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Synthesis of a Dinuclear Naphthalocyanine Analogue with Absorption in the NIR

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A dinuclear naphthalocyanine analogue containing two incomplete naphthalocyanine macrocycles connected by a shared benzene ring was synthesized in good yield. The long-wavelength absorption band in the electronic spectrum is observed at $\lambda = 965$ nm. As a consequence of the π-system extension caused by dimerization and addition of further peripheral benzene rings, this band is shifted bathochromically by approximately 300 nm compared to absorption bands of mononuclear phthalocyanines.

Introduction

Phthalocyanines (Pcs) have many applications such as dyes and pigments,[1] catalysts and photocatalysts,[2] photoconductors in laser printers[3] and photosensitizers in photodynamic therapy.[4] They are of significant interest as potential molecular conductors and semiconductors,[5] electrochromic[6] and non-linear optical materials,[7] components of organic photovoltaic cells[8] and field-effect transistors.[9] The high overall stability and exceptional electronic properties of Pcs are responsible for most of their real and potential applications. The synthesis of conjugated oligomers, as a way of Pc electronic structure modification, by increasing the extent of the conjugated π-electron system results in a bathochromic shift of the long wavelength absorption band, which is of substantial interest for the design of new functional materials.

Changes in the electronic structure of Pcs are well indicated by their electronic absorption spectra. Most Pcs in solution have a sharp intense absorption band (Q-band) in the red spectral region ($\lambda_{max} \approx 670$ nm). The extension of the Pc π-conjugated system causes a bathochromic shift of this band. One possible way to extend the Pc π-system is by annulation of further benzene rings on the periphery of the molecule leading to naphthalocyanines (Ncs),[10,11] anthracocyanines (Acs),[11] and different unsymmetrical analogues such as phthalonaphthalocyanines.[12] However, this approach leads to decreased compound stability. The other possibility is the construction of conjugated Pc oligomers. Some dimers of Pcs and their close analogues have been described.[13,14] It was shown by us that the strongest known interaction between Pc units is probably achieved if they are connected through a common annulated benzene ring. In our previous work, di- and trinuclear Pcs of this type were prepared that showed intense absorption in the NIR region.[15] In contrast, dinuclear Pcs covalently connected by benzene rings, exhibit no strong interactions between the two Pc units resulting in a shift of the Q-band of only 30 nm.[16]

In this work, the two approaches to construct large π-systems are combined: (i) connection of two π-systems by a shared benzene ring, and (ii) annelation of further benzene rings on the periphery of the conjugated molecule. An unsymmetrical compound of this type containing both Pc and incomplete Nc rings was described previously in a short communication,[13d] but no synthesis or yield details were given and, surprisingly, the compound did not show any long-wavelength absorption. In this work, the zinc(II) complex of the dinuclear Nc analogue **4**, which absorbs at $\lambda > 900$ nm, is synthesized for the first time in a good yield. Zn^{II} was selected as the metal ion in the core of the ligand of **4** because Zn^{II} complexes of Pcs are active sensitizers in photooxidation reactions and *p*-conductors in organic solar cells.[2,8]

Results and Discussion

The dinuclear Nc analogue **4** was prepared by a one-step procedure by the mixed co-cyclotetramerization of the bis(diiminoisoindoline) **1** and 6-*tert*-butylnaphthalene-2,3-dicarbonitrile (**2**) with lithium pentanolate in *n*-pentanol (Scheme 1). At first, a mixture of lithium Ncs is formed that are directly metalated in situ with zinc(II) acetate. The obtained statistical mixture of zinc complexes was separated by column chromatography on silica gel eluting with tolu-

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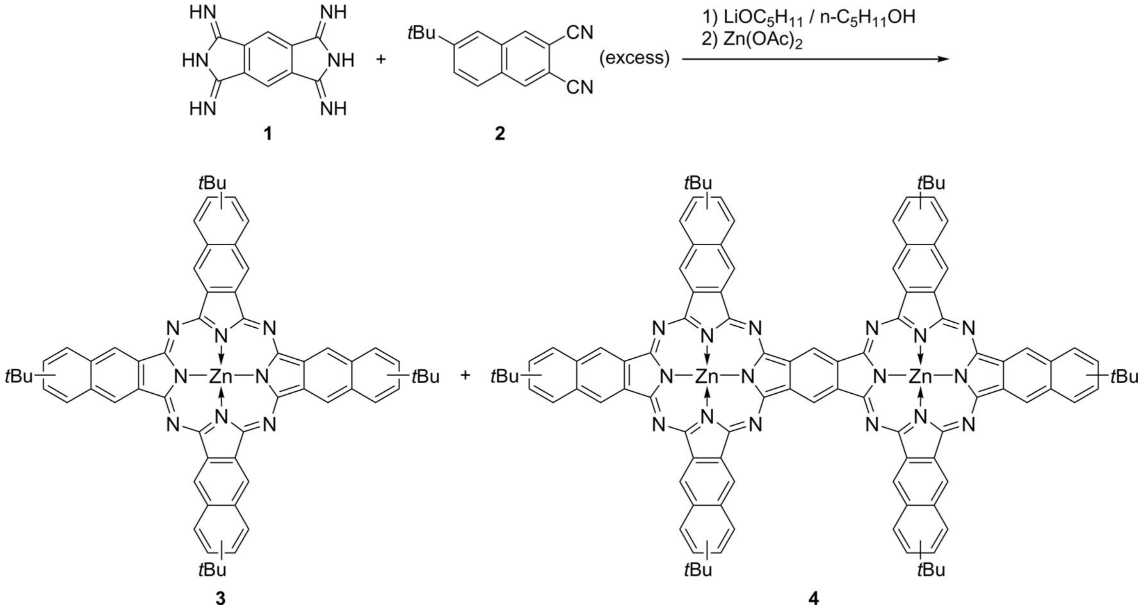
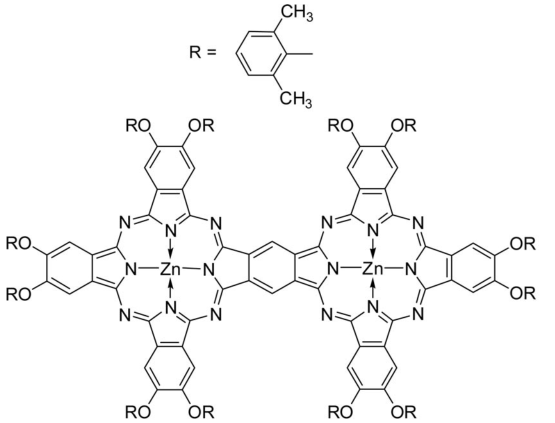


Scheme 1. Synthesis of the dinuclear Nc analogue **4**.

ene/THF, and **4** was isolated as the second fraction in 14% yield. A mixture of the metal-free ligands can also be obtained by demetalation of the lithium Ncs mixture with acetic acid. Attempts to separate this mixture were not successful due to strong aggregation, which is reduced for zinc complexes by a coordinating solvent such as THF. Other metal complexes can be prepared in the same way, but the possibility of separating the mixture strongly depends on the central metal ion.

Compound **4** can also be prepared by using diazabicyclo[5.4.0]undec-7-ene (DBU) as a basic catalyst in *n*-pentanol but this procedure leads to only a 3% yield of **4**. Another procedure using magnesium alkoxide as a basic catalyst followed by acidic removal of magnesium was employed to prepare the dinuclear Pc **5** in good yield.[15a] Surprisingly, magnesium Nc is stable in trifluoroacetic acid, and therefore the metal-free Nc analogue **4**, as well as its complexes with other metals, cannot be prepared by this method.



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Unexpectedly **4** is stable to exposure to air under room light in both the solid state and in solution, and this allows for chromatographic separation of the reaction mixtures. In contrast, other NIR-absorbing Pc analogues such as Acs decompose within a few days even when stored in the dark under nitrogen.[11c] Due to its bulky *tert*-butyl groups the dinuclear Nc analogue **4** is soluble in several organic solvents: aromatics, chloroform, THF, DMF, pyridine, and is soluble in DMSO but only in the presence of cyanide. In solution **4** is more strongly aggregated compared to the mononuclear Nc **3** and dinuclear Pc **5** with the same or similar substituents.[15] Compound **4** is monomolecular when dissolved in DMSO in the presence of cyanide, with Zn^{II} coordinated in the core of the ligand (Figure 1). However, in pyridine and THF some aggregation occurs that is visible in the UV/VIS/NIR spectra by a new absorption band at ca. 870 nm and a higher intensity of the Soret-band compared to the Q-band, this effect is more pronounce with THF. The evidence for aggregation is observed even in the ESI mass-spectrum of **4**. The molecular ion peak can be considered as a sum of M$^+$ and M$_2$$^{2+}$ (Figure 2).

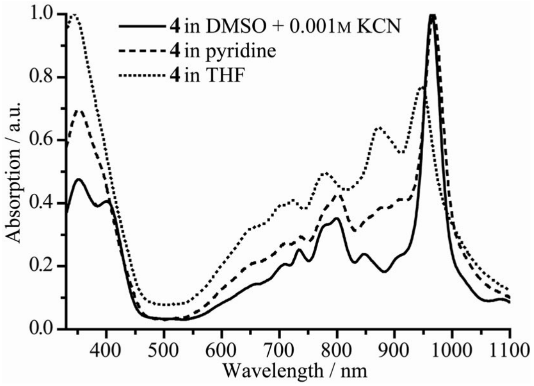

Figure 1. UV/Vis/NIR spectra of aggregated and nonaggregated **4**.

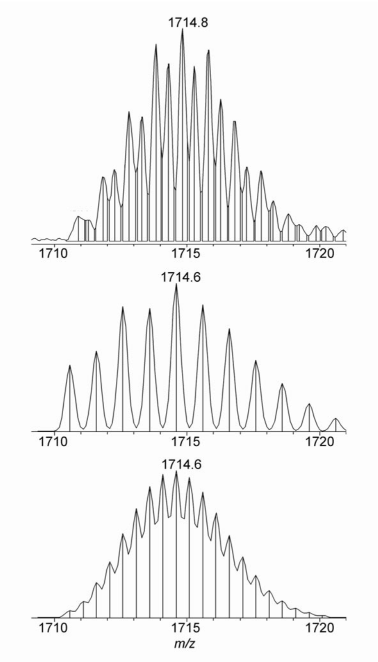

Figure 2. ESI mass-spectrum of **4** (top), simulated isotopic pattern of M^+ (middle) and M_2^{2+} (bottom).

The main electronic absorption band of **4** (λ = 965 nm, ε = 220000 $\text{M}^{-1}\,\text{cm}^{-1}$) is red-shifted by ca. 200 nm compared to the corresponding band for the mononuclear Nc **3** (λ = 760 nm), and by ca. 300 and ca. 120 nm when compared to bands for mononuclear and dinuclear Pcs (λ = 675 and 840 nm for **5**,[15b] respectively) which clearly reflects a very strong intramacrocyclic π-electron delocalization (Figure 3). Therefore, connection of the two macrocyclic rings by a common benzene ring and annelation of further benzene rings at the periphery results in an extended π-system with a significantly decreased HOMO–LUMO gap. The extinction coefficient of **4**, ε = 220.000 $\text{M}^{-1}\,\text{cm}^{-1}$, is higher than the value for the mononuclear Nc.[10,11a] The same trend was observed when comparing dinuclear and mononuclear Pcs.[15]

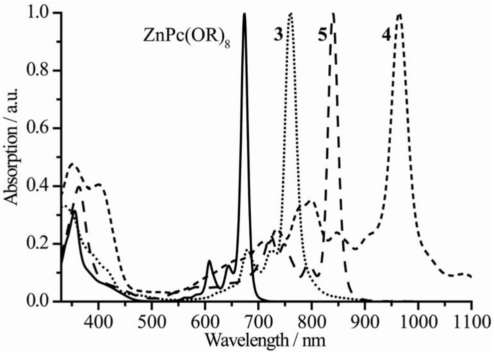

Figure 3. UV/Vis/NIR spectra of mono- and dinuclear Pcs and Ncs (**4** in DMSO and KCN, other compounds in THF).

For the unsubstituted analogues **4a** (R = H instead of *t*Bu) and **5a** (R = H instead of OR) of compounds **4** and **5** semiempirical calculations were carried out to predict the absorption bands in their UV/Vis/NIR spectra. The calculated spectra are shown in Figure 4 and the partial orbital diagrams in Figure 5. The shape of the theoretical spectra is in a good agreement with the experimental ones, the Q-band transition energies differ from the experimental ones by ≤ 5%. Also, the higher-energy transitions at ca. 700–750 nm calculated for **4a** and **5a** could be seen in the spectra of **4** and **5** as broad bands of low intensity. The observed strong Q-band changes can be explained using a simplified orbital model (Figure 5). The Pc Q-band arises from a HOMO–LUMO transition. For compound **5a** a series of two HOMOs and four LUMOs can be described as a linear combination of frontier orbitals of two mononuclear Pc molecules.[13b,13e] The splitting of the corresponding energy levels reduces the HOMO–LUMO gap. Addition of further benzene rings at the periphery of Pc macrocycle mainly increases the HOMO energy. It is known that the photooxidative stabilities of Pcs and their analogues are correlated with their HOMO energy.[17] This explains why Ncs and especially Acs are less stable than Pcs. In contrast, annulation of Pc or Nc macrocycles by a common benzene ring has stronger effect on LUMO rather than HOMO energy levels, which does not lead to significant loss of stability, but does strongly shift the Q-band to the red. It can be seen from Figure 5 that the orbital diagram of the dinuclear Nc analogue **4** can be explained as a combination of HOMO

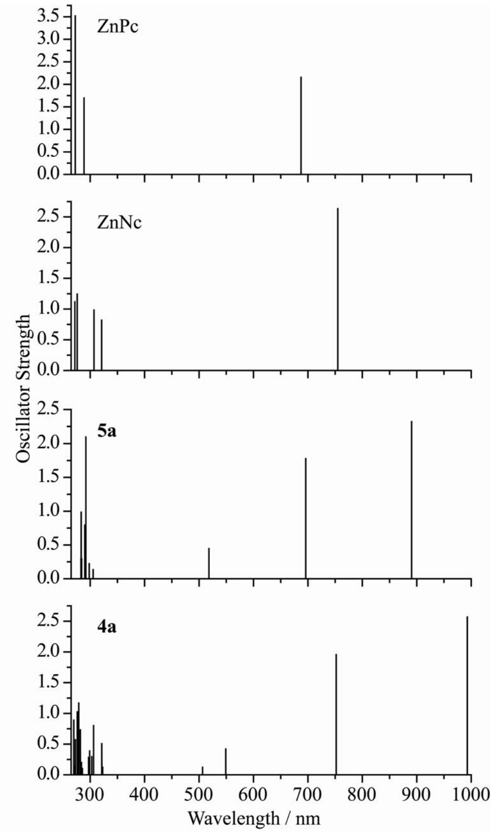

Figure 4. Calculated electronic absorption spectra of compounds **4a** and **5a** and for comparison their mononuclear analogues ZnPc and ZnNc.

level shifting due to addition of peripheral benzene rings and splitting of the frontier orbital levels (mainly LUMO), which is similar to the dinuclear Pc **5** orbital arrangement.

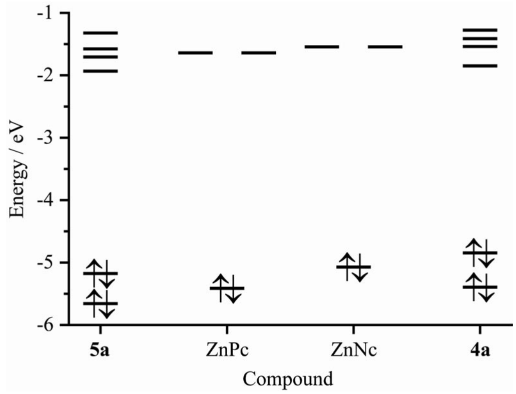

Figure 5. Partial orbital diagrams for compounds **4a** and **5a** and for comparison their mononuclear analogues ZnPc and ZnNc.

Conclusions

The dinuclear Nc analogue **4** containing two incomplete Nc rings connected by a common benzene ring was synthesized for the first time by the co-cyclotetramerization of compounds **1** and **2** in the presence of lithium alkoxide followed by metalation with Zn^{II}. Thus, two approaches to construct large π-systems are combined: (i) connection of two π-systems by a shared benzene ring and (ii) annulation of further benzene rings on the periphery of the conjugated molecule. This causes a large bathochromic shift of ca. 300 nm of the main absorption band in the UV/Vis/NIR spectra of mononuclear Pcs (λ ca. 670 nm). Such a bathochromic shift was also observed for trinuclear Pcs, with respect to similar bands observed in previously obtained spectra for trinuclear Pcs,[15b] which were prepared in 1% yield whereas the yield of **4** was 14%. Semiempirical MO calculations of the UV/Vis/NIR spectra are in good agreement with the experimental ones. Compounds with low orbital gaps, like **4**, are of interest to the field of molecular semiconductors.[18] They can be used as NIR sensors, as NIR photoconductors,[3] in organic solar cells,[8] and also as sensitizers[2] utilizing the NIR part of solar radiation.

Experimental Section

Measurements: ^{1}H NMR spectra were recorded with a Bruker Avance DPX-200 (200 MHz), MS-ESI with a Bruker Esquire LC. IR spectra were collected with a Perkin–Elmer Spectrum 1000 spectrometer, and UV/Vis/NIR spectra were recorded with a Perkin–Elmer Lambda 25 spectrophotometer. Elemental analysis was carried out with a EURO EA automatic analyzer.

Materials: Compound **1** was prepared from 1,2,4,5-tetracyanobenzene as described in the literature.[13b] Compound **2** was prepared by a published procedure.[19] The solvents used for the preparations (reagent grade) were dried, distilled, and stored under dry conditions. All syntheses were carried out under high purity dry nitrogen. Silica gel 60 (40–63 μm) (Merck) was used for chromatography procedures.

Semiempirical MO Calculation: For the spectra calculations, the ZINDO/S method in the HyperChem, rel. 7.1[20] software was used with the following parameters:[15b] total charge: 0; spin multiplicity: 1; state: lowest; convergence limit: 0.00001; spin pairing: RHF; overlap weighting factors: σ-σ: 1.267; π-π: 0.585; CI method: singly excited; energy criterion maximum excitation energy: 8 eV. The initial geometries were constructed from crystal structures of unsubstituted PcZn[21] and naphthalene as determined by XRD.[22]

Dinuclear Zinc Complex of Naphthalocyanine Analogue 4: Lithium metal (50 mg, 7 mmol) was dissolved in *n*-pentanol (5 mL). To this solution **1** (53 mg, 0.25 mmol) and **2** (0.47 g, 2 mmol) were added and the resulting mixture was heated under reflux for 2 h. Zinc acetate dihydrate (0.33 g, 1.5 mmol) was then added and the mixture was stirred at 100 °C for 15 h, then cooled and diluted with methanol (20 mL). The dark green precipitate was collected by centrifugation, washed with methanol, dried, and extracted with toluene containing 5 vol.% THF. The resulting solution was separated by column chromatography on silica gel eluting with toluene/THF, gradually increasing the THF content of the eluent from 5 to 30%. The second green fraction was collected, and the solvents removed under reduced pressure. The residue was dissolved in toluene and then precipitated with *n*-hexane. After drying under vacuum at 60 °C the final product was obtained as a dark green powder; yield 60 mg (14%). ^{1}H NMR ([D$_6$]DMSO + 0.01 M KCN, TMS): δ = 11.0–11.4 (2 H), 9.7–10.4 (10 H), 8.4–9.1 (14 H), 7.9–8.3 (6 H), 1.6–1.8 (54 H) ppm. UV/Vis (DMSO + 0.001 M KCN): $\lambda_{\max}$ (ε) = 965 (220000), 848 (53000), 800 (77000), 734 (55000), 710 (45000), 401 (89000), 351 nm (105000 $\mathrm{M^{-1}cm^{-1}}$). MS (ESI): *m*/*z* = 1710 [M^+], [M_2^{2+}]. IR (KBr): $\tilde{\nu}$ = 2954, 1617, 1457, 1418, 1353, 1304, 1258, 1098, 1063, 1019, 947, 906, 808, 738, 717 cm^{-1}. $C_{106}H_{86}N_{16}Zn_2{\cdot}2H_2O$ (1750.77): calcd. C 72.72, H 5.18, N 12.80; found C 72.34, H 5.54, N 12.41.

Acknowledgments

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