}), 7.25 (s, 2 H, H_{arom}), 7.58 (s, 2 H, $=CH$), 8.36 (s, 2 H, H_{arom}). – IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2924, 2855, 1659, 1608, 1574, 1524, 1514, 1466, 1425, 1377, 1327, 1281, 1177, 1161, 1096, 760, 694. – MS (FD; 70eV); *m/z*: 1226.8 [M^+]. – UV/Vis (toluene): λ_{max} = 299 nm, 340, 618, 688.

1,4,8,11,15,18-Hexaheptyltribenzo[b,g,l]-25,28-etheno-23,23a,24,29,29a,30-octahydro-26,27-dimethylene-23,30-epoxytetraceno[q]porphyrazinatonickel(II) (**6**): A solution of 10 mg (0.008 mmol) of dienophilic phthalocyanine **4** and 10 mg (0.06 mmol) of the tetraene **5** in 15 ml of toluene was stirred 3 d under nitrogen at 110°C. The solvent was removed under reduced pressure and the product purified by column chromatography on silica gel with toluene/hexane (1:1) as the mobile phase. – Yield: 9 mg (79%), R_f [toluene/hexane (1:1)] = 0.38. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.75–0.90 (m, 18 H, $-CH_3$), 1.15–1.60 (m, 24 H, $-CH_2-$), 1.65–2.80 (m, 42 H, $-CH_2-$ and $C-H$), 3.90–4.35 (m, 14 H, $-CH_2-$ and $C-H$), 4.89 (s, 2 H, $=CH_2$), 5.13 (s, 2 H, $=CH_2$), 5.41 (s, 2 H, $-O-CH$), 6.44 (t, 2 H, $-CH=CH-$), 7.59 (s, 4 H, H_{arom}), 7.72 (s, 2 H, H_{arom}), 8.68 (s, 2 H, H_{arom}). – IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1}, 3059, 2955, 2924, 2853, 1607, 1576, 1514, 1466, 1433, 1377, 1339, 1325, 1285, 1227, 1209, 1188, 1163, 1136, 1096, 926, 876, 760, 648. – MS (FD; 70eV); *m/z*: 1381.3 [M^+]. – UV/Vis (toluene): λ_{max} = 299 nm, 343, 619, 688.

1,4,8,11,15,18-Hexaheptyltribenzo[b,g,l]-27,28-(1,2-dihydrofullereno)-25,30-etheno-23,23a,24,25,26,29,30,31,31a,32-tetradecahydro23,32-epoxypentaceno[q]porphyrazinatonickel(II) (**7**): A solution of 7 mg (0.005 mmol) of enophilic phthalocyanine **6** and 25 mg (0.0035 mmol) of fullcrene in 15 ml of toluene was stirred for 5 d under nitrogen at 110°C. The solvent was removed under reduced pressure and the product purified by column chromatography on aluminium oxide with toluene/hexane (2:1) as the mobile phase. – Yield: 4 mg (62%), R_f (toluene) = 0.55. – ^{1}H NMR (250 MHz, C_6D_6/CS_2): δ = 0.94 (t, 18 H, $-CH_3$), 1.10–1.70 (m, 48 H, $-CH_2-$), 1.85–2.20 (m, 14 H, $-CH_2-$ and C–H), 2.45 (t, 2 H, $-CH_2-$), 2.70 (m, 2 H, $-CH_2-$), 3.50–4.60 (m, 16 H, $-CH_2-$), 4.62 (t, 2 H, –CH), 5.30 (s, 2 H, –O–CH), 7.01 (t, 2 H, –CH=CH–), 7.47–7.57 (dd, 4 H, H_{arom}), 7.78 (s, 2 H, H_{arom}), 8.42 (s, 2 H, H_{arom}). – IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2922, 2853, 1607, 1516, 1462, 1430, 1325, 1283, 1190, 1165, 1096, 928, 528, – MS (FD; 70eV); *m/z*: 2103.4 [M^+]. – UV/Vis (toluene): λ_{max} = 299 nm, 333, 435, 625, 693.

2,5;17,20-Bisepoxy-2,5,17,20-tetrahydro-2,5,17,20-tetrakis(2'-methylbutoxymethyl)hemiporphyrazinatonickel(II) (**10**): 2 g (5 mmol) of 6,7-dicyano-1,4-epoxy-1,4 dihydro-1,4-(2'-methylbutoxymethyl)naphthalene (**8**) and 550 mg (5 mmol) of Diaminopyridine (**9**) were stirred at 120°C in 20 ml of *n*-butanol until all NH_3 was removed. After the addition of 500 mg (2 mmol) of $Ni(OAc)_2$, the mixture was stirred for further 6 h at 120°C. Then excess *n*-butanol was removed and the precipitate was purified by column chromatography on silica gel with toluene/ethyl acetate (5:1) as the mobile phase. – Yield: 700 mg (27%) of a brown solid. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.92–0.99 (m, 24 H, $-CH_3$), 1.10–1.27 (m, 4 H, $-CH_2-$), 1.45–1.61 (m, 4 H, $-CH_2-$), 1.64–1.77 (m, 4 H, –CH), 3.23–3.43 (m, 8 H, $-CH_2-$), 3.99–4.18 (m, 4 H, $-CH_2-$), 6.43 (d, ^3J = 7.4 Hz, 4 H, H_{arom}), 6.78 (t, ^3J = 7.4 Hz, 2 H, H_{arom}), 6.88, 6.99 (2 s, 4 H, =CH–), 7.67 (s, 4 H, =CH–). – ^{13}C NMR (250 MHz, C_6D_6): δ = 1.5, 16.8, 26.6, 35.3, 68.8, 77.3, 92.1, 113.0, 121.2, 136.9, 139.2, 144.1, 154.6, 157.2, 159.2. – IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1}, 2930, 2874, 1670, 1622, 1578, 1541, 1448, 1429, 1366, 1310, 1205, 1186, 1105, 853, 891, 868, 802, 750, 719, 702, 646. – MS (FD; 70eV); *m/z*: 1028.9 [M^+]. – $C_{58}H_{66}N_8NiO_6$ (1029.92): calcd. C 67.6, H 6.5, N 10.9; found C 65.9, H 6.4, N 10.6.

Synthesis of the Diels-Alder Adduct **11** *of* **10** *with the Tetraene* **5**: 200 mg (0.19 mmol) of hemipophyrazinatonickel(II) **10** and 200 mg (1.3 mmol) of tetraene **5** were stirred in 20 ml of toluene for one week at 140°C. The toluene was removed under reduced pressure and the resulting green-brown product was purified by column chromatography on silica gel with toluene/ethyl acetate (5:1) as the mobile phase. – Yield: 200 mg (78%) of a green solid. – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.88–1.0 (m, 24 H, $-CH_3$), 1.12–1.25 (m, 4 H, $-CH_2-$), 1.47–1.58 (m, 4 H, $-CH_2-$), 1.60–1.70 (m, 4 H, –CH), 2.07 (m, 4 H, –CH), 2.28–2.32 (m, 4 H, $-CH_2-$), 2.46–2.51 (m, 4 H, $-CH_2-$), 3.12–3.37 (m, 8 H, $-CH_2-$), 3.86–3.89 (m, 4 H, –CH), 3.93–4.03 (m, 8 H, $-CH_2-$), 4.78–4.86 (2 s, 4 H, $=CH_2$), 5.05–5.19 (2 s, 4 H, $=CH_2$), 6.38–6.41 (m, 4 H, –CH=), 6.59 (d, ^3J = 7.4 Hz, 4 H, H_{arom}), 6.86 (t, ^3J = 7.4 Hz, 2 H, H_{arom}), 7.9 (s, 4 H, =CH–). – ^{13}C NMR (250 MHz, C_6D_6): δ = 11.5, 16.8, 26.5, 27.2, 35.3, 46.6, 54.1, 69.4, 77.3, 88.9, 101.4, 113.0, 120.9, 133.7, 137.7, 138.0, 139.3, 144.6, 152.1, 157.4, 159.3. – IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1}, 2930, 2874, 1670, 1620, 1578, 1541, 1458, 1431, 1375, 1317, 1263, 1204, 1121, 874, 806, 719. – MS (FD; 70eV); *m/z*: 1342.7 [M^+]. – $C_{82}H_{90}N_8NiO_6$ (1342.38): calcd. C 73.7, H 6.8, N 8.4; found C 74.2, H 7.5, N 8.1.

Synthesis of the Diels-Alder Bisadduct **12** *of* **11** *with [C_{60}]Fullerene:* 50 mg (0.03 mmol) of the bisadduct **11** and 220 mg (0.3 mmol) of C_{60} were stirred in 1-chloronaphthalene for 16 h at 140°C. The resulting brown product was purified by column chromatography on silica gel with toluene/ethyl acetate (10:1) as the mobile phase. – Yield: 10 mg (12%). – ^{1}H NMR (250 MHz, C_6D_6) δ = 0.91–1.01 (m, 24 H, $-CH_3$), 1.08–1.29 (m, 4 H, $-CH_2-$), 1.45–1.59 (m, 4 H, $-CH_2-$), 1.59–1.76 (m, 4 H, –CH), 2.49–2.58 (m, 4 H, –CH), 2.75–2.92 (m, 4 H, $-CH_2-$), 3.27–3.53 (m, 8 H, $-CH_2-$), 3.89–4.12 (m, 8 H, $-CH_2-$), 4.12–4.31 (m, 8 H, $-CH_2-$), 4.73 (m, 4 H, –CH), 6.60 (d, ^3J = 7.4 Hz, 4 H, H_{arom}), 6.81 (t, ^3J = 7.4 Hz, 2 H, H_{arom}), 7.2 (m, 4 H, =CH–), 8.07 (s, 4 H, =CH–). – IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1}, 2926, 2878, 1663, 1614, 1576, 1539, 1474, 1462, 1383, 1315, 1202, 1123, 870, 839,766, 696, 557, 527. – MS (FAB); *m/z*: 2782 [M^+]. – UV/Vis (toluene): λ_{max} = 327.5 nm, 405, 435, 463.

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