A Binuclear Phthalocyanine Containing Two Different Metals

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The unsymmetrical binuclear phthalocyanine **4a** and the symmetrical binuclear phthalocyanine **4b** with two different metals (Ni and Cu), as well as the correspondent binuclear phthalocyanines with two Ni atoms (**4c** and **4d**) were synthesized from the benzoannulated dicyano-substituted Ni phthalocyanine **2**. Atomic absorption spectroscopy verified unambiguously the presence of Ni and Cu in the binuclear phthalocyanines. The proposed synthetic route demonstrates great versatility towards substitution at the peripheral positions of the ring and the variation of the chelating central metal. Complexes **4a**–**4d** are soluble in common organic solvents of medium polarity.

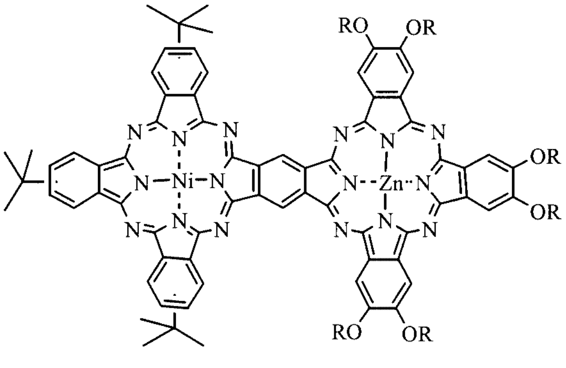
Introduction

Metallophthalocyanines (PcMs) have been widely studied for many years, mainly for their properties as dyes and catalysts.[1] The recent advances in materials science have identified many new applications for PcMs as active materials in various fields, for example in nonlinear optical (NLO) devices,[2,3] as semiconducting materials,[1b] as liquid crystals,[4] photosensitizers[5] and electrochromic devices,[6] amongst others.

PcMs possess an extended network of π-electrons, have planar or nearly planar structures in many cases, and show high thermal and photochemical stabilities. Since most PcMs are insoluble, and therefore difficult to process, the introduction of substituents at the Pc ring is a necessary approach to increase their solubility.[1b] Due to the growing interest in the properties of PcMs, it has become necessary to synthesize new systems, like binuclear PcMs, that can be used for the many possible applications listed above.

Results and Discussion

Planar or nearly planar binuclear Pcs, binuclear Pc-triazolhemiporphyrazinates (Thp)[7,8] or phthalocyanine-based dimers[8−19] {two Pcs linked, for example, by two butynes,[9] or oligo(phenylenevinylene)[10,11]} are known. Torres et al. reported the first preparation of heterodimetallic binuclear Pc derivatives with structure **1** (Scheme 1), having Ni and Zn as different metals.[8] The preparation of heterodimetallic binuclear Pc-Thp compounds with Ni and Zn has also been reported by the same authors.[7]



1 R = C_8H_{17}

Scheme 1

Among the reported binuclear Pcs, the metal-free compound with the basic structure of **4** and twelve dodecyloxy substituents was synthesized by mixed condensation of bis(dodecyloxy)(diimino)isoindoline with naphthalenebis(diiminoisoindoline) in 2-(dimethylamino)ethanol as solvent.[13] The reaction was carried out in one step, producing the mononuclear octadodecyloxy phthalocyanine, besides the desired binuclear Pc, which was isolated in a comparable low yield. A corresponding binuclear PcM was not prepared. In contrast to the binuclear Pc **1**, which can also be considered as an unsymmetrical substituted mononuclear Pc,[8] in **4** two complete Pc's are linked together.

We became interested in the preparation of new species with structure **4** because binuclear Pc's of this type are expected to show interesting linear optical and NLO properties,[2] and the starting material — the benzoannulated dicyano-substituted PcNi **2** — for an easy synthesis was available through our earlier work.[20]

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The synthesis described in Scheme 2 allowed us to obtain the binuclear Pc **4** containing different metals (Ni and Cu) in the same molecule, as well as to obtain unsymmetrically substituted binuclear PcMs.[8]

Depending on the functional groups in **2**, such as CN, these benzoannulated unsymmetrically substituted PcMs are desirable building blocks for the preparation of polymers,[19] for the linkage of PcMs with other materials, such as poly *p*-(phenylenevinylene) (PPV),[10,20] or, in our case, as the starting material for the synthesis of binuclear PcMs.

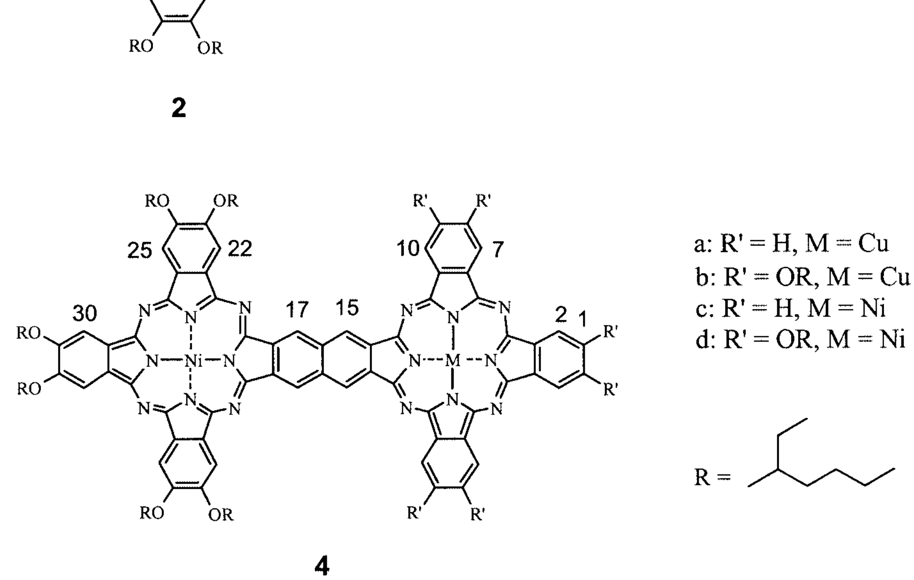
The benzoannulated PcNi **2** reacts with 1,2-dicyanobenzene (**3a**) or 1,2-dicyano-4,5-bis(2-ethylhexyloxy)benzene[21] (**3b**), in the presence of copper(II) chloride (route 1) to form the "second phthalocyanine ring" (**4a**, **4b**). Cu was used as the "second" metal in the binuclear PcMs **4a** and **4b** mainly due to its good chelating and stabilizing properties.[22] From reaction of, for example, dinitrile **3a** (**A**) and **2** (**B**), six different phthalocyanines are expected to be formed (statistical condensation,[23,24] **AAAA**, **AAAB**, **AABB**, **ABAB**, **ABBB** and **BBBB**). However, in the reaction of one equivalent of **2** with four equivalents of the dinitriles **3a** and **3b**, respectively, and $CuCl_2$ (route 1) in octan-1-ol in the presence of catalytic amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), only the **AAAB** and **AAAA** products are formed. The other isomers, for example **AABB** or **ABAB** are not obtained due to the high steric demand of dinitrile **2 (B)** in the process of the chelating ring formation[22] (pure **2** does not form any **BBBB** product in presence of $CuCl_2$. Force field calculations show a very high steric crowding of the hypothetical **BBBB** isomer). Separation of **AAAB** and **AAAA** was performed by column chromatography on silica gel,[24] with further purification by extracting the **AAAB** products (**4a** and **4b**) with methanol several times.

The binuclear PcMs **4c** and **4d**, with only Ni as central metals, have been obtained with $NiCl_2$ (route 2), using the same method as for the preparation and isolation of **4a** and **4b**.

Compounds **4a**−**4d** are soluble in common organic solvents with medium polarity, but practically insoluble in methanol, acetone and *n*-hexane. They were obtained in yields between 18% and 25%, based on **2**.

Flame Atomic Absorption Spectroscopy (FAAS)[25] has been applied for the quantitative determination of the metals Ni and Cu in **4a** and **4b,** respectively. Compounds **4a** and **4b** showed the calculated concentration of Ni and Cu in each binuclear Pc (see Exp. Sect.).

The UV/Vis maxima of **4a**−**4d** measured in CH_2Cl_2 are listed in Table 1. Due to aggregation caused by the essentially flat nature of the large molecules, broad absorptions in the Q-band region are observed, which differ characteristically from the sharp peaks of the mononuclear R_8PcCu and R_8PcNi (**AAAA** products, R = 2-ethylhexyloxy).[8] No, or only a small, red shift is observed for the Q-bands in PcMs **4a**−**4d** on account of only weak π-electron delocal-



Scheme 2

isation between two Pc rings. No mesomeric structures of compounds **4a**−**4d** including both rings can be drawn. A small shift of the Q-bands to lower wavelength is observed on going from **4a** to **4c**, and from **4b** to **4d**, due to the Cu in the binuclear PcMs **4a** and **4b**. This is also observed when comparing R_8PcCu and R_8PcNi (Table 1). In the case of **4a** and **4c**, the distance between the first and the second Q-band maxima, which is characteristic for unsymmetrical phthalocyanines,[26] is lowered on going from **4a** (Ni−Cu binuclear Pc) to **4c** (Ni−Ni binuclear Pc), due to the different metals in **4a**. This shift is even more pronounced in **4b** and **4d**, since these compounds are symmetric, and therefore the effect can be assigned to the metal only.

Table 1. UV/Vis absorptions (Q and B bands) for the listed compounds; all spectra were recorded in $CHCl_2$ as solvent (R = 2-ethylhexyloxy)

Compound	Q_{0-1} (nm)	Q_{0-0} (nm)	Q_{1-1} (nm)	B_{0-0} (nm)	B_{0-1} (nm)
3a	699.5	661.0	638.0 (sh)	–	326.0
3b	672.5	631.0 (sh)	–	–	304.0
3c	697.5	669.0	640.0 (sh)	–	321.0
3d	664.5	626.0 (sh)	–	–	312.5
R_8PcCu	679.0	611.5 (sh)	–	418.0	339.5
R_8PcNi	670.0	604.0 (sh)	–	410.0	310.0

The ^1H and ^{13}C NMR spectra of **4a** and **4b** (Ni−Cu Pc's) show respectively broad and weak resonances, due to the paramagnetic Cu. However, the spectra are in accordance with the structures **4a** and **4b** (see Exp. Sect.). The ^1H NMR spectra of **4c** and **4d** (Ni−Ni Pc's) also exhibit relatively broad signals of the ethylhexyloxy groups and broad aromatic signals. The obtained data are in agreement with the proposed structures.

The 2-ethylhexyloxy substituents in **4a**−**4d** are not stable under the conditions of FAB-MS, leading to a characteristic fragmentation pattern.[13] The PcMs **4a**−**4d** show a similar fragmentation pattern, corresponding to the molecular peak with loss of two substituents as the highest signal, followed by the loss of other fragments in a common pattern. The results are in agreement with the given structures (see Exp. Sect.).

Conclusion

In conclusion, we have presented the synthesis of symmetrical and unsymmetrical binuclear phthalocyanines of structure **4**, with two different metals incorporated in the same system. The described method is convenient and the products can easily be purified and characterized. This route is currently being extended to the synthesis of additional binuclear PcMs containing other different moieties, such as TiO, GaCl or InCl, to study their nonlinear optical properties.[2,27]

Experimental Section

General Method for the Preparation of Compounds 4a−4d: A mixture of **2** (210 mg, 140 µmol) and the appropriate dinitrile (1,2-dicyanobenzene) (**3a**), 70 mg, 530 µmol or 1,2-dicyano-4,5-bis(2-ethylhexyl)benzene[20] (**3b**), 110 mg, 280 µmol) and $CuCl_2$ (route 1, 20 mg, 150 µmol) or $NiCl_2$ (route 2, 20 mg, 145 mmol) was suspended in octan-1-ol (10 mL) in an argon-purged vessel and DBU (0.05 mL) was added. The mixture was stirred and heated to 175 °C for 24 h, allowed to cool down, and poured into MeOH (50 mL). The precipitate formed was isolated by centrifugation and was washed several times with MeOH. The crude mixture was separated by flash chromatography on silica gel with dichloromethane as eluent to obtain the desired compounds **4a**−**4d**.

Isolation of Products 4a and 4c (Unsymmetric Structures): The first fraction contained mostly unchanged **2** and was discarded. Compounds **4a** or **4c** (**AAAB** products) were eluted as the second fraction. The third fraction was eluted with a CH_2Cl_2/THF (5:1) mixture and identified as the **AAAA** product.

Isolation of Products 4b and 4d (Symmetric Structures): The first fraction from the chromatography contained the **AAAA** product and the second fraction was identified as the **AAAB** product (**4b** or **4d**). The third fraction (unchanged **2**) was discarded.

The solvent from each fraction was removed, and the greenish-blue solids were extracted with methanol for further purification. Drying in vacuo afforded **4a** (20%), **4b** (18%), **4c** (23%) and **4d** (20%); yields based on **2**.

Binuclear Metal Phthalocyanine 4a: FAAS (air/acetylene): Theory: 2.1 µg/l of Ni and 2.2 µg/l of Cu; found 1.9 µg/L of Ni and 2.3 µg/L of Cu. UV/Vis ($CHCl_2$): λ_{max} = 699.5, 661.0, 638.0, 326.0 nm. ^1H NMR ($CDCl_3$): δ = 0.86, 1.07 [br.,CH_3], 1.24, 1.41, 1.51, 1.66 [br., CH_2], 2.03 [br., CH], 4.18, 4.26 [br., OCH_2], 6.48−9.10 [br., PcH] ppm. ^{13}C NMR ($CDCl_3$): δ = 10.6, 11.5, 14.3 [CH_3], 22.7, 23.3, 23.7, 24.1, 24.5, 26.4, 29.3, 29.7, 30.4, 30.8, 31.9 [CH_2], 39.3, 39.4, 39.7, 40.2 [CH], 70.8, 71.7, 73.3 [OCH_2], 102.9−103.8 [C-2, C-7, C-8, C-9, C-10, C-22, C-25, C-30], 126.6−133.5 [C-22, C-25, C-30, C-3, C-6, C-11, C-14, C-16, C-18, C-21, C-26, C-29], 144.1−145.1 [C-4, C-5, C-12, C-13, C-19, C-20, C-27, C-28], 150.7−153.0 [C-1, C-8, C-9, C-23, C-24, C-31] ppm. MS (FAB): *m/z* (%) = 1651.9 (90) [$M^+ - 2C_8H_{16}$], 1602.7 (40) [$M^+ - 2OC_8H_{16}$], 1440.7 (30)[$M^+ - 4C_8H_{16}$]. $C_{110}H_{128}CuN_{16}NiO_6$: calcd. C 69.81, H 6.82, N 10.84; found C 69.17, H 7.16, N 9.33.

Binuclear Metal Phthalocyanine 4b: FAAS (air/acetylene): Theory: 2.0 µg/l of Ni and 2.1 µg/l of Cu; found1.8 µg/L for Ni and 2.1 µg/L for Cu. UV/Vis ($CHCl_2$): λ_{max} = 672.5, 631.0, 304.0 nm. ^1H NMR ($CDCl_3$): δ = 0.91, 0.93 [br., CH_3], 1.20, 1.33, 1.50 [br., CH_2], 1.78 [br., CH], 4.01, 4.49 [br., OCH_2], 7.35−8.51 [br., PcH] ppm. ^{13}C NMR ($CDCl_3$): δ = 11.2, 11.5, 14.1, 14.2 [CH_3], 22.6, 23.0, 23.3, 23.9, 29.1, 29.4, 29.7, 30.6, 30.9, 31.4[CH_2], 39.3, 39.6, 40.0 [CH], 71.6, 71.8, 72.1 [OCH_2], 104.4−108.1 [C-2, C-7, C-8, C-9, C-10, C-22, C-25, C-30], 115.4 [C-15, C-17], 129.2−132.9 [C-22, C-25, C-30], 133.1− 136.4 [C-3, C-6, C-11, C-14, C-16, C-18, C-21, C-26, C-29], 143.2−146.9 [C-4, C-5, C-12, C-13, C-19, C-20, C-27, C-28], 150.4−152.8 [C-1, C-8, C-9, C-23, C-24, C-31] ppm. MS (FAB): *m/z* (%) = 2442.8 (20) [$M^+ - 2C_8H_{16}$], 2133.7 (40) [$M^+ - 3OC_8H_{16} - C_8H_{16}$], 1141.9 (40)[$M^+ - 12OC_8H_{16}$]. $C_{158}H_{224}CuN_{16}NiO_{12}$: calcd. C 71.40, H 8.34, N 7.93; found C 72.59, H 8.39, N 7.48.

Binuclear Metal Phthalocyanine 4c: UV/Vis ($CHCl_2$): λ_{max} = 697.5, 669.0, 640.0, 321.0 nm. ^1H NMR ($CDCl_3$): δ = 0.86, 0.90, 1.09

[br., 36 H, CH_3], 1.24, 1.56, 1.66 [br., 48 H, CH_2], 1.98, 2.02 [br., 6 H, CH], 4.19, 4.29 [br., 12 H, OCH_2], 6.80, 6.95, 7.39, 7.52, 7.69, 7.75, 8.04 [br., PcH] ppm. ^{13}C NMR (THF): δ = 11.0, 11.2, 13.8, 13.9 [CH_3], 19.4, 22.8, 23.5, 23.8, 27.1, 29.3, 29.7, 29.9, 30.4, 31.1, 32.2, 32.9 [CH_2], 37.3, 39.9, 41.2 [CH], 71.4, 71.6, 72.1 [OCH_2], 104.1, 104.3, 104.8 [C-2, C-7, C-8, C-9, C-10, C-22, C-25, C-30], 124.7 [C-15], 125.1 [C-17], 127.7, 128.2, 128.6 [C-22, C-25, C-30], 129.0−133.5 [C-3, C-6, C-11, C-14, C-16, C-18, C-21, C-26, C-29], 143.6, 146.1, 147.5, 148.5 [C-4, C-5, C-12, C-13, C-19, C-20, C-27, C-28], 152.0, 152.3, 152.6 [C-1, C-8, C-9, C-23, C-24, C-31] ppm. MS (FAB): *m/z* (%) = 1686.7 (15) [$M^+ - C_8H_{16} - OC_8H_{16} + Na$], 1214.7 (100) [$M^+ - 6C_8H_{16}$]. $C_{110}H_{128}N_{16}Ni_2O_6$: calcd. C 69.94, H 6.83, N 10.87; found C 69.34, H 6.28, N 9.36.

Binuclear Metal Phthalocyanine 4d: UV/Vis ($CHCl_2$): λ_{max} = 664.5, 626.0, 398.5, 370.5, 312.5 nm. ^{1}H NMR ($CDCl_3$): δ = 0.84, 0.87, [br., 72 H, CH_3], 1.04, 1.24, 1.51, 1.76 [br., 96 H, CH_2], 2.02, 2.04, 2.10 [br., 12 H, CH], 4.16, 4.32, 4.50 [br., 24 H, OCH_2], 7.49, 7.92, 8.53, 8.82 [br., PcH] ppm. ^{13}C NMR (THF): δ = 10.4, 11.4, 13.6, 14.0 [CH_3], 22.9, 23.1, 23.8, 24.2, 29.0, 29.7, 29.9, 31.1, 31.4, 31.6, 32.1 [CH_2], 38.6, 39.9, 41.3 [CH], 71.3, 71.6, 71.9 [OCH_2], 102.7, 103.6, 104.2 [C-2, C-7, C-10, C-22, C-25, C-30], 117.7 [C-15], 125.2−133.9 [C-3, C-6, C-11, C-14, C-16, C-18, C-21, C-26, C-29], 143.2, 143.6, 144.1 [C-4, C-5, C-12, C-13, C-19, C-20, C-27, C-28], 151.1, 151.2, 151.5, 151.9 [C-1, C-8, C-9, C-23, C-24, C-31] ppm. MS (FAB): *m/z* (%) = 2537.4 (30) [$M^+ - 2C_8H_{16}$], 2305.8 (70) [$M^+ - 3C_8H_{16}$]. $C_{158}H_{224}N_{16}Ni_2O_{12}$: calcd. C 71.53, H 8.36, N 7.94; found C 72.05, H 5.56, N 7.19.

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