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Synthesis of Novel Covalently Linked Dimeric Phthalocyanines

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We report the syntheses of the dimeric homonuclear Pcs **9a** and **9b** and of the dimeric heteronuclear Pc **9c**, starting from the unsymmetrical phthalocyanines **7a** and **7b**, each containing a phenolic OH group in one of its substituents. Compounds **9a** and **9b** were obtained by single-step alkylations of **7a** and **7b** with 1,6-dibromohexane or, in better yields, by coupling of Pcs **7a** and **7b** with the bromoalkyl-derivatized Pcs **8a** and **8b**, while **9c** was prepared by treatment of **8a** with Pc-Ni complex **7b**. The dimeric Pcs **9a**–**9c** show strong cofacial intramolecular association in solution.

Introduction

Multinuclear phthalocyanine (Pc) systems, like their monomeric symmetrically and unsymmetrically substituted Pc counterparts, have recently attracted much attention because of their potential applications as semiconductors, nonlinear optical materials, and catalysts.[1] The synthesis of multinuclear phthalocyanine compounds has also provided new information contributing to the study of phthalocyanine aggregation.

A series of linked Pc structures in which the spacer length is systematically varied through a chain of one to five atoms was studied to examine the effect of the linkage length on the interaction between the two phthalocyanine terminal structures. When a sufficient length of the linking moiety is reached, a cofacial intramolecular association referred to as "clamshell behavior" is observed, with a dynamic equilibrium existing between open and closed conformations.[2]

Examples of covalently linked dimeric phthalocyanines containing spacer units have previously been reported by Lever[3–7] and Torres.[8–10] The spacers in these dimeric Pcs can be bis-alkoxy groups [e.g., $–OCH_2C(CH_3)(R)-CH_2O–$],[3–5] catechols with oxygen as bridging atoms,[6] methylene chains of different lengths [e.g., $–(CH_2)_n–$ with n = 2,4],[6] alkynyl chains of varying lengths [e.g., $–(C{\equiv}C)_m–$ with m = 1,2],[8,10] or double alkynyl chains with m = 2.[9] Similar dimeric systems have also been prepared with porphyrins taken as macrocycles instead.[11–13] Like the dimeric Pcs, these porphyrin-based systems are covalently linked with alkyl or aryl groups through a *meso* carbon in a pillared cofacial configuration[14] (Pacman-like systems).[15]

A first step in the synthesis of a covalently linked dimeric Pc can, for example, be to obtain an unsymmetrical phthalocyanine of the A_3B type with one functional group active for a nucleophilic substitution. This group can be either an alkyl or an aryl substituent containing, for example, a free hydroxy group. Subsequently this A_3B-type Pc can be treated with 4-nitrophthalonitrile to give a Pc substituted with a phthalonitrile group. Condensation of this with phthalonitriles affords the corresponding dimeric products.

The advantage of this method is its applicability to the synthesis of both symmetrical and asymmetrical (for instance heteronuclear) systems, while the same approach also offers the possibility of synthesizing mixed porphyrin-phthalocyanine systems.[16,17] However, application of the statistical condensation as the last step in this synthetic route results in low yields of the final products.

A compound containing an active group such as a hydroxy moiety – such as, for example, the Pcs **7a** or **7b** (Scheme 2) – can be used directly for dimerization through a bifunctional spacer. In our current research this approach has been applied to the synthesis of the dimeric phthalocyanines **9a**, **9b**, and **9c** (Scheme 3), linked through mixed alkyl–aryl spacers in order to avoid the second statistical cross-condensation step as described above. This method is distinguished by its simplicity and also provides an opportunity for synthesis of heteronuclear and/or heteroleptic dimeric systems and allows the extent and character of the spacer group to be varied easily.

Results and Discussion

For the synthesis of the dimeric Pcs **9a**, **9b**, and **9c** (Scheme 3) the routes shown in Scheme 1, 2, and 3 were chosen. The unsymmetrical monofunctionalized phthalocyanines **7a** and **7b** (Scheme 2) used as starting materials for **9a**–**9c** were prepared by statistical cross-condensation of the newly prepared 4-(*m*-hydroxyphenoxy)phthalonitrile (**3**) and 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (**5**). Compound **3** was in turn obtained by treatment of 4-nitro-

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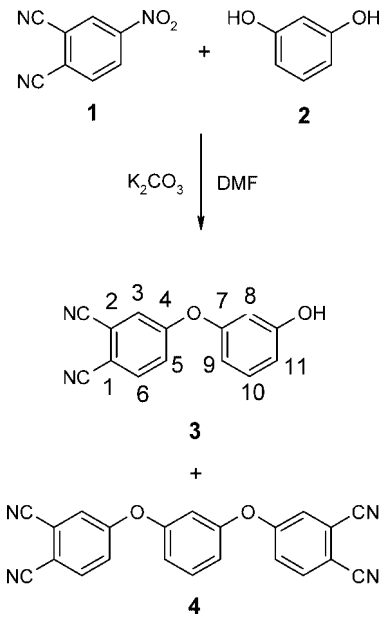
phthalonitrile (**1**) with an excess of resorcine (**2**) in DMF in the presence of K_2CO_3 (see Scheme 1 and Exp. Sect.) and was separated from the also formed 4,4′-(*m*-phenylenedioxy)bis(phthalonitrile) (**4**) by column chromatography.



Scheme 1.

The bis(phthalonitrile) **4** might also have served as a precursor for a dimeric phthalocyanine, but treatment of **4** with an excess of a substituted phthalonitrile (e.g., **5**) did not result in the corresponding dimer.

Condensation of **3** and **5** in a 1:3 ratio in hexanol in the presence of catalytic amounts of DBU resulted in a mixture of all possible metal-free phthalocyanines, among which **6a** and **7a** were dominant (Scheme 2). They were separated by column chromatography with dichloromethane as eluent.

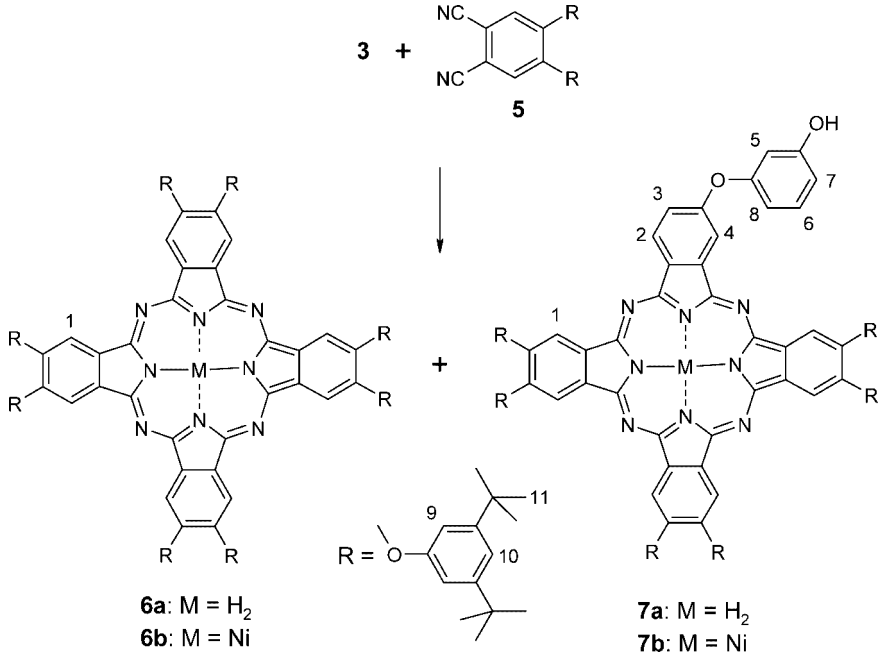
Nickel complexes **6b** and **7b** were obtained as a mixture by cross-condensation of phthalonitriles **3** and **5** in quinoline in the presence of $NiCl_2$ and catalytic amounts of ammonium molybdate. Separation of the PcNis by column chromatography with dichloromethane/hexane 7:3 as eluent gave pure Pc **7b**.

The UV/Vis spectra of **6a** and 7**a** are consistent with metal-free phthalocyanines and differ only slightly in the intensities of their absorption bands (see Exp. Sect.).The UV/Vis spectrum of **7b** is typical for a metal phthalocyanine, showing an unsplit Q-band (Figure 1), as in the case of **6b**.

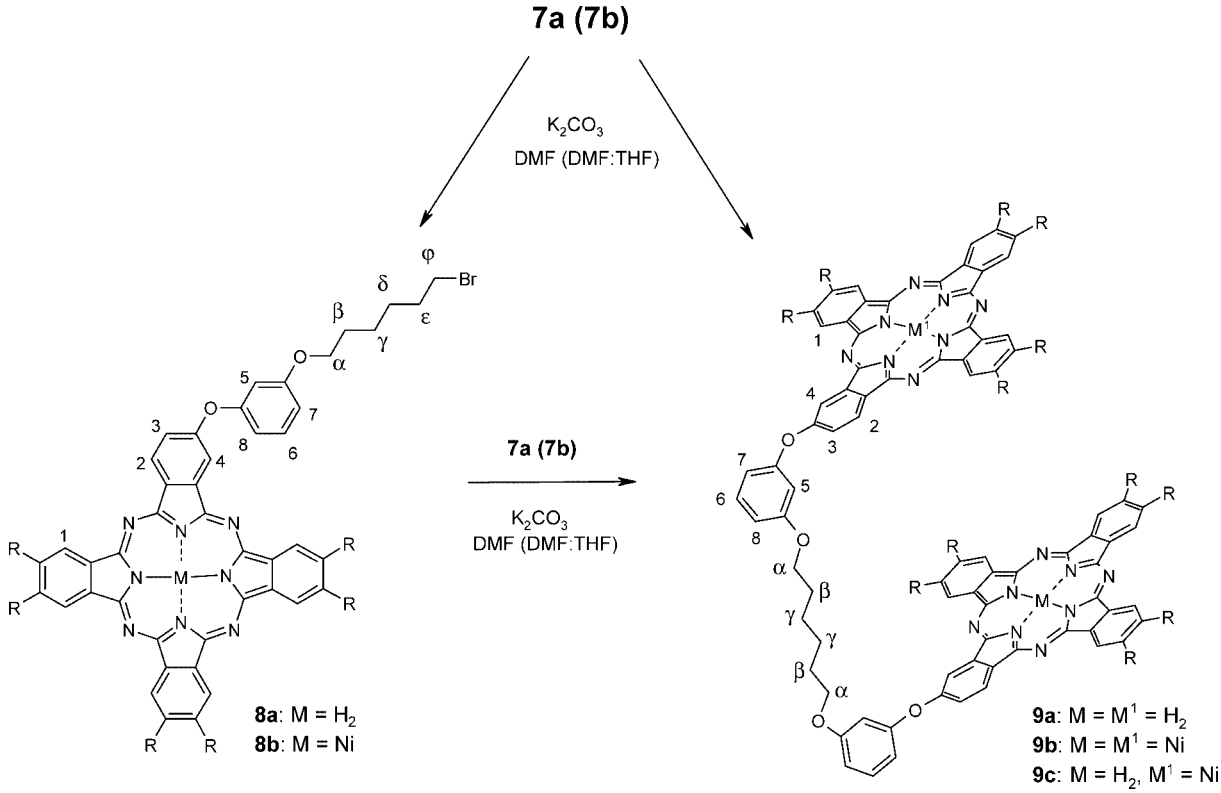
The ^1H NMR spectra ($CDCl_3$) of PcH_2 **7a** and PcNi **7b** are very similar, each with a peak corresponding to the free OH signal at $\delta \approx 5$ ppm and a multiplet of aromatic protons in the resorcine moiety appearing in the 6.7–6.9 ppm region. The signal of the inner NH protons of **7a** appears at $\delta = -0.78$ ppm and is absent in the spectrum of Ni complex **7b**.

Treatment of **7a** and **7b** with excess 1,6-dibromohexane in the presence of K_2CO_3, either in pure DMF or in a DMF/THF mixture (1:1), resulted mainly in the formation of the corresponding bromoalkyl derivatives **8a** and **8b** (Scheme 3).

Alkylation of the hydroxy groups in **7a** or **7b** did not result in any significant change in the UV/Vis spectra; the main evidence for the structures of **8a** and **8b** follows from their NMR and MALDI-TOF characteristics. The ^1H NMR spectra of Pcs **8a** and **8b** exhibit no signals in the 5 ppm region, which would be indicative of the presence of



Scheme 2.



Scheme 3.

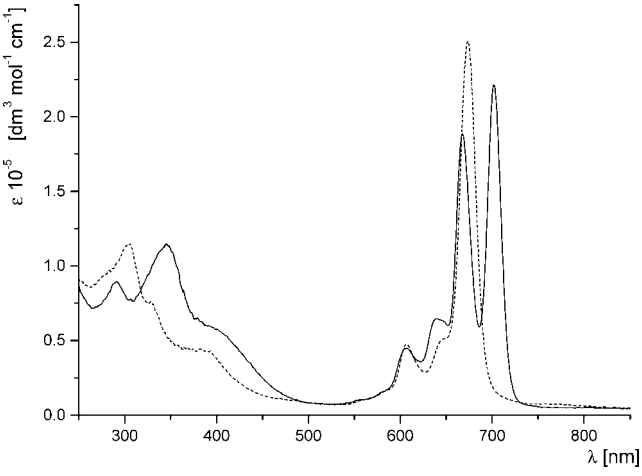


Figure 1. UV/Vis spectra (CH_2Cl_2) of **7a** (solid line) and **7b** (dashed line).

7a and **7b**, respectively. Two signals at approx. 4.0 and 3.3 ppm correspond to four alkyl protons, Hα and Hϕ of the bromohexyl fragments, whereas the signals of the other six protons (2 Hβ, 2 Hγ, 2 Hδ), expected in the 1.88–1.25 ppm region, are masked by the intense peaks of the peripheral *tert*-butyl groups. In the spectrum of **8a** the signals of the inner NH protons appear at –0.48 ppm.

The dimeric compounds **9a** and **9b** are also formed in small quantities under the synthesis conditions. They were separated by column chromatography and analyzed by MALDI-TOF and UV/Vis, which confirmed their structures.

Compounds **9a** and **9b** were more easily synthesized by coupling of the monomeric phthalocyanines **7a** and **7b** with Pcs **8a** and **8b**, respectively. They were also obtained by treatment of **7a** or **7b** with 0.5 equiv. 1,6-dibromohexane either in DMF or in a DMF/THF mixture (1:1) with subsequent purification by column chromatography.

The UV/Vis spectra of dimeric Pcs **9a** and **9b** (Figure 2) are different from the spectra of monomeric compounds **7a**,

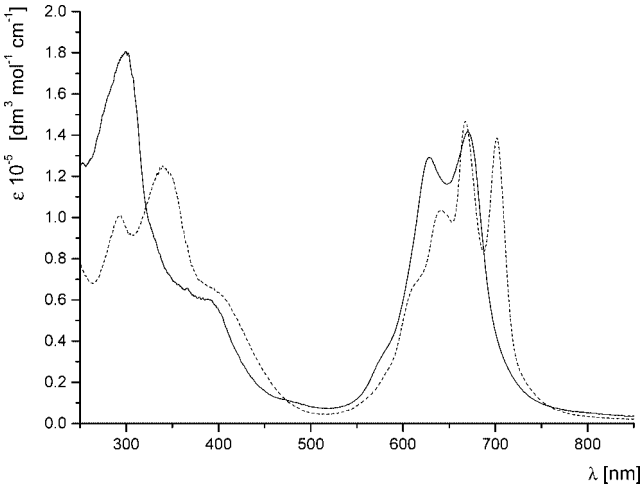


Figure 2. UV/Vis spectra (CH_2Cl_2) of **9a** (dashed line) and **9b** (solid line).

7b, **8a**, and **8b**. Compounds **9a** and **9b** each exhibit a more intense absorption in the B-band region and a broad pattern of the Q-band. The increased absorption at approx. 640 nm and 628 nm for **9a** and **9b** in CH_2Cl_2, and the independence of the intensity ratios of the Q-band components on the concentrations of **9a** and **9b** in solution indicate π–π interactions between the macrocycles with a strong tendency to co-facial orientation within the dimer molecules.

The ^{1}H NMR spectra of dimeric phthalocyanines **9a** and **9b** each show a characteristic triplet in the area of 4 ppm, corresponding to four alkyl protons Hα. In the metal-free complex **9a** the NH protons appear at approx. –0.69 ppm (see Figure 3).

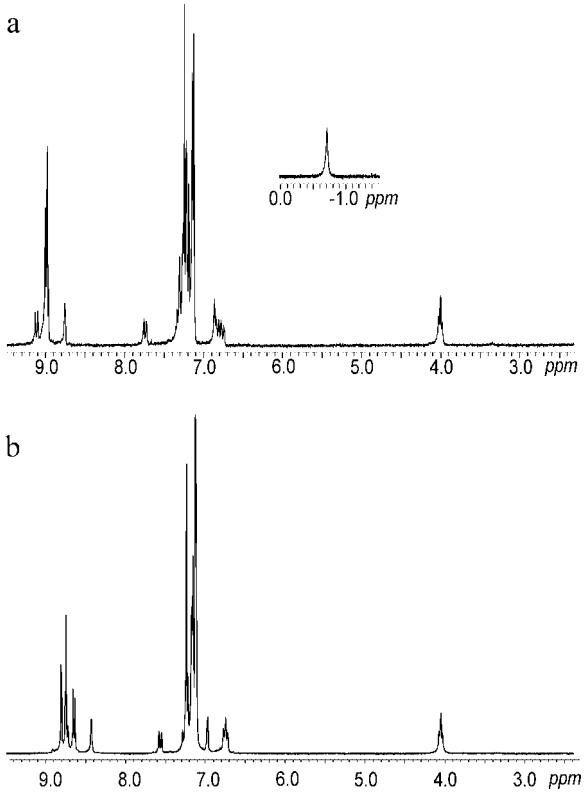


Figure 3. ^{1}H NMR spectra of dimeric phthalocyanines **9a** (a) and **9b** (b) in $CDCl_3$.

The heteronuclear dimeric phthalocyanine **9c** was obtained in good yield by treatment of **8a** with an excess of Pc-Ni complex **7b** in DMF/THF in the presence of K_2CO_3 (see Exp. Sect.). Purification of Pc **9c** was carried out by column chromatography. As expected, its UV/Vis spectrum is very similar to the superposed spectra of dimers **9a** and **9b** (see Figure 4).

In the ^{1}H NMR, the four Hα alkyl protons of the heteronuclear dimer **9c** give two overlapping triplets in the 4 ppm region (Figure 5). The characteristic singlet for the inner NH protons of the metal-free macrocycle was observed in the dimer at –0.98 ppm. In the MALDI-TOF spectra, none of the synthesized dimers **9a**–**9c** exhibited fragmentation: only isotopic cluster peaks of molecular ions were observed, which provides additional confirmation of the purities of the synthesized Pcs **9a**–**9c**.

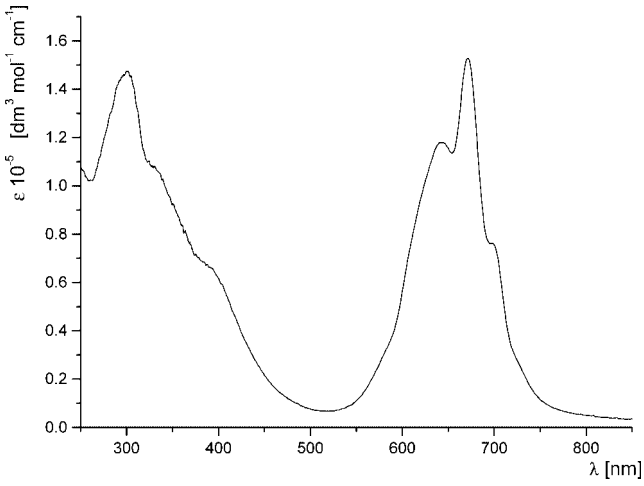


Figure 4. UV/Vis spectrum (CH_2Cl_2) of dimer **9c**.

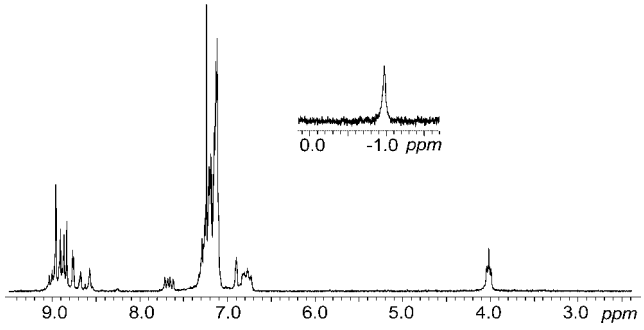


Figure 5. ^{1}H NMR spectrum of heteronuclear dimeric phthalocyanine **9c**.

Conclusions

The synthesis of the unsymmetrical substituted phthalocyanines **7a** and **7b**, each containing one active (phenolic) hydroxy group, is reported. These compounds were further converted into dimeric phthalocyanine systems **9a**, **9b**, and **9c**, exhibiting noticeable co-facial intramolecular interactions of the Pc-macrocycles in their UV/Vis spectra in solution.

The method described for the synthesis of **9a**–**9c** is easy to carry out, proceeds with good yields, and represents a convenient pathway to both homonuclear and heteronuclear dimeric phthalocyanine compounds. Additionally, this method allows the spacer group, metal cations, and peripheral substitution pattern to be varied for tuning of the properties of the dimers.

Experimental Section

General: All solvents were dried by standard methods. Quinoline was first purified on a column (basic alumina). Commercially available reagents were used as purchased. 4,5-Bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (**5**) was prepared by a previously described procedure.[18] NMR spectra were recorded on a Bruker AC 250 spectrometer. The UV/Vis spectra were taken in CH_2Cl_2 with a Shimadzu UV-365 spectrometer and IR spectra with a Bruker Tensor 27. Mass spectra (EI, MALDI-TOF) were obtained on a Finnigan

TSQ 70 MAT and a Bruker Autoflex spectrometer, and elemental analyses on a Euro EA 3000.

4-(*m*-Hydroxyphenoxy)phthalonitrile (3): A mixture of 4-nitrophthalonitrile (**1**, 1 g, 6 mmol), resorcine **2** (4 g, 36 mmol), and K_2CO_3 (5.5 g, 0.04 mol) was heated to 85–90 °C with stirring in anhydrous DMF (10 mL) for 1 h. After cooling, the reaction mixture was filtered and the brown filtrate was added dropwise to water (50 mL). The formed creamy colored precipitate was filtered off and washed with water, and the mixture was subjected to column chromatography on silica gel with dichloromethane/acetonitrile (9:1), resulting in the elution of 4,4′-(*m*-phenylenedioxy)-bis(phthalonitrile) (**4**) (R_f = 0.9) and subsequently 4-(*m*-hydroxyphenoxy)phthalonitrile (**3**, R_f = 0.6). The solvent was completely evaporated and products were dried under vacuum at 90 °C.

Compound 3: Yield: 0.74 g (54%). ^{1}H NMR ([D$_6$]DMSO, numbering according to Scheme 1): δ = 8.07 (d, ^3J = 8.8 Hz, 1 H, H^6), 7.75 (d, ^4J = 2.2 Hz, 1 H, H^3), 7.36 (dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz, 1 H, H^5), 7.27 (t, ^3J = 8.1 Hz, 1 H, H^{10}), 6.71 (dd, ^3J = 8.1 Hz, ^4J = 2.2 Hz, 1 H, H^9), 6.58–6.51 (m, 2 H, H^{11}, H^8) ppm. IR (KBr): $\tilde{\nu}$ = 3372 (OH), 2252, 2231 (C≡N), 1602, 1566, 1479, 1421, 1340, 1310 1287, 1252, 1172, 1134, 975, 931, 882, 799, 693, 522 cm^{-1}. MS (electron ionization, EI): *m*/*z* (%) = 236.1 (100) [M]$^+$, 208.1 (27), 179.1 (23), 65.2 (16), 39.2 (6). Elemental analysis calcd. (%) for $C_{14}H_8N_2O_2$: C 71.18, H 3.41, N 11.86; found: C 70.94, H 3.29, N 11.89.

Compound 4: Yield: 0.07 g. IR (KBr): $\tilde{\nu}$ = 2232 (C≡N), 1568, 1563, 1478, 1455, 1422, 1404, 1304, 1284, 1247, 1201, 1175, 1123, 1090, 1003, 980, 950, 917, 900, 888, 864, 851, 843, 792, 775, 720, 685, 525 cm^{-1}. MS (electron ionization, EI): *m*/*z* (%): 362.1 (100) [M]$^+$, 218.1 (14), 191.1 (41), 164.1 (26), 40.1 (15). Elemental analysis calcd. (%) for $C_{22}H_{10}N_4O_2$: C 72.93, H 2.78, N 15.46; found: C 72.66, H 2.70, N 15.70.

Synthesis of 7a: 4-(*m*-Hydroxyphenoxy)phthalonitrile (**3**, 0.2 g, 0.84 mmol) and 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (**5**, 1.35 g, 2.52 mmol) were mixed with a catalytic quantity of DBU under nitrogen in hexanol. The mixture was heated up to 170–175 °C and was allowed to react for 16 h. After cooling, the reaction product was added to methanol (50 mL) containing H_2O (0.5 mL), filtered off, washed thoroughly with methanol, dried, and subjected to column chromatography on silica gel with CH_2Cl_2 as eluent. The symmetrical Pc **6a** was eluted first, followed by the unsymmetrical PcH_2 **7a**.

Compound 7a: Yield: 0.22 g (14.2%). ^{1}H NMR ($CDCl_3$, numbering according to Scheme 2): δ = 9.10 (d, ^3J = 8.5 Hz, 1 H, H^2), 9.01–8.96 (m, 6 H, H^1), 8.74 (s, 1 H, H^4), 7.75 (d, ^3J = 8.5 Hz, 1 H, H^3), 7.35–7.14 (m), 6.90–6.71 (m, 22 H, H^5, H^6, H^7, H^8, 12 H^9, 6 H^{10}), 5.01 (s, 1 H, H_{OH}), 1.38–1.32 (m, 108 H, H^{11}), –0.78 (s, 2 H, H_{NH}) ppm. IR (KBr): $\tilde{\nu}$ = 3442 (OH, NH), 2964, 2868, 1608, 1589, 1500, 1467, 1443, 1423, 1398, 1364, 1317, 1297, 1276, 1246, 1198, 1137, 1089, 1013, 961, 902, 866, 757, 706 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 702.0 (5.35), 667.5 (5.28), 640.5 (4.81), 606.0 (4.65), 400 (sh), 345.0 (5.6), 291.5 nm (4.95). MS (MALDI-TOF): *m*/*z* = 1847 [M]$^+$. Elemental analysis calcd. (%) for $C_{122}H_{142}N_8O_8$: C 79.27, H 7.74, N 6.06; found: C 78.43, H 7.71, N 6.15.

Synthesis of 7b: 4-(*m*-Hydroxyphenoxy)phthalonitrile (**3**, 0.2 g, 0.84 mmol) and 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (**5**, 1.35 g, 2.52 mmol) were mixed under nitrogen with $NiCl_2$ (0.44 g, 3.36 mmol) in quinoline (4 mL). The mixture was heated up to 185–195 °C and was allowed to react for 16 h. After cooling, the reaction product was added to methanol (50 mL) containing concd. aqueous HCl (0.5 mL), filtered off, washed thoroughly with methanol, dried, and subjected to column chromatography on silica gel with CH_2Cl_2/*n*-hexane (7:3) as eluent. The symmetrically substituted Pc **6b** was eluted first, followed by the unsymmetrical PcH_2 **7b**.

Compound 6b: Yield: 0.22 g (15.6%). ^{1}H NMR ($CDCl_3$, numbering according to Scheme 2): δ = 8.94 (s, 8 H, H^2), 7.22 (s, 8 H, H^{10}), 7.09 (s, 16 H, H^9), 1.3 (s, 144 H, H^{11}) ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2905, 2869, 1608, 1588, 1533, 1459, 1418, 1363, 1297, 1275, 1246, 1198, 1145, 1095, 1055, 1002, 961, 903, 864, 837, 756, 729, 707 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 674.0 (5.40), 648.0 (sh), 608.0 (4.66), 391.0 (4.62), 305.0 nm (5.06). MS (MALDI-TOF): *m*/*z* = 2203 [M]$^+$.

Compound 7b: Yield: 0.2 g (12.5%). ^{1}H NMR ($CDCl_3$, numbering according to Scheme 2): δ = 8.92–8.75 (m, 7 H, H^2, 6 H^1), 8.55 (s, 1 H, H^4), 7.64 (d, ^3J = 8.5 Hz, 1 H, H^3), 7.34–7.11 (m), 6.88–6.70 (m) (22 H, H^5, H^6, H^7, H^8, 12 H^9, 6 H^{10}), 5.15 (s, 1 H, H_{OH}), 1.34–1.29 (m, 108 H, H^{11}) ppm. IR (KBr): $\tilde{\nu}$ = 3444 (OH), 2964, 2905, 2869, 1608, 1589, 1533, 1460, 1421, 1362, 1352, 1297, 1277, 1246, 1198, 1138, 1096, 1056, 1002, 961, 903, 864, 756, 728, 707 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 673.5 (5.40), 647.0 (sh), 606.5 (4.68), 382.5 (sh), 329.0 (sh), 305.5 nm (5.06). MS (MALDI-TOF): *m*/*z* = 1903 [M]$^+$. Elemental analysis calcd. (%) for $C_{122}H_{140}N_8NiO_8$: C 76.91, H 7.41, N 5.88; found: C 76.63, H 7.49, N 5.89.

Alkylated Phthalocyanines 8a and 8b. General Method: Compound **7a** or **7b** (0.016 mmol) was mixed with excess 1,6-dibromohexane in DMF (2 mL; for **7b** in a 1:1 DMF/THF mixture) in the presence of K_2CO_3 (0.02 g, 0.145 mmol). The mixture was heated to 50–55 °C for 4 h. After cooling, the reaction product was added to water/methanol (1:1, 20 mL), filtered off, washed thoroughly with methanol, dried, and subjected to column chromatography on silica gel with CH_2Cl_2/*n*-hexane (65:35) as eluent. Phthalocyanines **8a** and **8b** were isolated as the largest fractions (second).

Compound 8a: Yield: 0.021 g (65%). ^{1}H NMR ($CDCl_3$, numbering according to Scheme 3): δ = 9.20 (d, ^3J = 8.5 Hz, 1 H, H^2), 9.07–8.96 (m, 6 H, H^1), 8.82 (d, ^4J = 2.2 Hz, 1 H, H^4), 7.79 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1 H, H^3), 7.39–7.13 (m, 19 H, H^6, 12 H^9, 6 H^{10}), 6.90 (dd, ^3J = 8.1 Hz, ^4J = 2.2 Hz, 1 H, H^8), 6.83 (t, ^4J = 2.2 Hz, 1 H, H^5), 6.79 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 1 H, H^7), 3.99 (t, ^3J = 6.3 MHz, 2 H, Hα), 3.36 (t, ^3J = 6.6 Hz, 2 H, Hϕ), 1.88–1.25 (m, 116 H, 108 H^{11}, 2 Hβ, 2 Hγ, 2 H*δ*), –0.48 (s, 2 H, H_{NH}) ppm. IR (KBr): $\tilde{\nu}$ = 3444 (NH), 2963, 2869, 1608, 1588, 1467, 1443, 1423, 1398, 1363, 1297, 1275, 1246, 1199, 1139, 1089, 1013, 961, 902, 866, 756, 707 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 702.0 (5.27), 668.0 (5.20), 639.5 (4.75), 607.0 (4.49), 400 (sh), 344.5 (4.99), 291.5 nm (4.88). MS (MALDI-TOF): *m*/*z* = 2011 [M]$^+$. Elemental analysis calcd. (%) for $C_{128}H_{153}BrN_8O_8$: C 76.43, H 7.67, N 5.57; found: C 75.77, H 7.71, N 5.71.

Compound 8b: Yield: 0.023 g (71%). ^{1}H NMR ($CDCl_3$, numbering according to Scheme 3): δ = 8.95 (d, ^3J = 8.4 Hz, 1 H, H^2), 8.88–8.79 (m, 6 H, H^1), 8.60 (d, ^4J = 2.2 Hz, 1 H, H^4), 7.66 (dd, ^3J = 8.4 Hz, ^4J = 2.2 Hz, 1 H, H^3), 7.36–7.11 (m), 6.90–6.75 (m, 22 H, H^5, H^6, H^7, H^8, 12 H^9, 6 H^{10}), 3.98 (t, ^3J = 6.2 Hz, 2 H, Hα), 3.36 (t, ^3J = 6.9 Hz, 2 H, Hϕ), 1.86–1.22 (m, 116 H, 108 H^{11}, 2 Hβ, 2 Hγ, 2 H*δ*) ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2868, 1608, 1589, 1533, 1464, 1421, 1363, 1297, 1276, 1246, 1198, 1139, 1116, 1056, 962, 903, 865, 755, 728, 707 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 674.0 (5.41), 646.0 (sh), 607.0 (4.71), 382.5 (sh), 329.0 (sh), 300.0 nm (5.12). MS (MALDI-TOF): *m*/*z* = 2067 [M]$^+$. Elemental analysis calcd. (%) for $C_{128}H_{151}BrN_8NiO_8$: C 74.33, H 7.36, N 5.42; found: C 74.52, H 6.98, N 5.89.

Synthesis of Homonuclear and Heteronuclear Dimeric Phthalocyanines 9a, 9b, and 9c

Method A: Phthalocyanine **7a** or **7b** (0.05 g) and K_2CO_3 (0.01 g) were added to a solution of 1,6-dibromohexane in DMF (0.012 M, 1 mL). The mixture was heated up to 50–55 °C and stirred for 48 h. After cooling, the reaction product was added to water (10 mL), filtered off, washed thoroughly with water and methanol, dried, and subjected to column chromatography on silica gel with CH_2Cl_2/*n*-hexane (65:35) as eluent. Phthalocyanines **9a** and **9b** were isolated as first fractions.

Method B: Phthalocyanine **8** (0.025 mmol) and phthalocyanine **7** (0.05 mmol) were mixed with K_2CO_3 (0.1 mmol) in DMF (2 mL, or DMF/THF 1:1). The mixture was heated up to 80–85 °C for 12 h. After cooling, the product was added to water (20 mL), filtered off, washed thoroughly with water and methanol, dried, and subjected to column chromatography on silica gel with CH_2Cl_2/*n*-hexane (65:35) as eluent. Dimer **9a** was obtained from PcH_2 **7a** by **Method A** in 89% yield. By starting from mononuclear phthalocyanines **8a** and **7a** in DMF, **9a** was also obtained in 63% yield by **Method B**.

Compound 9a: ^{1}H NMR ($CDCl_3$, numbering according to Scheme 3): δ = 9.11 (d, ^3J = 8.5 Hz, 2 H, H_2), 9.00–8.96 (m, 12 H, H^1), 8.75 (d, ^4J = 2.2 Hz, 2 H, H^4), 7.74 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 2 H, H^3), 7.34–7.12 (m), 6.87–6.74 (m, 44 H, 2 H^5, 2 H^6, 2 H^7, 2 H^8, 24 H^9, 12 H^{10}), 4.00 (t, ^3J = 6.3 Hz, 4 H, Hα), 1.82–1.24 (m, 224 H, 216 H^{11}, 4 Hβ, 4 Hγ), –0.69 (s, 4 H, H_{NH}) ppm. IR (KBr): $\tilde{\nu}$ = 3451 (NH), 2963, 2869, 1608, 1588, 1467, 1443, 1423, 1397, 1363, 1297, 1274, 1247, 1199, 1139, 1089, 1012, 961, 902, 865, 759, 707 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 701.5 (5.16), 667.5 (5.20), 640.5 (5.02), 611.0 (sh), 393.5 (sh), 339.5 (5.10), 293.0 nm (5.00). MS (MALDI-TOF): *m*/*z* = 3776 $[M]^+$. Elemental analysis calcd. (%) for $C_{250}H_{294}N_{16}O_{16}$: C 79.46, H 7.84, N 5.93; found: C 79.66, H 7.87, N 6.08.

Dimer **9b** was prepared from PcNi **7b** by **Method A** in 86% yield. By **Method B**, starting from mononuclear phthalocyanines **7b** and **8b** in DMF/THF, **9b** was obtained in 71% yield.

Compound 9b: ^{1}H NMR ($CDCl_3$, numbering according to Scheme 3): δ = 8.81–8.64 (m, 14 H, 12 H^1, 2 H^2), 8.43 (d, ^4J = 1.8 Hz, 2 H, H^4), 7.56 (dd, ^3J = 8.5, ^4J = 1.8 Hz, 2 H, H^3), 7.29–7.11 (m), 6.97 (t, ^4J = 2.2 Hz), 6.78–6.72 (m, 44 H, 2 H^5, 2 H^6, 2 H^7, 2 H^8, 24 H^9, 12 H^{10}), 4.05 (t, 4 H, Hα, ^3J = 6.2 Hz), 1.87–1.27 (m, 224 H, 216 H^{11}, 4 Hβ, 4 Hγ) ppm. IR (KBr): $\tilde{\nu}$ = 2963, 2868, 1608, 1589, 1533, 1462, 1421, 1385, 1362, 1297, 1276, 1246, 1198, 1139, 1095, 1055, 962, 903, 864, 755, 707 cm^{-1}. MS (MALDI-TOF): *m*/*z* = 3891 $[M]^+$. Elemental analysis calcd. (%) for $C_{250}H_{290}N_{16}Ni_2O_{16}$: C 77.14, H 7.51, N 5.76; found: C 77.63, H 7.60, N 6.02. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 670.5 (5.15), 628.5 (5.11), 577.0 (sh), 383.0 (sh), 299.5 nm (5.26).

Dimeric heteronuclear phthalocyanine **9c** was obtained from mononuclear phthalocyanines **8a** and **7b** by **Method B** in DMF/THF in 70% yield.

Compound 9c: ^{1}H NMR ($CDCl_3$, numbering according to Scheme 3): δ = 9.03–8.57 (m, 16 H, 12 H^1, 2 H^2, 2 H^4), 7.72–7.61 (m, 2 H, H^3), 7.29–7.12 (m), 6.90–6.73 (m, 44 H, 2 H^5, 2 H^6, 2 H^7, 2 H^8, 24 H^9, 12 H^{10}), 4.02 (t, ^3J = 6.2 Hz, 4 H, Hα), 1.85–1.21 (m, 224 H, 216 H^{11}, 4 Hβ, 4 Hγ), –0.98 (s, 2 H, H_{NH}) ppm. IR (KBr): $\tilde{\nu}$ = 3443 (NH), 2963, 2868, 1607, 1588, 1532, 1465, 1421, 1385, 1363, 1297, 1275, 1246, 1198, 1139, 1118, 1093, 1055, 1012, 961, 902, 865, 756, 706 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 699 (sh), 671.0 (5.18), 644.0 (5.07), 392.0 (sh), 331.0 (sh), 300.5 nm (5.17). MS (MALDI-TOF): *m*/*z* = 3831 $[M]^+$. Elemental analysis calcd. (%) for $C_{250}H_{292}N_{16}NiO_{16}\cdot H_2O$: C 77.92, H 7.71, N 5.82; found: C 77.63, H 7.65, N 5.97.

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