Synthesis of an Oligo(phenylenevinylene)-Bridged Phthalocyanine Dimer

Reiner Jung,[a] Karl-Heinz Schweikart,[a] and Michael Hanack*[a]

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The nickel phthalocyanine **4**, which is soluble in common organic solvents, has been synthesized from the corresponding tetracyclone monoadduct **1** and acrolein (**3**). Reaction of **4** with *p*-toluenesulfonic acid leads to the modified phthalocyanine monoaldehyde **5**. The capability of **5** to undergo a Wittig reaction has been demonstrated with benzyltriphenylphosphonium bromide (**6**). Furthermore, a dimer **9** has been synthesized by treating **5** with 0.5 equiv. of xylylenebis(triphenylphosphonium bromide) (**8**). Dimer **9** constitutes a model compound for corresponding PPV polymers containing phthalocyanine subunits.

Introduction

Since the discovery of light emission from poly *p*-(phenylenevinylene) (PPV) and analogous polymers,[1] semiconducting, π-conjugated polymers have attracted widespread research interest,[2] which has resulted in many applications, for example in microelectronic and optoelectronic devices.[3] Modification of the PPV allows variation of the optical and electronic properties of the polymer: Besides the introduction of substituents, a partial or complete replacement of the phenylene rings in the PPV backbone by different moieties (for example by naphthalene, anthracene, heterocycles)[4] offers the possibility of influencing these properties in a controlled manner. This plays an important role in applications of PPV and analogous compounds in the field of organic light-emitting diodes (OLEDs) for example, where the electroluminescence (EL) maxima and thus the colours of the resulting diodes can be tuned.[5] Nevertheless, in general, such organic polymer-based diodes still lack long-term stability.[6]

Recently, great efforts have been directed towards the introduction of macrocyclic moieties into conjugated polymers, since macromolecular chromophoric structures such as porphyrins and phthalocyanines (Pcs) exhibit remarkable electrical and optical properties as well as high stabilities.[7] To date, PPV-analogous polymers containing macrocyclic subunits in the backbone have only been described in the literature in the case of porphyrins.[8]

Pc subunits can be expected to improve the properties of a given phthalocyanine−PPV polymer (hereafter abbreviated as PcPPV), especially with regard to its stability. Moreover, the absorption spectra of Pcs show two major absorption bands, which are located in quite favourable regions: the B-band at around 340 nm and the Q-band at approximately 650 nm. Therefore, a PcPPV can be expected to exhibit an increased absorption range compared to PPV (402 nm).[9] This characteristic, along with the stability and high absorption coefficients of Pcs, make PcPPV particularly interesting for applications in solar cells for example, where these properties are prerequisites for high efficiency.[10]

On the other hand, the El emissions of PPV (520, 551 nm)[2] and many related polymers peak in a range where Pcs are essentially transparent. This is advantageous for applications in OLEDs, where Pcs are still employed as hole-transporting layers in multistructure devices.[11] For the most part, the Pc absorptions do not interfere with the emission of the organic polymer layer.

The properties of Pcs can be varied in many ways by introducing substituents at the periphery of the macrocycle and by variation of the central metal.[7] The same can be expected for PcPPVs.

However, the synthesis of a PPV polymer or oligomer with Pc moieties linked to phenylenevinylene units has not yet been achieved. Here, we report on a dimer that represents the first step en route to the preparation of PcPPV.

Results and Discussion

We found a suitable method for linking Pcs with phenylenevinylene moieties by employing the Wittig reaction. The model compound **9** presented in this paper represents the first oligophenylenevinylene-linked Pc dimer that contains two Pc units substituted by solubilizing groups. In comparison to corresponding PcPPV polymers, a satisfying characterization of **9**, e.g. by mass spectrometry or NMR, proved to be easier. For the synthesis of **9**, we first had to find a means of preparing the monoaldehyde **5**, which can be converted into **9** by a Wittig reaction. To the best of our knowledge, **5** is the first example of a modified Pc aldehyde. Compound **9** can be considered both as a phenylenevinylene trimer with Pc moieties as annulated substituents and as a *p*-[bis(vinylene)]phenylene-linked Pc dimer. We found a suitable method for preparation of the monoaldehyde **4** based on our work on unsymmetrically substituted Pcs.[12]

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[a] Institut für Organische Chemie, Universität Tübingen,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany
Fax: (internat.) + 49-(0)7071/295244
E-mail: hanack@uni-tuebingen.de
WWW: http://www.uni-tuebingen.de/hanack/index.html

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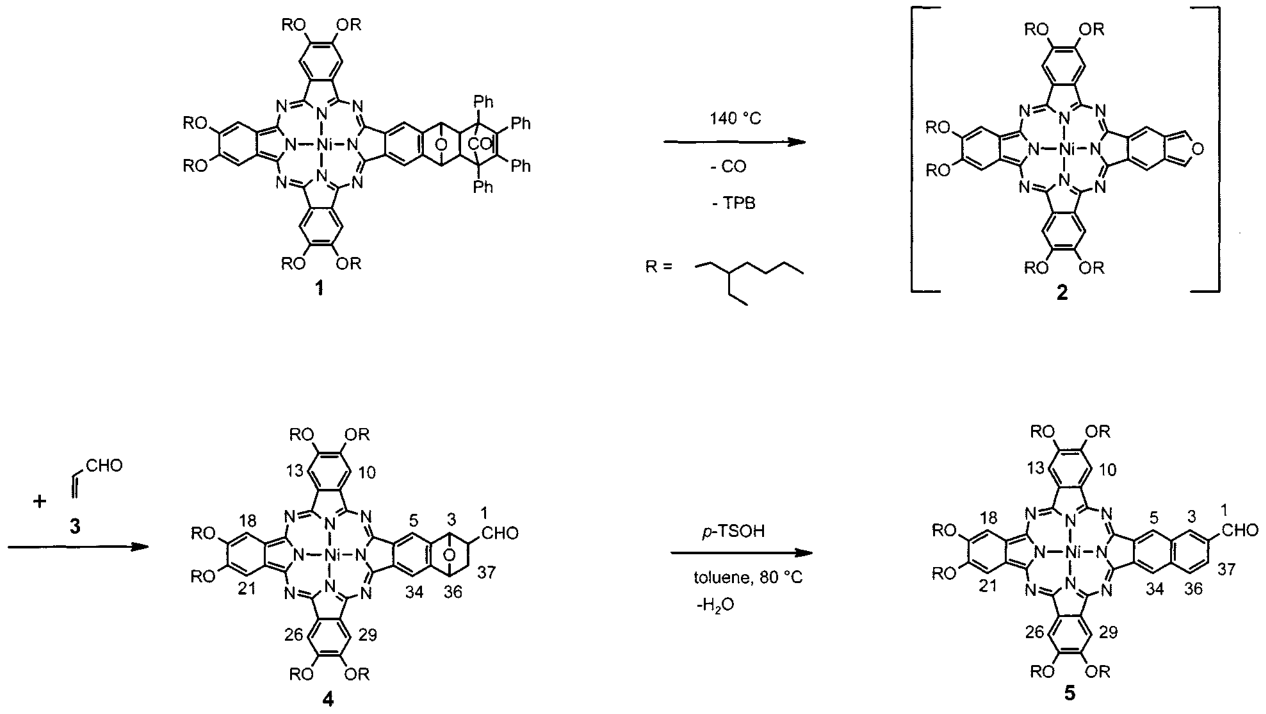
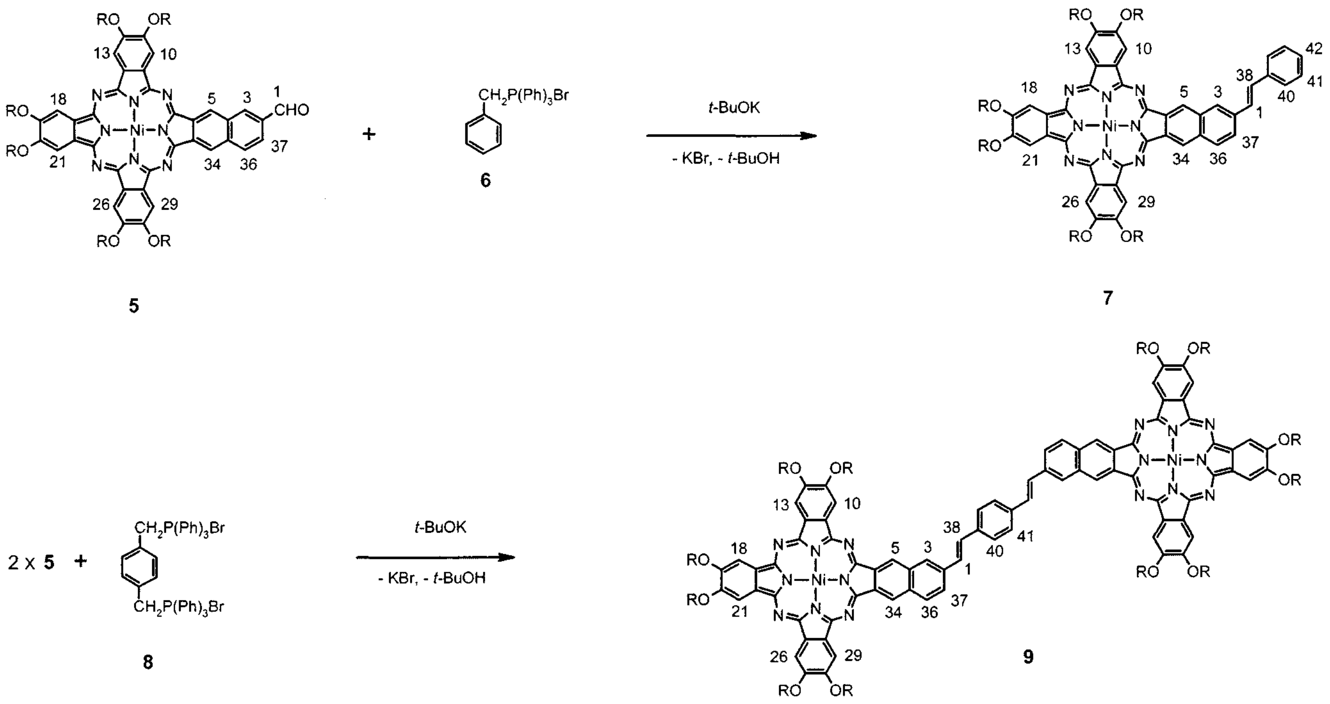


Scheme 1. Synthesis of the Pc monoaldehyde **5**

The starting compound **1** was prepared according to our previously reported procedure,[12] by treating an unsymmetrical monodienophilic Pc with 1,2,3,4-tetraphenylcyclopentadienone (tetracyclone). Compound **1** is a precursor of the reactive isobenzofuran derivative **2**, which is formed in situ by loss of CO and 1,2,3,4-tetraphenylbenzene (TPB) upon heating, for example in refluxing toluene. Isobenzofuran **2** reacts with acrolein (**3**) in a Diels−Alder reaction, forming the corresponding acrolein adduct **4** (Scheme 1). The reaction was performed in an autoclave at 140°C. As the hexakis(2-ethyl)hexyloxy-substituted tetracyclone monoadduct **1** is freely soluble in most organic solvents, an excess of **3** was used to act as both reactant and solvent. The adduct **4** was obtained in 80% yield and was identified on the basis of its NMR and FAB-MS data. Two isomers with *exo* and *endo* orientations of the acrolein fragment were formed, which was evident from two carbonyl proton signals due to 1-H at $\delta = 9.07$ and 10.02. The epoxybenzo units were characterized by the ^{1}H-NMR signals due to 2-H, 37-H, 3-H, and 36-H (see Experimental Section). The appearance of two signals for 2-H was in accordance with the aforementioned *exo*/*endo* orientations. In the case of 3-H, 36-H, and 37-H, only slightly differing chemical shifts were seen for the *exo* and *endo* forms, these protons appearing as multiplet-type signals. All other NMR data and integral values were in agreement with the proposed structure. A separation of the *exo* and *endo* isomers was not pursued because both isomers were expected to form the same product in the subsequent dehydration reaction.

Dehydration was accomplished by treating **4** with a sixfold excess of *p*-toluenesulfonic acid in toluene at 80°C for 1 h (Scheme 1). The reaction was monitored by TLC (silica gel, CH_2Cl_2) and the Pc monoaldehyde **5** was obtained in 65% yield after chromatographic workup. In the FAB mass spectrum, the expected [M^+] peak was observed at m/z = 1416.4. Complete dehydration was also clearly evident from the absence of any residual NMR signals due to 2-H. Two downfield-shifted doublets at $\delta = 7.77$ and 7.88 were observed for 36-H and 37-H. The aldehyde proton signal appeared at $\delta = 10.36$. All NMR data are in agreement with the proposed structure, including those derived from an additionally performed H,C-COSY experiment. In the IR spectrum, the carbonyl band was found to be shifted from 1724 cm^{-1} (**4**) to 1695 cm^{-1} (**5**), which provided a clear indication of the change from an aliphatic to an aromatic aldehyde. As expected, the Q transitions in the electronic spectrum of **5** were found to be bathochromically shifted [692 nm, 631 nm (sh)] compared to those of the parent molecule **4** (668 nm, 602 nm). For the linkage of Pc aldehyde **5** to a phenylenevinylene moiety, the Wittig reaction was used (Scheme 2).

In order to assess the reactivity of **5** under Wittig conditions, it was first treated with an equimolar amount of benzyltriphenylphosphonium bromide (**6**)[13] for 30 min in dry THF at room temperature, using potassium *tert*-butoxide as the base. The Wittig adduct **7** was obtained in 60% yield and could be unequivocally characterized. An assignment of *cis* or *trans* configuration on the basis of NMR- or IR-spectroscopic data was not possible, but usually both isomers tend to be formed under these reaction conditions.[14] Due to aggregation phenomena, the NMR spectra of **7** were difficult to interpret. Nevertheless, all the signals found in the ^{1}H- and ^{13}C-NMR spectra were consistent with the proposed structure. The FAB mass spectrum fea-



Scheme 2. Synthesis of Wittig adduct **7** and Pc dimer **9**

tured not only the [M$^+$] peak, but also several fragment-ion peaks that matched the proposed structure very well (see Experimental Section). In the IR spectrum, the carbonyl band was completely absent. The structure of **7** bears a resemblance to those of phenylenevinylene-substituted Pcs, which have recently been prepared by condensing two different dinitriles in a statistical manner.[15]

The reaction of **5** with 0.4 equivalents of *p*-xylylenebis(triphenylphosphonium bromide) (**8**)[13] in dry THF furnished the oligophenylenevinylene-bridged dimer **9** in 50% yield. As in the case of compound **7**, the NMR spectra are only of moderate quality due to the aggregation tendencies of the molecules and the probable presence of a mixture of different isomers (**9**: *cis-cis*, *cis-trans*, *trans-trans*). The vinyl proton signals are broad between δ = 6.74 and δ = 7.16 in the ^{1}H-NMR spectrum, while the carbon atoms of the phenylenevinylene subunit gave rise to signals between δ = 124 and δ = 129 in the ^{13}C-NMR spectrum. The proposed structure was corroborated by the [M$^+$] peak and the fragment-ion peaks found in the FAB mass spectrum. The UV/Vis spectrum of **9** had to be interpreted as a typical Pc spectrum, although the compound can be considered both as a phenylenevinylene trimer with Pc moieties as annulated substituents and as a *p*-[bis(vinylene)]phenylene-linked Pc dimer. Nevertheless, the absorption between 300 and 500 nm had increased compared to the spectra of the parent molecule **5** and of Wittig adduct **7** (Figure 1).

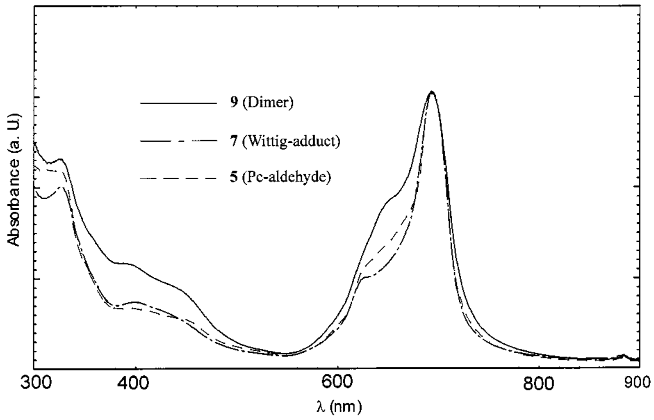


Figure 1. UV/Vis spectra of compounds **5**, **7**, and **9**

The photoluminescence of **9** was measured in solution as well as in the solid state. As expected, the phenylenevinylene-bridged phthalocyanine dimer **9** does not show detectable luminescence under the conditions employed. Detailed investigations of the PL and EL effects of phthalocyanines[16] have shown that luminescence is normally observed if stacking effects, which lead to quenching, can be avoided by incorporating large substituents in the peripheral positions of the phthalocyanines.[17] Although we do not as yet have a crystal structure for the short-chain model compound **9**, we assume a stacked arrangement of the phthalocyanine subunits, which would lead to quenching effects and thus to an absence of luminescence. Stacking arrangements of the phthalocyanine units will be more hindered in a PcPPV polymer containing **9** as a subunit. Work aimed at synthesizing this polymer is currently in progress.

A strategy for achieving enhanced luminescent behaviour of short-chain phenylenevinylene-bridged phthalocyanine model compounds would be to insert longer phenylenevinylene segments between the peripheral Pc subunits. This could lead, as in the case of the aforementioned PcPPV polymer, to a hindrance of stacking of the phthalocyanine units or might induce luminescence effects only from the longer chain phenylenevinylene bridges between the end-on attached Pc rings. Work relating to the synthesis of compounds of this type, as well as of bifunctional Pc moieties, is also currently under way.

In conclusion, by synthesizing **9** we have shown how the preparation of longer PcPPV oligomers and polymers with end-on attached Pc subunits may become possible for the first time. Furthermore, using **9** as a model compound for PcPPVs simplifies the interpretation of the spectroscopic data.

Experimental Section

FT-IR: Jasco FT/IR-430. − UV/Vis: Shimadzu UV-2102 PC. − NMR: Bruker AC 250, Bruker ARX 250 (^{1}H: 250.1 MHz; ^{13}C: 62.9 MHz). − MS: Finnigan ISQ 70, Varian MAT 711A (modified by AMD Intectra). − Elemental analyses were performed with Carlo Erba Elemental Analyzers 1104 or 1106, they are all in agreement with the given structures. All chemical shifts are referenced to the signals of $CDCl_3$. All solvents were dried according to standard procedures.

PcNi (4; Pc−Acrolein Adduct): 1.0 g (560 μmol) of **1** was dissolved in 4 mL of freshly distilled acrolein (**3**) and the solution was stirred in an autoclave for 5 h at 140°C. After cooling and evaporation of the unreacted **3**, the crude product was purified by means of flash column chromatography. After first eluting with CH_2Cl_2 (TPB and traces of unreacted **1**), product **4** was eluted with CH_2Cl_2/ethyl acetate (4:1). The solvent was removed from this second fraction and the residual blue-green solid was extracted several times with methanol to achieve further purification. Drying in vacuo furnished a yield of 645 mg (80%). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2959, 2929, 2872, 2720, 2651, 1724, 1606, 1532, 1481, 1462, 1428, 1385, 1278, 1228, 1200, 1155, 1109, 1063, 1032, 897, 852, 750. − UV/Vis (CH_2Cl_2): λ_{max} = 668 nm, 602, 392, 308. − ^{1}H NMR ($CDCl_3$): δ = 0.95, 1.00, 1.03, 1.05, 1.17, 1.20, 1.23 (br., 36 H, CH_3), 1.45, 1.51, 1.68 (br., 48 H, CH_2), 2.06, 2.14 (br., 6 H, CH), 2.69 (m, 2 H, 37-H), 2.87, 3.56 (br., 1 H, 2-H), 4.33 (br., 12 H, OCH_2), 6.03, 6.08, 6.14 (br., 2 H, 3-H, 36-H), 8.22, 8.28, 8.46, 8.53, 8.71 (br., 8 H, 5-H, 10-H, 13-H, 18-H, 21-H, 26-H, 29-H, 34-H), 9.07, 10.02 (1 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 11.4, 11.5, 11.6, 14.2, 14.3 (CH_3), 23.2, 23.3, 24.0, 24.2, 29.2, 29.4, 29.5 (CH_2), 30.1, 30.3 (C-37), 30.8 (CH_2), 39.8, 39.9 (CH), 52.3, 53.3 (C-2), 71.7, 71.9 (OCH_2), 79.7, 80.1, 80.3 (C-3, C-36), 103.6, 104.1, 104.6 (C-10, C-13, C-18, C-21, C-26, C-29), 111.8, 113.1 (C-5, C-34), 130.2, 130.5, 130.7, 130.8, 135.6, 135.8, 136.2 (C-4, C-6, C-9, C-14, C-17, C-22, C-25, C-30, C-33, C-35), 142.1, 142.9, 144.1, 144.4, 145.4, 145.7, 146.2, 146.6 (C-7, C-8, C-15, C-16, C-23, C-24, C-31, C-32), 151.8, 152.0, 152.1 (C-11, C-12, C-19, C-20, C-27, C-28), 201.5 (C-1). − MS (FAB); *m/z* (%): 1436.3 (90) [M$^+$], 1407.3 (40) [M$^+$ − CO], 1380.2 (100) [M$^+$ − C_3H_4O], 1266.9 (40) [1380.2 − C_8H_{17}].

PcNi (5; Pc Monoaldehyde): To a solution of 300 mg (209 μmol) of **4** in 40 mL of freshly distilled dry toluene in a nitrogen-purged vessel, was added 240 mg (1260 μmol) of *p*-toluenesulfonic acid. The mixture was stirred at 80°C for 1 h. Then, 1 mL of triethylamine was added. After 15 min, the solvent was evaporated. Subsequent flash chromatography (SiO_2, CH_2Cl_2/ethyl acetate, 4:1) furnished **5** in a second fraction. Drying in vacuo gave 195 mg (65%) of **5** as an olive-green powder. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2958, 2927, 2872, 2858, 1694, 1606, 1534, 1461, 1429, 1385, 1278, 1203, 1156, 1104, 1062, 1033, 899, 853, 749. − UV/Vis (CH_2Cl_2): λ_{max} = 692 nm, 632, 393, 331. − ^{1}H NMR ($CDCl_3$): δ = 1.05, 1.06, 1.22 (br., 36 H, CH_3), 1.53, 1.67, 1.78 (br., 48 H, CH_2), 2.00 (br., 6 H, CH), 4.00, 4.07, 4.21, 4.42 (br., 12 H, OCH_2), 7.32, 7.42 (br., 2 H 10-H, 29-H), 7.77 (d, 1 H, 37-H), 7.86 (d, 1 H, 36-H), 7.90 (br., 2 H, 13-H, 26-H), 8.02 (br., 2 H, 5-H, 34-H), 8.11 (br., 1 H, 3-H), 8.29 (br., 2 H, 18-H, 21-H), 10.12 (s, 1 H, 1-H). − ^{13}C NMR ($CDCl_3$): δ = 11.5, 11.6, 14.2, 14.3 (CH_3), 23.2, 23.3, 24.1, 24.2, 29.4, 29.7, 30.8, 31.0 (CH_2), 39.8, 40.0 (CH), 71.6, 71.9, 72.1 (OCH_2), 103.0, 103.2, 103.6, 104.0, 104.4 (C-10, C-13, C-18, C-21, C-26, C-29), 119.5, 121.3, 121.9 (C-3, C-5, C-36), 129.7 (C-37), 129.9, 130.3, 130.6, 131.2, 133.1, 133.4, 133.8, 134.7, 134.8 (C-2, C-4, C-6, C-9, C-14, C-17, C-22, C-25, C-30, C-33, C-35), 136.3 (C-34), 143.2, 143.4, 143.9, 144.0, 144.2, 144.4, 144.6, 145.3 (C-7, C-8, C-15, C-16, C-23, C-24, C-31, C-32), 151.5, 151.7, 152.0 (C-11, C-12, C-19, C-20, C-27, C-28), 191.5 (C-1). − MS (FAB); *m/z* (%): 1416.4 (70) [M$^+$], 1389.4 (30) [M$^+$ − CO], 1303.2 (15) [M$^+$ − C_8H_{17}].

PcNi (7; Wittig Adduct): 70 mg (49.4 μmol) of **5** and 24 mg (55.4 μmol) of **6** were dissolved in 5 mL of dry THF under nitrogen and the resulting mixture was stirred at room temperature. A solution of *t*BuOK in dry THF was then added dropwise until **5** had been completely consumed (TLC control). After a further 10 min, the solvent was evaporated and the crude product was purified by flash chromatography (SiO_2, CH_2Cl_2). After extraction with methanol for further purification, drying in vacuo furnished 44 mg (60%) of **7**. − IR (KBr): $\tilde{\nu}$ = 3081 cm^{-1}, 2958, 2926, 2871, 2858, 1606, 1532, 1461, 1430, 1385, 1361, 1278, 1205, 1159, 1103, 1062, 1035, 896, 853, 750, 737. − UV/Vis (CH_2Cl_2): λ_{max} = 694 nm, 628, 398, 326. − ^{1}H NMR ($CDCl_3$): δ = 1.01, 1.15, 1.24 (br., 36 H, CH_3), 1.48, 1.73 (br., 48 H, CH_2), 2.03 (CH), 4.31 (br., 12 H, OCH_2), 6.82−7.12 (br., 1-H, 38-H), 7.33, 7.41, 7.50, 7.66, 7.79, 7.97, 8.16, 8.26, 8.42, 9.01, 9.19 (3-H, 5-H, 10-H, 13-H, 18-H, 21-H, 26-H, 29-H, 34-H, 36-H, 40-H, 41-H, 42-H). − ^{13}C NMR ($CDCl_3$): δ = 11.4, 11.5, 11.6, 12.0, 14.2 (CH_3), 23.2, 24.1, 24.5, 28.6, 29.4, 29.7, 30.8 (CH_2), 39.9 (CH), 71.7, 71.8 (OCH_2), 103.5, 103.8, 104.2 (C-10, C-13, C-18, C-21, C-26, C-29), 120.8 (C-3, C-5, C-36), 126.6, 127.5, 128.5, 128.8 (C-1, C-2, C-38, C-39, C-40, C-41, C-42), 129.2, 129.9, 130.2, 130.5, 133.4, 133.7, 135.6 (C-4, C-6, C-9, C-14, C-17, C-22, C-25, C-30, C-33, C-34, C-35, C-37), 144.2, 144.8, 145.6 (C-7, C-8, C-15, C-16, C-23, C-24, C-31, C-32), 151.8 (C-11, C-12, C-19, C-20, C-27, C-28). − MS (FAB); *m/z* (%): 1490.9 (100) [M$^+$], 1388.0 (70) [M$^+$ − C_8H_7], 1377.9 (40) [M$^+$ − C_8H_{17}], 1276.8 (50) [M$^+$ − C_8H_7 − C_8H_{17}].

PcNi (9; Dimer): 105 mg (74 μmol) of **5** and 25 mg (35 μmol) of **8** were dissolved in 10 mL of dry THF under nitrogen and the resulting mixture was stirred at room temperature. A solution of *t*BuOK in dry THF was then added dropwise until **5** had been completely consumed (TLC control). After a further 15 min, the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, CH_2Cl_2). After extraction with methanol for further purification, drying in vacuo furnished 51 mg (50%) of **9**. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2958, 2926, 2871, 2859, 1606, 1533, 1461, 1433, 1385, 1362, 1278, 1205, 1159, 1102, 1062, 1033, 959, 901, 853, 750, 729. − UV/Vis (CH_2Cl_2): λ_{max} = 693 nm, 648, 388, 328. − ^{1}H NMR ($CDCl_3$): δ = 1.01, 1.17, 1.25 (br., 36 H, CH_3), 1.48, 1.73, 1.79 (br., 48 H, CH_2), 2.00 (CH), 4.25 (br., 12 H, OCH_2), 6.74, 6.82, 7.12, 7.16 (br., 1-H, 38-H), 7.31−8.76 (br., 3-H, 5-H, 10-H, 13-H, 18-H, 21-H, 26-H, 29-H, 34-H, 36-H, 40-H, 41-H). − ^{13}C NMR ($CDCl_3$): δ = 11.5, 11.7, 14.2, 14.4, 14.5 (CH_3), 23.3, 24.1, 29.4, 30.8 (CH_2), 39.8 (CH), 71.6, 71.9, 72.1 (OCH_2), 103.5, 103.6, 103.8, 103.9, 104.2 (br., C-10, C-13, C-18, C-21, C-26, C-29), 120.3, 120.8 (C-3, C-5, C-36), 124.0, 126.8, 128.3, 128.5 (C-1, C-2, C-38, C-39, C-40, C-41), 129.2, 129.8, 129.9, 130.1, 130.3, 130.4, 132.6, 133.4, 133.7, 134.0, 134.9 (C-4, C-6, C-9, C-14, C-17, C-22, C-25, C-30, C-33, C-34, C-35, C-37), 144.1, 144.3, 144.5, 144.6, 144.8, 144.9, 145.0, 145.2, 145.4 (C-7, C-8, C-15, C-16, C-23, C-24, C-31, C-32), 151.7 (C-11, C-12, C-19, C-20, C-27, C-28). − MS (FAB); *m/z* (%): 2904.6 (80) $[M^+]$, 2790.9 (50) $[M^+ - C_8H_{17}]$, 1516.8 (50) $[M^+ - C_{84}H_{112}N_8NiO_6]$, 1506.2 (100) $[M^+ - C_{85}H_{113}N_8NiO_6]$, 1388.2 (50) $[C_{84}H_{112}N_8NiO_6]$, 1276.2 (50) $[C_{84}H_{112}N_8NiO_6 - C_8H_{17}]$.

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