DOI: 10.1002/ejic.200600843

Linear and Rectangular Trinuclear Phthalocyanines

Sergey G. Makarov,[a,b] Olga N. Suvorova,[b] Christian Litwinski,[c] Eugeny A. Ermilov,[c] Beate Röder,[c] Olga Tsaryova,[a] Thomas Dülcks,[a] and Dieter Wöhrle*[a]

Keywords: Phthalocyanines / NIR absorption / UV/Vis spectroscopy / Semiempirical calculations / Fused-ring systems

Isomeric linear and rectangular trinuclear metal-free and zinc(II) phthalocyanine complexes connected by common annulated benzene rings have been synthesized by the mixed cyclotetramerization of a 1,2,4,5-tetracyanobenzene derivative and 4,5-bis(2,6-dimethylphenoxy)phthalonitrile. Their electronic-absorption and fluorescence spectra have been studied in comparison with the corresponding mono- and dinuclear phthalocyanines. For the zinc complexes, the molecular orbitals and electronic spectra have been calculated semi-empirically. The trinuclear phthalocyanines exhibit absorptions up to 940 nm with extinction coefficients up to about 700000 $M^{-1}cm^{-1}$, which shows the extension of the π-electron system.

Introduction

Conjugated porphyrin oligomers are the subject of significant interest due to their potential uses as molecular wires, materials for optical limiting, and other advanced technologies.[1] Accordingly, many compounds have been synthesized and studied in recent years. However, much less is known[2] about such systems based on phthalocyanines (Pcs) − the most common porphyrin analogues. Pcs have many applications, such as in dyes and pigments,[3a] catalysts and photocatalysts,[3b–3d] photoconductors in laser printers,[3e] and photosensitizers in photodynamic therapy.[3f] They are also of significant interest as potential molecular conductors and semiconductors,[4a] electrochromic[4b,4c] and non-linear optical[4d,4e] materials, components of organic photovoltaic cells,[4f] and light-emitting diodes.[4g] The high overall stability and exceptional electronic properties of Pcs are responsible for most of their actual and potential applications. The synthesis of conjugated oligomers as a way of modifying the electronic structure of phthalocyanines by increasing the dimensions of the conjugated π-electron system 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 ($\lambda_{max} \approx 680$ nm). The extension of the Pc π-conjugated system causes a bathochromic shift and, depending on the resulting symmetry, splitting of the Q band. To understand these spectral changes MO calculations, which are normally in good agreement with experimental data, are often performed.

One possible way to extend the Pc π-system is annulation of further benzene rings at the periphery of the molecule, which leads to naphthalocyanines (Ncs), anthracocyanines (Acs),[5a] and different unsymmetrical analogues such as phthalonaphthalocyanines.[5b,5c] Unsymmetrical annulation gives more flexibility when it comes to tuning the electronic properties. However, this approach also leads to decreased stability.[5a,5b] The other possibility is the construction of conjugated Pc oligomers. Some dimers of Pcs and their close analogues have been described[2] but only a very few conjugated trimers are known: a diacetylene-bridged "Pc triangle", a benzo-annulated SubPc trimer, and only one conjugated benzo-annulated Pc trimer (described by us).[2a,2b,2g–2i,2l] It has been shown that the strongest known interaction between Pc units is probably achieved if they are connected through a common annulated benzene ring.[2b] It is interesting to point out that further annulation of a Pc ring to a dimer of this type will lead to isomeric linear and rectangular trimers with different symmetries and electronic properties. In our previous work,[2b] a substituted metal-free dimer and a linear metal-free trimer were prepared and their photophysical properties were described. To the best of our knowledge, a rectangular trimer of this type has not yet been reported and neither have metal-containing linear and rectangular trimers. In this work, we describe the preparation and basic photophysical properties of linear and rectangular metal-free and zinc Pc trimers in comparison

[a] FB2, Biologie/Chemie
Universität Bremen
P. O. Box 330440, 28334 Bremen, Germany
Fax: +49-421-218-4935
E-mail: woehrle@chemie.uni-bremen.de
[b] G.A. Razuvaev Institute of Organometallic Chemistry
Russian Academy of Sciences
Nizhniy Novgorod, Russia
[c] Institut für Physik, Photobiophysik
Humboldt-Universität zu Berlin
Newtonstr. 15, 12489 Berlin, Germany

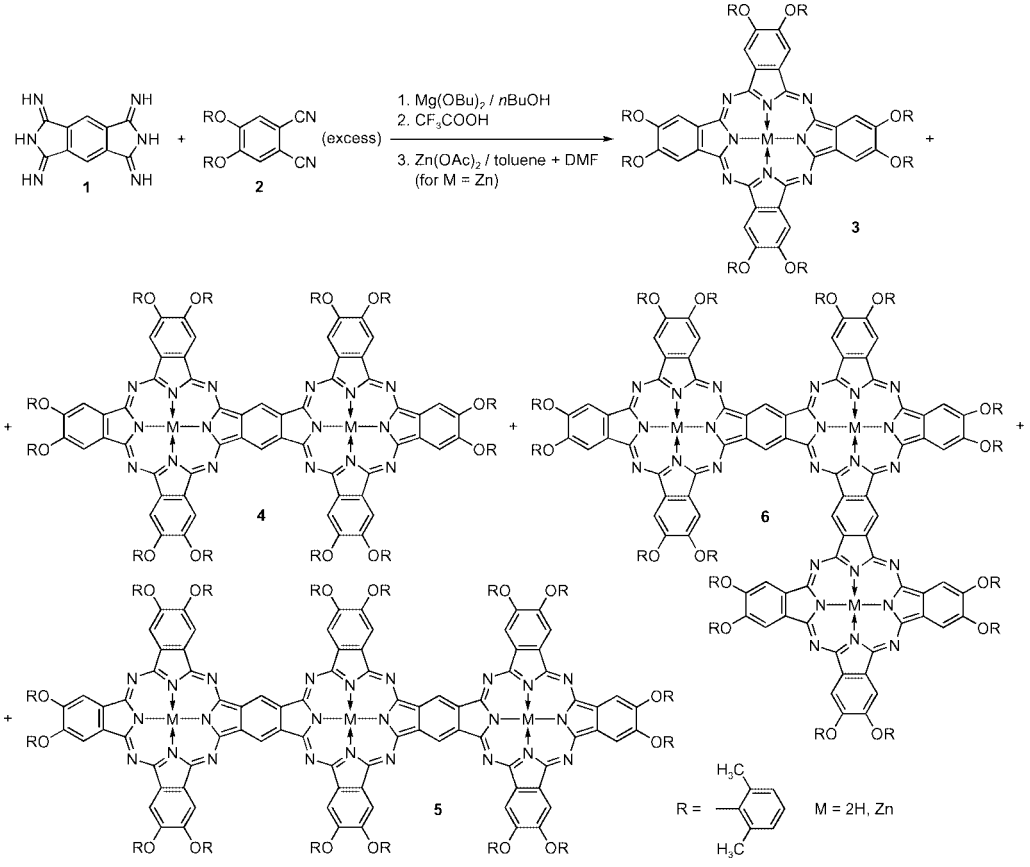
with their mono- and dinuclear analogues. For the zinc complexes, molecular orbitals and electronic spectra have been calculated semi-empirically.

Results and Discussion

The metal-free linear trinuclear phthalocyanine H_6**5** was described in our previous work.[2b] It was isolated in 0.2% yield from the Pc mixture obtained by co-cyclotetramerization of the tetracyanobenzene derivative **1** and the substituted phthalonitrile **2**. Bulky 2,6-dimethylphenoxy groups in the phthalonitrile derivative **2** were selected to avoid or reduce aggregation of the corresponding Pcs. Compared to Pcs prepared from a mono-substituted phthalonitrile, a Pc synthesized from **2** exists as single isomer, which allows easier isolation and better characterization. The corresponding rectangular metal-free trimer was not isolated but was detected from a peak at around 900 nm in the UV/Vis/NIR spectrum of the reaction mixture.[2b] In the present work more careful gradient elution from a silica gel column with a toluene/hexane mixture, followed by column chromatography of all mixed fractions, allowed us to isolate both H_6**5** and H_6**6** in yields of 0.9 and 1.7%, respectively. Their zinc complexes were prepared by the usual metalation with zinc acetate in toluene/dmf (Scheme 1).

All compounds prepared in this work are stable in air and to light in solution as well as in the solid state. They are soluble in aromatic solvents, thf and halogenated hydrocarbons. Linear trinuclear Pcs, especially Zn_3**5**, have significantly lower solubility and higher aggregation tendency than the other Pcs described previously and here.[2b] This becomes significant in toluene (concentration dependence of the extinction coefficient, broad bands at around 850 and 1000 nm) at concentrations higher than 10^{-6} M. This tendency is not so pronounced in chloroform for H_6**5** or in thf for both H_6**5** and Zn_3**5**. Generally, zinc complexes Zn_2**4**–Zn_3**6** tend to aggregate more strongly than the corresponding free ligands.

The electrospray ionization (ESI) method was used for mass-spectrometric characterization of the prepared compounds. This method is widely employed for high-molecular-weight ($M > 1000$) compounds such as biomacromolecules,[6a] supramolecular systems,[6b] fullerenes[6c,6e] etc. It is known that ESI is sensitive only to ions already present in the solution or compounds that easily ionize through acid/base (Brønsted or Lewis) or redox chemistry.[6c,6d] To enhance the sensitivity to compounds that are more difficult to ionize, different reagents that convert the substrate into an ionic form (oxidants,[6c] salts,[6b,6d,6e] even in combination with chemical derivatization of analyte[6b,6d]) are used. In the present work, we found that the use of pyridine as a basic co-solvent for H_6**6**, or a small amount of sodium cyanide ($\approx 10^{-4}$ M) for Zn_3**5** and Zn_3**6**, facilitates their ionization to produce [M^{2-} – 2H] and [M^{2-} + 2CN], respectively. Pyridine is expected to deprotonate pyrrole fragments and cyanide coordinate to Zn. An interesting example of using



Scheme 1. Synthesis of **3**–**6** (M = 2 H, Zn).

NaCN in ESI MS is the analysis of higher fullerenes.[6e] In this case the nucleophilic addition of cyanide to fullerene is responsible for ionization. In summary, the molecular ions of the annulated dinuclear and trinuclear Pcs were clearly identified by the ESI MS method, although it was not possible to distinguish by mass spectrometric means between the isomeric trinuclear linear **5** and rectangular **6**.

The difference between linear and rectangular trinuclear Pcs can be clearly seen in their ^{1}H NMR spectra, where Pc ring currents help to resolve the spectra of di- and trinuclear Pcs by deshielding the protons of the neighboring Pc fragments.[2b] The ^{1}H NMR spectrum of H_6**5** has been described previously.[2b] The spectrum of H_6**6** (Figure 1) is more complicated due to its lower symmetry. The signals of the methyl protons are only partially resolved,[7a] in contrast to the clearly resolved group of four singlets in the case of the linear H_6**5**. In the aromatic region of the spectrum, two signals of (two types of) protons of the bridging benzene rings appear at δ = 11.46 and 11.25 ppm, and two groups of signals of the other Pc aromatic protons (eight types, resolved only partially) at δ = 8.99–9.08 and 8.17–8.37 ppm. In the case of H_6**5** there are only five types of Pc ring protons that give separate singlets. The aromatic protons of the substituents show a broad signal at δ = 7.32–7.54 ppm. In the rectangular trimer, one pair of substituents get very close to each other and, in one of the possible conformations, their tails can be located over the neighboring benzene rings of the remote Pc fragments. The doublet at δ = 6.96 ppm and the triplet at δ = 6.63 ppm in the spectrum of H_6**6**, which disappear upon increasing temperature, can be assigned to the aromatic protons of these substituents. Zinc complexes Zn_3**5** and Zn_3**6** show similar spectra to the corresponding free ligands except for the two signals of the pyrrole protons near δ = 0 ppm (1:2 ratio), which belong to central and peripheral Pc rings, respectively.

The UV/Vis/NIR absorption spectra of **3**–**6** (M = Zn) are shown in Figure 2. The values for the most intense bands are given in Table 1. The spectrum of H_6**6** is very similar to that of Zn_3**6** [for **3**–**5** (M = 2 H) see ref.[2b]]. The spectral changes on going from Zn**3** to Zn_2**4** and further to Zn_3**5** are similar to the changes reported[2b] for their metal-free analogues, namely a strong red shift of the Q band [166 nm (2900 cm^{-1}) from Zn**3** to Zn_2**4** and 102 nm (1300 cm^{-1}) from Zn_2**4** to Zn_3**5**], and an increase of its ex-

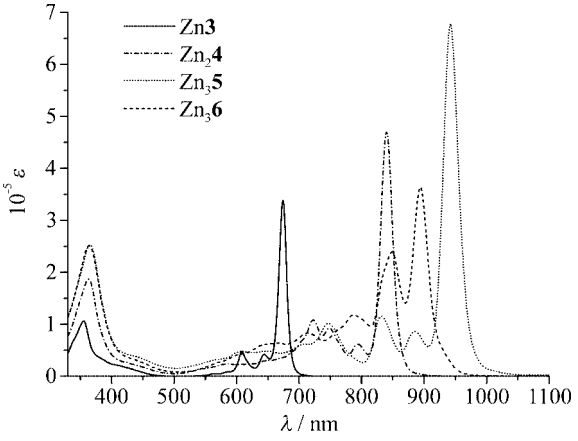


Figure 2. Electronic absorption spectra of **3**–**6** (M = Zn) in thf.

Table 1. Main electronic absorption bands of **3**–**6** (M = Zn).

	Q band		B band	
	λ [nm] (cm^{-1})	ε [M^{-1} cm^{-1}]	λ [nm] (cm^{-1})	ε [M^{-1} cm^{-1}]
Zn**3**	674 (14800)	338000	355 (28200)	106000
Zn_2**4**	840 (11900)	470000	363 (27500)	187000
Zn_3**5**	942 (10600)	680000	365 (27800)	253000
Zn_3**6**	894 (11200)	364000	364 (27500)	251000
	849 (11800)	239000		

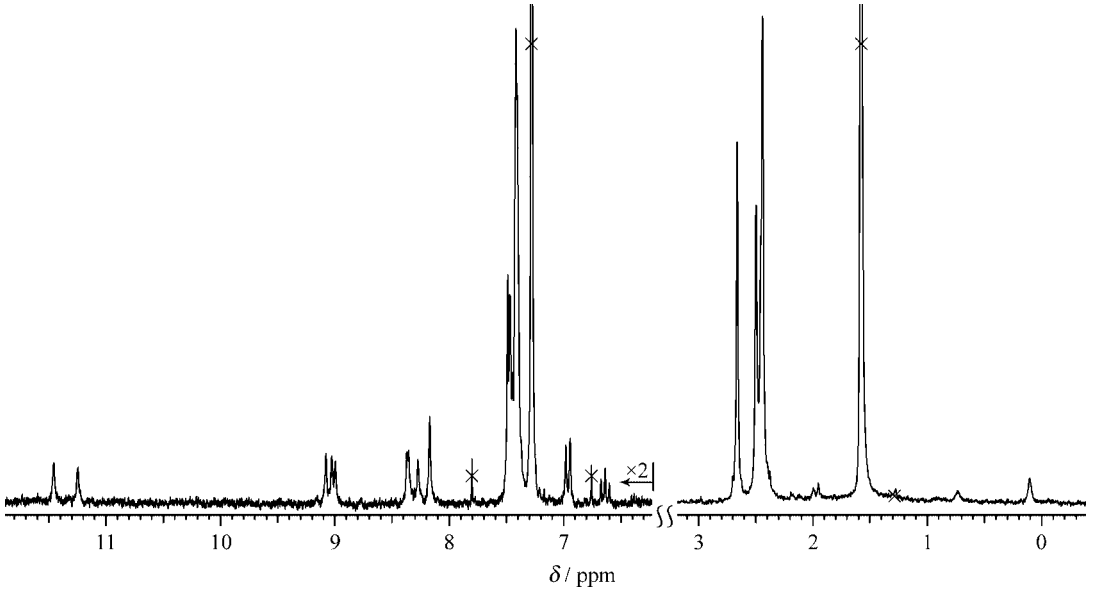


Figure 1. ^{1}H NMR spectrum of H_6**6** in $CDCl_3$.

tinction coefficient. The spectrum of Zn_3**6** is more complex. The Q band appears between those of Zn_2**4** and Zn_3**5**, thus indicating that the rectangular annulation of the third Pc ring has less effect on the frontier orbitals than the linear one. In contrast to D_{2h}-symmetric Zn_2**4** and Zn_3**5**, the Q band of C_{2v}-symmetric[8] Zn_3**6** is split into two sub-bands of similar intensity; its maximal extinction coefficient is lower than that of Zn_3**5**. The Soret band position is not significantly influenced by π-system extension, which indicates only a weak perturbation of the higher excited singlet state. The intensity of the Soret band increases with molecular size − the intensity ratios for Zn**3**/Zn_2**4**/Zn_3**5**/Zn_3**6** are 1:1.76:2.38:2.36, i.e. not proportional to the number of Pc rings but more likely to the number of benzene rings (ratios 1:1.75:2.50:2.50).

For better understanding of the observed spectral changes semi-empirical MO calculations (ZINDO/s method) were carried out for the unsubstituted analogues Zn**3a**–Zn_3**6a** of Zn**3**–Zn_3**6**, respectively. The initial geometries were constructed from the crystal structure of the unsubstituted ZnPc (Zn**3a**)[9] by making the molecules perfectly planar and adopting D_{4h} (Zn**3a**), D_{2h} (Zn_2**4a** and Zn_3**5a**), or C_{2v} symmetry (Zn_3**6a**), as described for dinuclear Pc.[2f] The distance between the closest hydrogen atoms located at the first and the third Pc ring of Zn_3**6a** is only 2.8 Å, which means that bulky substituents at these positions in **6** have to escape each other (see discussion of NMR spectra), perhaps also distorting the Pc rings. This more sterically hindered and less symmetrical structure could be the reason for the much higher solubility of **6** compared to **5**. The calculated spectra are shown in Figure 3 and the partial orbital diagrams in Figure 4. The results obtained for Zn**3a** and Zn_2**4a** are similar to data reported previously.[2c,2e,2f] The shapes of the theoretical spectra are in good agreement with the experimental ones, although the transition energies are underestimated by around 10% for the Q bands of Zn_2**4**–Zn_3**6**. The splitting of the Q band for Zn_3**6** is predicted. Also, the higher-energy transitions at around 700 nm calculated for Zn_2**4**–Zn_3**6** can be seen in their spectra as broad bands of low intensity. The observed strong Q band changes can be explained by considering a simplified orbital model (Figure 4). The Pc Q band is essentially a HOMO–LUMO transition. A series of two HOMOs and four LUMOs of **4a** can be described as a linear combination of frontier orbitals of two mononuclear Pc molecules.[2f] The splitting of the corresponding energy levels reduces the HOMO–LUMO gap, and this effect increases with addition of the third Pc ring. Whereas the HOMO splitting pattern is similar for Zn_3**5a** and Zn_3**6a**, the LUMO splitting is different: it is stronger for Zn_3**5a**, and in the case of Zn_3**6a** two lowest unoccupied levels have very similar energy values, which is responsible for the Q band splitting. This is very similar to the observed difference between opposite and adjacent annulation of benzene rings at the Pc:[5b,5c] the splitting of the LUMO (and, as a consequence, of the Q band) in the latter case is much weaker. This can be explained by the orthogonality of the Pc LUMOs (E_{gx} and E_{gy}). In the case of rectangular (adjacent) annulation they interact with the orbitals of annulated fragments (Pc or benzene rings) almost independently, which results in a rather small splitting. This is in contrast to linear (opposite) annulation along the x axis, where the E_{gx} LUMO interacts

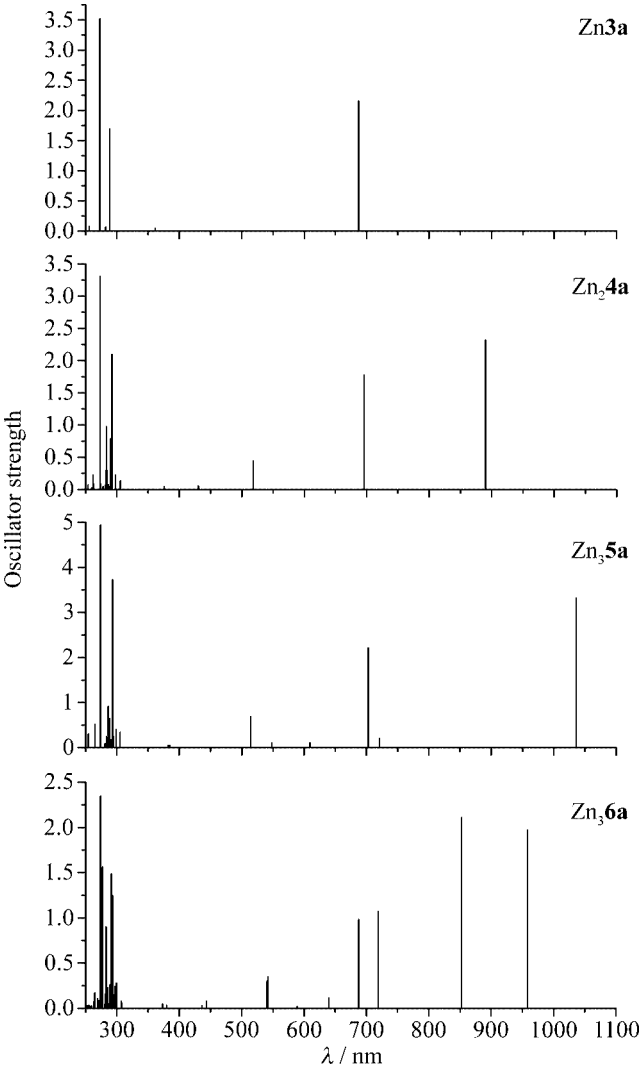


Figure 3. Calculated electronic spectra (ZINDO/s method) for unsubstituted analogues **3a**–**6a** (M = Zn) of **3**–**6** (M = Zn).

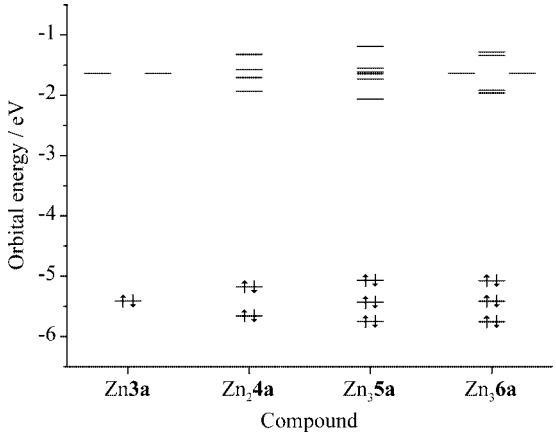


Figure 4. Partial orbital diagrams of **3a**–**6a** (M = Zn).

strongly with both fragments, resulting in strong red shift of the *x*-polarized Q sub-band. Since the Pc HOMO (A_{1u}) is symmetric relative to all four C_2 axes within the plane, its interaction with the orbitals of additional Pc or benzene rings, which results in splitting or destabilization[5b] of the corresponding energy levels, is similar for both types of annulation. Each trimer has one occupied and two unoccupied orbitals with energies very similar to the HOMO and LUMOs of Zn**3a**. These "unperturbed" orbitals are located on peripheral Pc rings.

The fluorescence spectra of compounds **3**–**6** (M = Zn) in thf are shown in Figure 5. The maximum of the fluorescence spectrum of the mononuclear Pc Zn**3** (λ_{max} = 687 nm) shifts to 846 nm for the dinuclear Pc Zn_2**4**, 902 nm for the rectangular trimer Zn_3**6**, and to 948 nm for the linear trimer Zn_3**5** (Table 2). The fluorescence quantum yield (Φ_{fl}) of the mononuclear Pc Zn**3** is 0.28, that of the dinuclear Pc Zn_2**4** is 0.08, and those for the linear (Zn_3**5**) and rectangular (Zn_3**6**) trinuclear Pcs less than 0.03 (Table 2). The fluorescence lifetime (τ_{fl}) of Zn**3** is 3.05 ns, whereas it is 0.68 ns for Zn_2**4**, 0.35 ns for Zn_3**5**, and 0.56 ns for Zn_3**6**. The values of the fluorescence quantum yield of the dinuclear and trinuclear ZnPcs are reduced compared with that of the mononuclear Pc. This reduction is in agreement with a decrease of the fluorescence lifetime. The decrease of the HOMO–LUMO gap and a more extended vibrational level structure of larger molecules, which increase the probability of nonradiative decay, are the reasons for this effect.[2b,2f,2j,10] Compared to the values for H_2**3** reported in our previous publication,[2b] the fluorescence lifetime and fluorescence quantum yield of Zn**3** are strongly reduced due to the heavy-atom effect, which is usual for Pcs with a closed-shell central metal.[10] Due to the strongly increased probability of nonradiative deactivation of the first excited singlet state of **4** and **5**, the difference between the fluorescence lifetime and quantum yield for metal-free and Zn di- and trinuclear Pcs becomes negligible.[11]

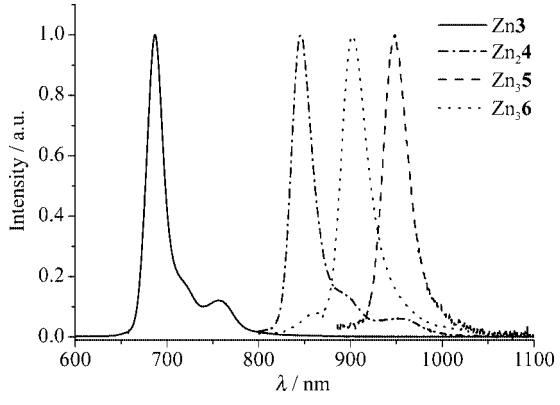


Figure 5. Fluorescence spectra (uncorrected) of **3**–**6** (M = Zn) in thf.

Table 2. Photophysical properties of **3**–**6** (M = Zn) in thf.

	Fluorescence max. λ [nm] (cm^{-1})	Φ_{fl}	τ_{fl} [ns]
Zn**3**	687 (14550)	0.28	3.05
Zn_2**4**	846 (11800)	0.08	0.68
Zn_3**5**	948 (10550)	<0.03	0.35
Zn_3**6**	902 (11100)	<0.03	0.56

Conclusions

Isomeric linear and rectangular trinuclear phthalocyanines connected through common annulated benzene rings have been obtained by the mixed condensation of a tetracyanobenzene derivative and 4,5-bis(2,6-dimethylphenoxy)-phthalonitrile together with mono- and dinuclear Pcs. The different annulated Pcs could be separated by column chromatography. Metal-free rectangular and zinc linear and rectangular trinuclear Pcs of this type have been prepared for the first time. The annulated zinc complexes show intense ($\varepsilon = 2\times10^5$–$7\times10^5$ $M^{-1}cm^{-1}$) NIR absorption bands at $\lambda \approx 950$ nm for the linear and $\lambda \approx 850$ and 900 nm for the rectangular trimer, whereas the dinuclear Pc absorbs at $\lambda \approx 850$ nm. This clearly reflects the extension of the π-electron system. An exceptionally long wavelength shift and decreasing HOMO–LUMO gap is also observed for triply linked fused porphyrins due to conjugation over the whole planar π-system.[1b,1e,1f] Compared to the linear trimer, the less symmetrical rectangular one shows a more complex spectrum with a splitting of the lowest energy absorption band. The observed spectral changes are in good agreement with semi-empirical MO calculations (ZINDO/s method). The difference between the orbitals and spectra of linear and rectangular trinuclear Pcs is analogous to that in opposite and adjacent dibenzo-annulated Pc analogues.[5b,5c] The fluorescence quantum yields and lifetimes decrease with increasing molecular size. The rectangular trimer Zn_3**6** has a longer fluorescence lifetime than the linear Zn_3**5**. Work is now in progress to study the electronic properties of these trinuclear Pcs in more detail.

Experimental Section

Measurements: Electronic absorption spectra were recorded with a Perkin–Elmer Lambda 2 spectrophotometer, IR spectra with a Perkin–Elmer Spectrum 1000 FT-IR spectrometer, NMR spectra with a Bruker Avance DPX 200 (200 MHz), and ESI mass spectra with a Bruker Esquire LC mass spectrometer. The experimental setups for steady-state and time-resolved fluorescence measurements have been described previously.[2b] The excitation source for the time-resolved measurements was a pulsed frequency doubled linear polarized Nd:VO_4 laser (Cougar, Time Bandwidth Products) with a wavelength of 532 nm, a pulse width of 12 ps, and a repetition rate of 60 MHz. The steady-state fluorescence spectra of **3**–**6** were recorded at an excitation wavelength of 360 nm.

Molecular Orbital Calculations were performed using the ZINDO/s method within the HyperChem R 5.02[12] software program. The σ–σ and π–π overlap weighing factors were 1.267 and 0.585, respectively. The electronic spectra were calculated using the configuration interaction method including all singly excited configurations with excitation energies up to 8 eV, as described previously.[2c] The initial geometries were constructed from the X-ray crystal structure

of the unsubstituted PcZn[9] by making the molecules perfectly planar and adopting D_{4h} (Zn**3a**), D_{2h} (Zn_2**4a** and Zn_3**5a**), or C_{2v} symmetry (Zn_3**6a**), as described previously for Zn_2**4a**.[2f]

Materials: Zinc acetate dihydrate (Fluka) purchased in the highest available grade was used without further purification. The solvents (Fluka, analytical reagent grade) were dried, distilled, and stored under nitrogen. Merck silica gel 60 (40–63 μm) was used for chromatographic separations. The compounds Zn**3** and Zn_2**4** were prepared as described previously.[2l]

The phthalocyanines **3**–**6** (M = 2 H) were prepared by the mixed condensation procedure described by us previously.[2b] After demetalation of the obtained mixture of MgPcs with trifluoroacetic acid, the resulting mixture of metal-free Pcs was chromatographed on silica gel eluting with toluene/hexane and *very slowly* reducing the hexane content from 15 to 5 vol.-%. The eluate content was analyzed by UV/Vis/NIR spectroscopy, the fractions containing peaks at about 900 and 950 nm were collected, and the ones with almost identical spectra were mixed and re-chromatographed to obtain two fractions whose spectra did not change during elution from the column. The solvents were then evaporated under reduced pressure. Compound H_6**5** (less soluble) was recrystallized from toluene and H_6**6** re-precipitated from toluene with hexane; both were then dried under vacuum (10^{-2} mbar) at 60 °C.

$H_6$5: Dark-green powder; yield: 8.5 mg (0.9%). ^{1}H NMR: identical to previous data.[2b] UV/Vis (thf): λ_{max} (ε) = 944 (400000), 890 (89000), 836 (100000), 754 (85000), 660 (sh, 45000), 608 (41000), 418 (sh, 72000), 356 nm (215000 $M^{-1}cm^{-1}$).[13] MS (ESI, CH_2Cl_2/dmf, 1:10, negative mode): *m*/*z* 1652.5 [M^{2-} – H].

$H_6$6: Dark-green powder; yield: 16 mg (1.7%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS):[7a] δ = 11.46 (s, 2 H), 11.25 (s, 2 H), 9.08 (s, 2 H), 9.02 (s, 2 H), 8.99 (s, 2 H), 8.37 (s, 2 H), 8.35 (s, 2 H), 8.27 (s, 2 H), 8.17 (br., 4 H), 7.32–7.54 (br. m, 42 H), 6.96 (d, $J_{H,H}$ = 7.6 Hz, 4 H), 6.63 (t, $J_{H,H}$ = 7.6 Hz, 2 H), 2.36–2.72 (m, 96 H), 0.73 (br. s, 2 H), 0.10 (br. s, 4 H) ppm. UV/Vis (thf): λ_{max} (ε) = 907 (288000), 860 (209000), 810 (118000) 773 (sh, 102000), 729 (107000), 668 (sh, 66000), 420 (sh, 84000), 357 nm (232000 $M^{-1}cm^{-1}$). MS (ESI, pyridine/dmf, 1:10, negative mode): *m*/*z* 1652 [M^{2-} – 2 H].

Compound $Zn_3$5: H_6**5** (5.1 mg, 1.5 μmol) was suspended in toluene (2 mL) by sonication. A solution of zinc acetate dihydrate (30 mg, 0.14 mmol) in dmf (1 mL) was then added and the resulting mixture was refluxed for 15 h. The cooled mixture was diluted with methanol (10 mL) and the precipitate was collected by centrifugation, washed with methanol, vacuum-dried, dissolved in toluene containing 8 vol.-% of diethyl ether, and chromatographed on silica gel eluting with toluene/diethyl ether (approx. 10 vol.-% of diethyl ether). The solvents were then evaporated under reduced pressure and the compound was recrystallized from toluene and vacuum-dried (10^{-2} mbar, 60 °C) to obtain a black powder. Yield: 2.3 mg (42%). ^{1}H NMR (200 MHz, C_6D_6, 65 °C, TMS):[7b] δ = 11.71 (s, 4 H), 9.82 (s, 4 H), 8.68 (br., 8 H), 7.25–7.49 (br. m, 48 H), 2.73 (s, 24 H), 2.64 (s, 24 H), 2.40 (s, 24 H), 2.28 (s, 24 H) ppm. UV/Vis (thf): λ_{max} (ε) = 942 (680000), 885 (86000), 832 (115000), 746 (102000), 709 (sh, 62000), 648 (48000), 607 (48000), 365 nm (253000 $M^{-1}cm^{-1}$). MS (ESI, dmf + NaCN, negative mode): *m*/*z* 1772 [M^{2-} + 2CN].

Compound $Zn_3$6: Similarly, a mixture of H_6**6** (10.9 mg, 3.3 μmol) in toluene (2 mL) was treated with zinc acetate dihydrate (44 mg, 0.20 mmol) in dmf (1 mL). The crude product was chromatographed on silica gel eluting with toluene/diethyl ether (approx. 9 vol.-% of diethyl ether), re-precipitated from toluene with hexane, and vacuum-dried (10^{-2} mbar, 60 °C) to obtain Zn_3**6** as a dark-green powder. Yield: 5.1 mg (44%). ^{1}H NMR (200 MHz, C_6D_6, 60 °C, TMS):[7a] δ = 11.91 (s, 2 H), 11.81 (s, 2 H), 9.77 (s, 2 H), 9.74 (s, 2 H), 9.55 (s, 2 H), 8.71 (br., 10 H), 7.24–7.52 (m, 48 H), 2.25–2.80 (m, 96 H) ppm. UV/Vis (thf): λ_{max} (ε) = 894 (364000), 849 (239000), 787 (118000), 715 (83000), 664 (sh, 64000), 364 nm (251000 $M^{-1}cm^{-1}$). MS (ESI, dmf + NaCN, negative mode): *m*/*z* 1772 [M^{2-} + 2CN].

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft for financial support (WO 237/32-3, RO 1042/9-4).

[1] a) P. D. Harvey, in *The Porphyrin Handbook*, vol. 18 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, California, **2003**, pp. 63–250; b) H. L. Anderson, *J. Am. Chem. Soc.* **2002**, *124*, 14642–14654; c) H. L. Anderson, *Chem. Commun.* **1999**, 2323–2330; d) M. G. Vicente, L. Jaquinod, K. M. Smith, *Chem. Commun.* **1999**, 1771–1782; e) A. Tsuda, H. Furuta, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 10304–10321; f) A. Tsuda, A. Osuka, *Adv. Mater.* **2002**, *14*, 75–79; g) A. K. Burrell, D. L. Officer, P. G. Plieger, D. C. W. Reid, *Chem. Rev.* **2001**, *101*, 2751–2796.

[2] a) N. Kobayashi, *Coord. Chem. Rev.* **2002**, *227*, 129–152; b) S. Makarov, Ch. Litwinski, E. A. Ermilov, O. Suvorova, B. Röder, D. Wöhrle, *Chem. Eur. J.* **2006**, *12*, 1468–1474; c) N. Kobayashi, H. Ogata, *Eur. J. Inorg. Chem.* **2004**, 906–914; d) M. Calvete, M. Hanack, *Eur. J. Inorg. Chem.* **2003**, 2080–2083; e) N. Kobayashi, T. Fukuda, D. Lelievre, *Inorg. Chem.* **2000**, *39*, 3632–3637; f) N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, T. Koyama, A. Monden, H. Shirai, *J. Am. Chem. Soc.* **1994**, *116*, 879–890; g) M. J. Cook, M. J. Heeney, *Chem. Eur. J.* **2000**, *6*, 3958–3964; h) E. M. Garcia-Frutos, F. Fernandez-Lazaro, E. M. Maya, P. Vazquez, T. Torres, *J. Org. Chem.* **2000**, *65*, 6841–6846; i) C. G. Claessens, T. Torres, *Angew. Chem.* **2002**, *114*, 2673–2677; *Angew. Chem. Int. Ed.* **2002**, *41*, 2561–2565; j) N. Kobayashi, Y. Higashi, T. Osa, *Chem. Lett.* **1994**, 1813–1816; k) G. de la Torre, V. M. Martinez-Diaz, T. Torres, *J. Porphyrins Phthalocyanines* **1999**, *3*, 560–568; l) S. G. Makarov, A. V. Piskunov, O. N. Suvorova, G. Schnurpfeil, G. A. Domrachev, D. Wöhrle, *Chem. Eur. J.*, in press.

[3] a) P. Erk, H. Hengelsberg, in *The Porphyrin Handbook*, vol. 19 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, California, **2003**, pp. 105–149; b) D. Wöhrle, O. Suvorova, R. Gerdes, O. Bartels, Ł. Łapok, N. Baziakina, S. Makarov, A. Słodek, *J. Porphyrins Phthalocyanines* **2004**, *8*, 1020–1041; c) J. H. Zagal, *Coord. Chem. Rev.* **1992**, *119*, 89–136; d) R. Gerdes, O. Bartels, G. Schneider, D. Wöhrle, G. Schulz-Ekloff, *Polym. Adv. Technol.* **2001**, *12*, 152–160; e) K.-Y. Law, *Chem. Rev.* **1993**, *93*, 449–486; f) E. Ben-Hur, W. Shun Chan, in *The Porphyrin Handbook*, vol. 19 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, California, **2003**, pp. 1–36.

[4] a) T. Inabe, H. Tajima, *Chem. Rev.* **2004**, *104*, 5503–5533; b) R. J. Mortimer, *Chem. Soc. Rev.* **1997**, *26*, 147–156; c) M. M. Nicholson, in *Phthalocyanines – Properties and Applications*, vol. 3 (Eds.: C. C. Leznoff, A. B. P. Lever), VCH Publishers, New York, **1993**, pp. 71–117; d) G. de la Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, *Chem. Rev.* **2004**, *104*, 3723–3750; e) S. Flom, in *The Porphyrin Handbook*, vol. 19 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, California, **2003**, pp. 179–190; f) D. Wöhrle, L. Kreienhoop, D. Schlettwein, in *Phthalocyanines – Properties and Applications*, vol. 4 (Eds.: C. C. Leznoff, A. B. P. Lever), VCH Publishers,

New York, **1996**, pp. 219–284; g) W. H. Flora, H. K. Hall, N. R. Armstrong, *J. Phys. Chem. B* **2003**, *107*, 1142–1150.
[5] a) N. Kobayashi, S. Nakajima, H. Ogata, T. Fukuda, *Chem. Eur. J.* **2004**, *10*, 6294–6312; b) N. Kobayashi, H. Miwa, V. N. Nemykin, *J. Am. Chem. Soc.* **2002**, *124*, 8007–8020; c) N. Kobayashi, J. Mack, K. Ishii, M. J. Stillman, *Inorg. Chem.* **2002**, *41*, 5350–5363.
[6] a) J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, C. M. Whitehouse, *Science* **1989**, *246*, 64–71; b) K. C. Russell, E. Leize, A. V. Dorsselaer, J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 209–213; c) S. R. Wilson, Y. Wu, *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 596–603; d) G. I. Van Berkel, F. Zhou, *Anal. Chem.* **1994**, *66*, 3408–3415; e) G. Khairallah, J. B. Peel, *Int. J. Mass Spectrom.* **2000**, *194*, 115–120.
[7] a) The low-intensity, temperature-dependent satellites around the signals of the methyl protons in the spectra of H_6**6** and Zn_3**6** could be due to aggregation and/or hindered rotation of the substituents; b) The peaks in the spectrum of Zn_3**5** appear on a background of broad bands of aggregates; the integration is only approximate.
[8] C_{2v} is the symmetry of the idealized flat structure. The real symmetry is probably lower (C_2) due to the steric hindrance of the substituents.
[9] J. F. Kirner, W. Dow, W. R. Scheidt, *Inorg. Chem.* **1976**, *15*, 1685–1690.
[10] K. Ishii, N. Kobayashi, in *The Porphyrin Handbook*, vol. 16 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, California, **2003**, pp. 1–42.
[11] There is an error in our previous paper (ref.[2b]): The fluorescence quantum yield of H_2**3** is 0.66 and that of H_4**4** is 0.08.
[12] *HyperChem. R.5.02 Pro*, Hypercube Inc., Gainesville, FL, USA, **1997**.
[13] The ε values were underestimated in our previous work,[2b] probably due to incomplete disaggregation: the sample dissolution requires sonication, then the solution must stand for several hours until the slowly increasing optical density stabilizes; the reported values (ref.[2b]) were obtained immediately after dissolution.

Received: September 11, 2006
Published Online: December 11, 2006

