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Synthesis and Photophysical Properties of Annulated Dinuclear and Trinuclear Phthalocyanines

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Abstract: Metal-free mononuclear, dinuclear and trinuclear phthalocyanines were prepared by a mixed cyclotetramerisation of a 1,2,4,5-tetracyanobenzene derivative and 4,5-bis(2,6-dimethylphenoxy)phthalonitrile. For the first time, a π-electron-conjugated trinuclear phthalocyanine was synthesised with phthalocyanine units connected by common annulated benzene rings. The Q band of the trinuclear compound in solution occurs at $\lambda = 944$ nm whereas those of the dinuclear and mononuclear compounds are at $\lambda = 853/830$ and 701/664 nm, respectively. Fluorescence quantum yields, fluorescence lifetimes and singlet-oxygen quantum yields of the compounds were determined.

Keywords: fluorescence · N ligands · photophysical properties · phthalocyanines · UV/Vis spectroscopy

Introduction

Some of the most important applications of phthalocyanines (Pcs) are based on the interaction of visible light with the chromophore: dyes and pigments,[1] photoconductors in laser printers,[2] photosensitisers in the photodynamic therapy of cancer[3] and degradation of pollutants of waste and natural water.[4] Pcs as thin films or adsorbed on inorganic semiconductors have potential applications in photovoltaic or dye-sensitised solar cells.[5] Based on these applications and taking into account the increasing interest in near-infrared (NIR) absorbing systems,[6] it is important to make compounds with absorptions over a broad region of visible light down to the NIR region.

Most dissolved monomolecular metal-free or metal-containing Pcs have a Q-band absorption at $\lambda \approx 680$ nm with high extinction coefficients $\varepsilon > 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$. Substituted Pcs, especially those containing electron-donating substituents such as alkoxy groups in positions 1, 4, 8, 11, 14, 18, 22 and 25, exhibit a bathochromic shift of their Q band up to $\lambda \approx 760$ nm.[7] By annulation of further benzene rings at the Pc moiety the π system is extended, and strong redshifts of the Q band are observed for naphthalocyanines (Nc) at $\lambda \approx 740$–810 nm and anthracocyanines (Ac) at $\lambda \approx 830$–860 nm that are dependent on the substituents on the naphthalene or anthracene rings.[8] A great disadvantage is the decreasing stability of the compounds going from Pc to Nc and then to Ac. Anthracocyanines are particularly unstable in solution and also in the solid state.[8b]

Another possibility to extend the π-electron system and thus to shift the Q band into the NIR region is the dimerisation of Pcs and related macrocycles through a common annulated benzene ring or another fully conjugated linker. Conjugated dimers and oligomers are well known in the porphyrin family and are of special interest as potential molecular wires and photosynthetic antenna models.[9] Some examples are known among phthalocyanines and related porphyrazine derivatives: Pc–Pc, Pc–Nc, Pc–pyrazinoporphyrazine dimers sharing a common benzene ring; Pc–Pc sharing a common naphthalene ring; dimeric Pc fused with anthraquinone.[10] Their Q bands are shifted up to $\lambda \approx 850$ nm into the NIR region, thus indicating the extension of the π-electron system. Besides electronic absorption spectra, the dinuclear compounds were characterized by magnetic circular dichroism (MCD) spectra,[10a,c,d] electrochemical redox behav-

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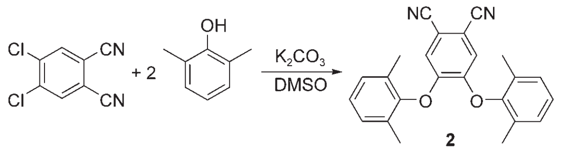
iour,[10a,d] time-resolved electron paramagnetic resonance (TREPR),[10b] mesophase behaviour[10g] and molecular orbital calculations.[10a,c,d]

In this paper, the synthesis and photophysical properties of a metal-free dinuclear phthalocyanine $H_2Pc–H_2Pc$ **4** and its mononuclear analogue H_2Pc **3** are presented and compared. To the best of our knowledge, the synthesis of a trinuclear phthalocyanine $H_2Pc–H_2Pc–H_2Pc$ **5** is described here for the first time. All annulated Pcs containing the same bulky substituents are bridged through shared benzene rings and consist of extended π-electron systems. This structural situation allows the comparison of their photophysical properties such as fluorescence quantum yields, fluorescence lifetimes and singlet-oxygen quantum yields.

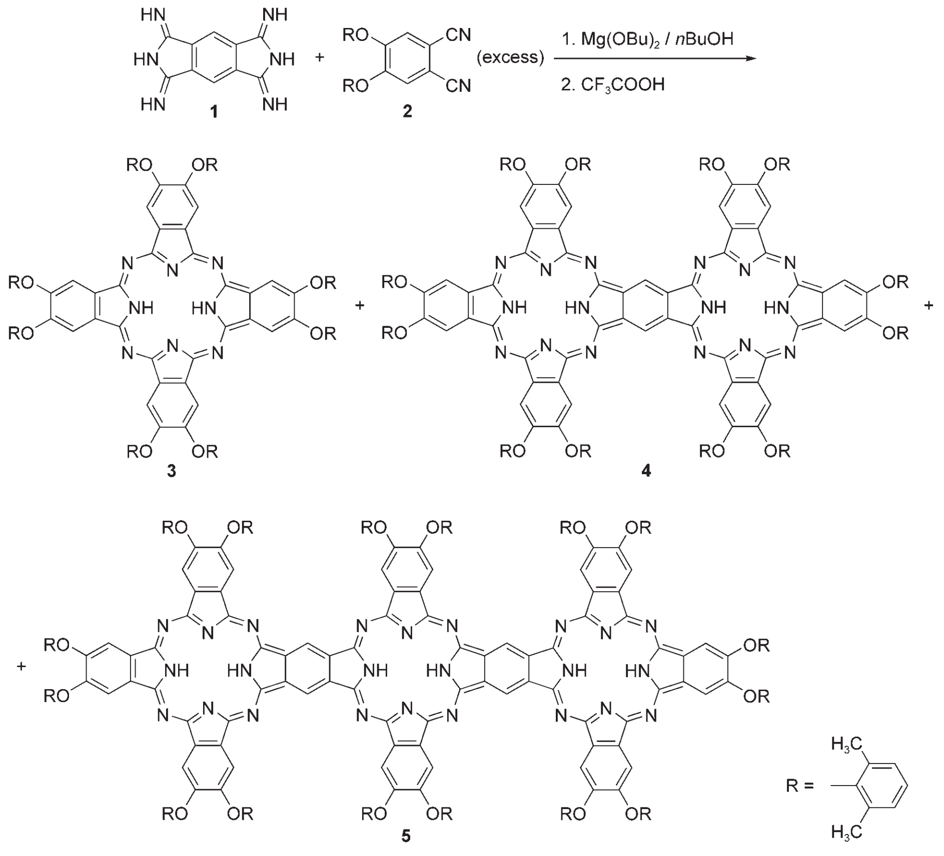
Results and Discussion

Synthesis: 4,5-Bis(2,6-dimethylphenoxy)phthalonitrile (**2**) as one precursor for the synthesis of the phthalocyanines was synthesized according to a well-known method[11] (aromatic nucleophilic substitution) from 4,5-dichlorophthalonitrile and 2,6-dimethylphenol (Scheme 1). Introducing bulky substituents onto the phthalocyanine ring is a common method used to increase the solubility, reduce aggregation and allow easier chromatographic separation of the phthalocyanines. In comparison with monosubstituted (e.g., *tert*-butyl- or neopentoxy-[12]) phthalonitriles, phthalocyanines formed from 4,5- or 3,6-disubstituted phthalonitriles exist as single isomers, with the advantages of easier separation and characterisation. In contrast to alkoxy[13] and most other types of substituents,[14] phenoxy groups can be introduced into phthalonitrile by a simple one-step procedure starting from commercially available compounds. Thus, the 2,6-dimethylphenoxy group was found to be a suitable peripheral substituent. The bis(diiminoisoindoline) compound **1** of 1,2,4,5-tetracyanobenzene was prepared as described in the literature[10d] and used directly in the phthalocyanine synthesis without further purification. The yield of **1** was quantitative, but the mass spectrum indicated traces of alkoxyiminoisoindolenines.



Scheme 1. Synthesis of 4,5-bis(2,6-dimethylphenoxy)phthalonitrile (**2**).

On the whole, annulated phthalocyanine dimers are prepared by mixed condensation of two diiminoisoindoline derivatives, obtained by reaction of 1,2,4,5-tetracyanobenzene and an alkoxy-substituted phthalonitrile.[10,15] Annulated phthalocyanines studied in this work were prepared by a method for binuclear porphyrazines described by Hoffmann et al.[16] As shown in Scheme 2, the employed method is based on a mixed cyclotetramerisation of the bis(diiminoisoindoline) **1** and the substituted phthalonitrile **2** in a molar ratio of 1:7, with magnesium butoxide in boiling butanol. Attempts to use other molar ratios of **1** and **2** were unsuccessful for the isolation of the trinuclear compound **5**. For example, the theoretical molar ratio of 1:4 for synthesising **5** led to a larger amount of higher oligomeric phthalocyanines thus preventing the isolation of the trinuclear Pc. Resulting mixtures of magnesium phthalocyanines were demetallated with trifluoroacetic acid. The obtained mixture of metal-free phthalocyanines was separated by chromatography on silica gel. As main products, an octasubstituted mononuclear phthalocyanine H_2Pc **3** (24 % yield) and an annulated dinuclear phthalocyanine $H_2Pc–H_2Pc$ **4** (11 % yield)



Scheme 2. Synthesis of mononuclear, dinuclear and trinuclear phthalocyanines **3**, **4** and **5** by mixed condensation of **1** and **2**.

were isolated. The linear, annulated trinuclear phthalocyanine H_2Pc–H_2Pc–H_2Pc **5** showed a small peak near $\lambda = 950$ nm in the UV/Vis spectrum of the obtained phthalocyanine mixture. Compound **5** was eluted from the chromatographic column in a mixture with **4**, and then isolated by recrystallisation from toluene (0.2 % yield). In the reaction mixture an additional peak near $\lambda = 900$ nm was also seen, but the corresponding compound expected to be a Γ-type trimer was not isolated. Compound **5** is the first example of a conjugated trinuclear Pc–Pc–Pc compound bridged by common annulated benzene rings. Favoured by the bulky substituents, all phthalocyanines are soluble in several organic solvents ($CHCl_3$, aromatics and THF, but not in alcohols or hexane), with an aggregation tendency low enough for chromatographic separation and NMR characterisation (see below). In the solid state the phthalocyanines are intensively green coloured. In solution, **3** is intensively green coloured whereas **4** and **5** of the same concentration exhibit only a weak yellow-green colour as a result of their low absorption intensities in the visible region (Figure 2, see below).

The phthalocyanines exhibit molecular-ion peaks in their mass spectra (electrospray ionization (ESI) for **3** and **4** and matrix-assisted laser desorption/ionization (MALDI) for **5**) without significant fragmentation. The MALDI spectrum of trinuclear **5** contains no peaks of mononuclear **3** and dinuclear **4**, which is a sign of the good purity of **5**.

^{1}H NMR spectra of metal-free phthalocyanines **3**, **4** and **5** were recorded in $CDCl_3$ at room temperature. They show no evidence of aggregation (broadening of the signals of Pc aromatic protons) at the concentrations used (10^{-4} M). All phthalocyanines show relatively simple ^{1}H NMR spectra due to their high symmetry. The aromatic protons of 2,6-dimethylphenoxy substituents give broad, nonresolved multiplets for all compounds. For **5**, two broad peaks with a 1:3 ratio (at $\delta = 7.48$–7.53 and 7.32–7.44 ppm, respectively) can be assigned to the substituents at central and side phthalocyanine rings, respectively. The chemical shifts of aromatic protons on phthalocyanine rings, pyrrole protons and methyl protons are shown in Table 1. In the symmetrical mononuclear compound **3**, both methyl and Pc aromatic protons give one singlet each. In the dinuclear compound **4**, three types of methyl groups and four types of Pc aromatic protons lead, as expected, to separate singlets taking into account ring-current effects. The protons closer to the centre of the molecule are deshielded by the ring currents of both phthalocyanine subunits and their signals are more downfield-shifted. In the trinuclear compound **5**, four types of methyl groups and five types of Pc aromatic protons are clearly resolved in the spectrum (Figure 1). In both dinuclear and trinuclear phthalocyanines, the most downfield-shifted signals are those of the protons on the common bridging benzene rings. They appear as singlets near $\delta = 11$ ppm, which is comparable to what was previously observed for dinuclear Pc[10g] and subphthalocyanine.[19] For **4** and **5** the signals of the pyrrole protons are less upfield-shifted than those in **3** which indicates the deshielding effect of the neighbouring phthalocyanine rings. The NMR spectrum is a rather clear proof that the trinuclear Pc **5** has a linear annulated and not a rectangular annulated structure. The NMR spectra of **5** does not contain the pattern of other phthalocyanines such as **3** and **4**. For *tert*-butyl-substituted metal-free phthalocyanines (Pc), naphthalocyanine (Nc) and anthracocyanine (Ac), the pyrrole protons are less upfield-shifted with increasing size of the macrocycle, which indicates that the ring current decreases the larger the macrocycle.[8b]

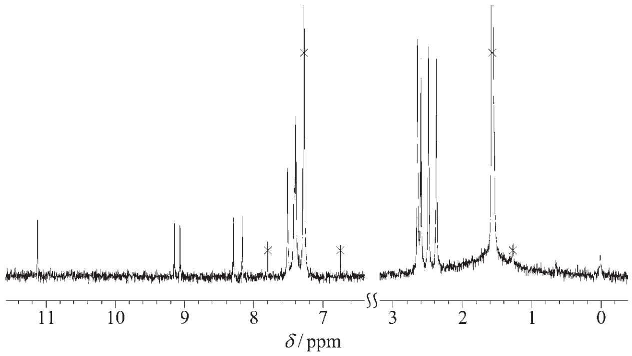


Figure 1. ^{1}H NMR spectrum of **5** in $CDCl_3$.

The NIR-absorbing **4** and **5** exhibit, in contrast to other NIR-absorbing phthalocyanine analogues like Nc and Ac in air and daylight, good stability in the solid state and in solution which enables their chromatographic purification. Acs decompose quickly even during chromatography, which is necessary for their purification.[8b] Solid CoAc can be stored in the dark whereas solid H_2Ac decomposes within a few days even if stored in the dark under nitrogen. The photooxidative stabilities of ZnAcs and ZnNcs are one and a half and one order of magnitude lower than ZnPcs, respectively.[17]

Photophysical properties: The UV/Vis-NIR spectra of **3**, **4** and **5** in solution are shown in Figure 2, and values are given in Table 2. The two most intense Q bands (Q_1 and Q_2) are bathochromically shifted going from the mononuclear **3** ($\lambda = 664/701$ nm) to the dinuclear **4** ($\lambda = 830/853$ nm) and to the trinuclear **5** ($\lambda = 944$ nm), which clearly reflects the extension of the π-electron system by the three connected phthalocyanines rings.[8b,10c,16] Surprisingly, two-dimensional poly(phthalocyanines) show no apparent redshift of the Q band which may due to some

Table 1. ^{1}H NMR chemical shifts (δ in ppm) for the phthalocyanines **3**, **4** and **5** in $CDCl_3$.

	Methyl protons	Pc aromatic protons	Pyrrole protons
3 (M = 2H)	2.43	8.18	−0.76
4 (M = 2H)	2.38, 2.48, 2.62	8.15, 8.29, 9.06, 11.14	−0.04
5 (M = 2H)	2.37, 2.49, 2.60, 2.64	8.16, 8.29, 9.06, 9.15, 11.12	0.01, 0.65

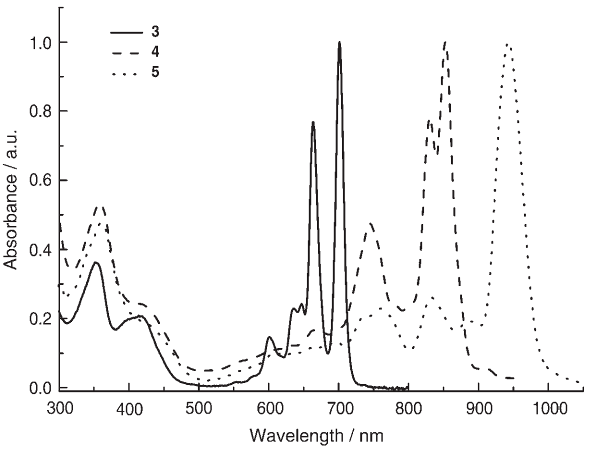


Figure 2. Absorption spectra of the phthalocyanines **3**, **4** and **5** in toluene (a.u. = arbitrary units).

Table 2. Absorption bands [nm] of phthalocyanines **3**, **4** and **5** in toluene; values in parentheses are given in cm^{-1}.

	Q_1	Q_2	Q_3	Q_4	Q_5	B
3	701 (14250)	664 (15050)	647 (15450)	636 (15700)	601 (16650)	353 (28350)
4	853 (11750)	830 (12050)	745 (13400)	–	–	358 (27800)
5	944 (10600)	–	887 (11300)	833 (12000)	760 (13150)	362 (27600)

Table 3. Shifts [cm^{-1}] between absorption bands of the phthalocyanines **3**, **4** and **5** in toluene.

	B band	Q band
3–4	550	2750 (Q_1/Q_2 for **3** and Q_1/Q_2 for **4**)
4–5	200	1300 (Q_1/Q_2 for **4** and Q_1 for **5**)

defects in the structure of the polymer, but this is still a point of discussion.[18] Taking the centre between the maximum of the Q_1 and Q_2 bands of **3** and **4**, and the maximum of the Q_1 band of **5**, the bathochromic shift decreases from 2750 cm^{-1} going from **3** to **4** to 1300 cm^{-1} going from **4** to **5** (Table 3). The first value is comparable with 2700 cm^{-1} reported for similar mono- and dinuclear metal-free Pcs (with other substituents).[10c] Also, for *tert*-butyl-substituted metal-free phthalocyanine (Pc), naphthalocyanine (Nc) and anthracocyanine (Ac) absorbing at $\lambda = 664/698$, 784 and 858 nm, respectively, the Q bands are observed at longer wavelengths with increasing number of annulated benzene rings on the macrocycles.[8b] The shift of the Q bands on going from H_2Pc to H_2Nc and to H_2Ac are 1939 and 1100 cm^{-1}, respectively. Therefore the extension of the π-electron system by annulation of phthalocyanines bridged by benzene rings leads to a larger bathochromic shift than the annulation of benzene rings at the phthalocyanine. An interesting long wavelength shift was also observed for annulated subphthalocyanines ($\lambda_{\max} = 575$ (monomer), 693 (dimer), 755 nm (trimer)[19a]).[19] For a Pc–triazolehemiporphyrazine dimer absorbing at $\lambda = 730$ nm a shift of only 900 cm^{-1} with respect to the corresponding Pc monomer absorbing at $\lambda = 685$ nm and a further shift of only 450 cm^{-1} from the dimer to a Pc–triazolehemiporphyrazine–Pc trimer absorbing at $\lambda = 755$ nm are observed.[20] The reason for this is that the bridging hemiporphyrazine is nonaromatic thus giving only a weak contribution to the extension of the conjugated π-electron system. A Pc dimer connected by a dehydro[12]annulene fragment shows only a 1550 cm^{-1} redshift of the Q band compared with its monomeric analogue.[21] Triphthalocyaninodehydro[18]annulenes exhibit no pronounced long wavelength shift of the Q band.[21] Therefore, using a benzene ring as a linker provides the best conjugation between Pc rings.

Compounds **3**, **4** and **5** additionally exhibit small absorption bands (Q_3, Q_4, Q_5) of low extinctions outside the main Q-band region (Q_1, Q_2) due to normal vibrational splitting and (for **4** and **5**) electronic splitting of Q bands.[10c] For all compounds **3**–**5** the change of the Soret (B) band position around $\lambda = 360$ nm is very small compared with that of the Q bands (Tables 2 and 3). The very small shift of the B band indicates that linking of two or three Pcs results only in a weak perturbation of the high excited singlet states of the Pc moiety.[10c,16]

The extinction coefficients are $1.38 \times 10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ ($\lambda = 707$ nm, in toluene) for **3**, $1.65 \times 10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ ($\lambda = 853$ nm, in toluene) for **4** and $3.00 \times 10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ ($\lambda = 944$ nm, in THF) for **5**. For *tert*-butyl-substituted metal-free Pc, Nc and Ac the extinction coefficients of the longest wavelength Q bands in pyridine are 1.41×10^5 ($\lambda = 698$ nm), 2.04×10^5 ($\lambda = 784$ nm) and only $0.89 \times 10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ ($\lambda = 858$ nm), respectively.[8b] Surprisingly, the extinction coefficient of H_2Ac is lower than that of H_2Nc. The values of **3**, **4** and **5** increase with extension of the π-electron system which is a usual effect of increasing transition dipole moment.

As metal-free Pcs have a D_{2h} symmetry, the Q band of the mononuclear Pc **3** is split into two sub-bands Q_1 and Q_2 with an energetic distance of 800 cm^{-1} (Table 2). A small (300 cm^{-1}) splitting of the main peak in Q band was also observed for the dinuclear Pc **4**, probably due to the presence of isomers with different positions of inner hydrogen atoms[10c] (this splitting is solvent-dependent and absent, for instance, in DMF). The Q_1 band of the trinuclear phthalocyanine Pc **5** shows no visible splitting (Figure 2). For metal-free Pcs and their analogues it was found that the splitting of the Q band decreases with increasing absorption wavelength.[8b,22]

The fluorescence spectra of compounds **3**, **4** and **5** are shown in Figure 3. The maximum of the fluorescence spectrum of the mononuclear Pc **3** at $\lambda = 706$ nm shifts to $\lambda = 860$ nm for the dinuclear Pc **4** and to $\lambda = 956$ nm for the trinuclear Pc **5** (Table 4). The Stokes shifts between the maxima of the lowest energetic absorption and fluorescence

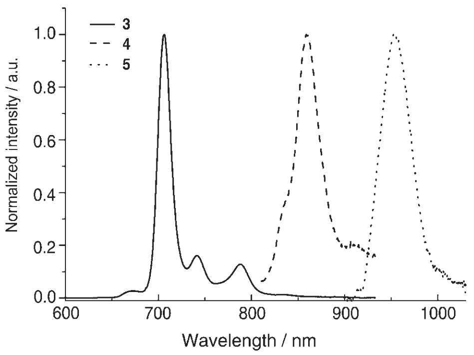


Figure 3. Fluorescence spectra of the phthalocyanines **3**, **4** and **5** in toluene.

Table 4. Photophysical properties of the phthalocyanines **3**, **4** and **5** in toluene.

	Fluorescence band[a]	Stokes shift [cm^{-1}]	Φ_{fl}	τ_{fl} [ns]	Φ_{Δ}
3	706 (14150)	100	0.33	6.2	10
4	860 (11600)	100	0.04	0.8	<0.02
5	956 (10450)	150	<0.02	0.4	<0.02

[a] Fluorescence in nm; values in parentheses are given in cm^{-1}.

band are comparably low for **3**, **4** and **5**, which is usual for such rigid molecules like Pcs and their analogues.

The fluorescence quantum yield (Φ_{fl}) of the mononuclear Pc **3** is 0.33, of the dinuclear Pc **4** 0.04 and for the trinuclear Pc **5** less than 0.02 (Table 4). The fluorescence lifetime (τ_{fl}) of **3** is 6.2 ns compared with 0.8 ns for **4** and 0.4 ns for **5**. The values of the fluorescence quantum yield of the dinuclear and trinuclear Pcs are reduced compared with that of the mononuclear Pc. The reduction is in good agreement with the decrease of the fluorescence lifetime. Similarly, for a differently substituted metal-free Pc and an analogously substituted metal-free Nc with an enlarged π-electron system, a decrease of the fluorescence quantum yield from 0.85 to 0.14 and a decrease of the fluorescence lifetime from 7.2 to 3.2 ns was reported.[23] This usual effect is due to the decrease of the HOMO–LUMO gap and a more extended vibrational level structure of larger molecules, thus increasing the probability of nonradiative decay.

Singlet oxygen ($^1O_2$, $^1\Delta_g$) is generated by energy transfer from the excited triplet state of a sensitiser molecule to the ground-state triplet oxygen ($^3O_2$, $^3\Sigma_g^-$). As the $^1O_2$ state lies 0.98 eV above the triplet ground state, the energy difference between T_1 and S_0 of a sensitiser should be above or around this value to allow the generation of singlet oxygen.[23,24] This prerequisite holds for 5,10,15,20-tetraphenylporphyrins with a triplet energy (E_T) of ≈1.59 eV and phthalocyanines with E_T of ≈1.2 eV.[25] For ZnPc and H_2Pc singlet-oxygen quantum yields (Φ_{Δ}) of 0.55 and 0.13, respectively, were found.[26] The triplet energy of Ncs is ≈0.94 eV, thus below 0.98 eV.[23a] The singlet-oxygen quantum yields of **3**, **4** and **5** were determined by time-resolved measurement of the photosensitised-generated singlet-oxygen luminescence at $\lambda =$ 1270 nm.[26,27] For the mononuclear **3**, the Φ_{Δ} value of 0.10 is in good agreement with the values known for other metal-free phthalocyanines.[26] Due to the low triplet energy of dinuclear **4** and trinuclear **5**, the signal of singlet-oxygen luminescence was below the resolution of the measurement setup (<0.02) for these compounds (Table 4).

Conclusion

The mixed cyclotetramerisation of the bis(diiminoisoindoline) compound **1** from 1,2,4,5-tetracyanobenzene and 4,5-bis(2,6-dimethylphenoxy)phthalonitrile (**2**) in *n*BuOH in the presence of magnesium butoxide with a precursor molar ratio of 1:7 is suitable to isolate the mononuclear H_2Pc **3** and the dinuclear H_2Pc-H_2Pc **4**, in addition to the trinuclear H_2Pc-H_2Pc-H_2Pc **5** in a low yield. The phthalocyanine rings in **4** and **5** are connected by common annulated benzene rings. To the best of our knowledge, a trinuclear benzo-bridged π-electron conjugated phthalocyanine is described here for the first time. UV-visible-NIR spectra in solution document a very strong extension of the conjugated π-electron system by a shift of the Q bands at $\lambda = 664/701$ nm for H_2Pc **3** to $\lambda = 830/853$ nm for H_2Pc–H_2Pc **4** and then to $\lambda =$ 944 nm for H_2Pc–H_2Pc–H_2Pc **5**. Furthermore, the extinction coefficients increase with molecular extension. In the series of mononuclear Pc **3** to dinuclear Pc **4** and then to trinuclear Pc **5**, the fluorescence quantum yields, fluorescence lifetimes and singlet-oxygen quantum yields decrease. Work is now in progress to synthesise metal complexes of mononuclear, dinuclear and trinuclear phthalocyanines connected either by annulated benzene rings or by single bonds in order to study the influence of the binding type on the photophysical properties in more detail.

Experimental Section

Measurements: IR spectra were recorded on a Perkin–Elmer Spectrum 1000 FTIR spectrometer, ^1H NMR spectra were recorded on a Bruker Avance DPX-200 (200 MHz), MS MALDI-TOF spectra were recorded on a Applied Biosystems Voyager System 6033, MS-ESI spectra were recorded on a Bruker Esquire LC and MS-EI spectra were recorded on a Finnigan MAT 95.

Steady-state absorption and fluorescence: The ground-state absorption spectra were recorded at room temperature by using the Shimadzu UV160 A spectrophotometer. The emission spectra were recorded at room temperature in optical quartz cells (1×1 cm) using a xenon lamp (OSRAM) with monochromator for excitation and a polychromator with a cooled charge coupled device (CCD) matrix for detection (LOT-Oriel, Instaspec IV).[28] The mononuclear Pc **3** and binuclear Pc **4** were measured relative to pheophorbide a in ethanol ($\Phi_{fl} = 0.28$).[29] The fluorescence quantum yield of the trinuclear compound **5** was estimated by comparison with the dye IR140 in dimethyl sulfoxide (DMSO).[30]

Time-resolved fluorescence: The time-resolved fluorescence decays were obtained by using a time-correlated single-photon-counting technique (TCSPC) (Becker & Hickl GmbH, SPC 600) with frequency-doubled pulses of a Ti:sapphire laser (Coherent Mira 900, 350–460 nm, FWHM 120 fs) for excitation. The response function of the system, which was measured with a scattering Ludox solution (Aldrich), had a full width at half-maximum height (FWHM) of spectral peak of about 60 ps. The setup was previously described in reference [31].

Time-resolved singlet-oxygen detection: Photosensitised-generated singlet-oxygen luminescence (SOLM) was measured time-resolved at 1270 nm. A nanosecond Nd-YAG laser (BMI) was used to excite the samples at $\lambda = 355$ nm and the luminescence signal was recorded by using a germanium pin diode (Northcoast). For calculating the singlet-oxygen quantum yield of both samples the solution of the H_2TPP in toluene was used as reference ($\Phi_\Delta = 0.68$).[27] The setup and details are described elsewhere.[26]

Materials: 4,5-Dichlorophthalonitrile (Aldrich), 2,6-dimethylphenol (Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich), magnesium turnings (Merck) and anhydrous potassium carbonate (Merck) purchased in the highest available purity were used without further purification. The bis(diiminoisoindoline) compound **1** was prepared as described[10d] from 1,2,4,5-tetracyanobenzene.[32] The solvents used for the preparations (reagent grade) were dried, distilled and stored under dry conditions. All syntheses were carried out under dry high purity nitrogen. Silica gel 60 (40–63 µm; Merck) was used for chromatographic analyses.

4,5-Bis(2,6-dimethylphenoxy)phthalonitrile (2): 4,5-Dichlorophthalonitrile (4.0 g, 20 mmol) and 2,6-dimethylphenol (14.6 g, 120 mmol) in dry DMSO (40 mL) were stirred under dry nitrogen at 95 °C. Dry potassium carbonate (5 × 12 g) was added (every 5 min) and the solution was stirred at 95 °C for an additional 1.5 h, then cooled and poured into ice–water (400 mL). The sticky precipitate was filtered, washed with cold water, ethanol, and then dissolved in dichloromethane and precipitated with ethanol with subsequent evaporation of dichloromethane. The precipitate was filtered and vacuum-dried to give white crystals (5.77 g, 77 %). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.20$ (br s, 6 H), 6.74 (s, 2 H), 2.19 ppm (s, 12 H); MS (EI, 70 eV): m/z (%): 368 (100) [$M^{+\bullet}$], 105 (55) [R^+] (see Scheme 2).

Phthalocyanines 3–5: Magnesium turnings (0.14 g) were heated in *n*BuOH (40 mL) under reflux for 2 h (until all magnesium was consumed). Compounds **1** (prepared from 101 mg (0.57 mmol), 1,2,4,5-tetracyanobenzene)[10d] and **2** (1.47 g, 4 mmol) were added to this cooled suspension and the mixture was heated under reflux for 48 h. After the reaction mixture had been cooled, methanol (200 mL) was added and the resulting mixture was stirred for 1 h. The precipitate was collected by centrifugation, washed with methanol, dried and then extracted with toluene. After evaporation of toluene the solid was dissolved in trifluoroacetic acid (25 mL) and stirred in the dark for 1 h. The solution was poured into ice–water (100 mL), the precipitate collected, washed successively with water, 5 % $NaHCO_3$, water and methanol, then dried under vacuum, extracted with toluene/hexanes (4:1 v/v) and subjected to chromatography on silica gel eluting with toluene/hexanes gradually reducing the hexanes content from 20 to 5 vol %. From the first green fraction containing **3** the solvents were evaporated, and the resulting solid was recrystallised from toluene. From the main (front) part of the second green fraction the solvents were evaporated and the solid **4** was reprecipitated from toluene with hexanes. From the tail of the second fraction a part having an absorption peak near 950 nm in the UV-visible-NIR spectrum was collected and the solvents were evaporated; the solid was recrystallised twice from toluene. Thus **5** was obtained. Solids **3**, **4** and **5** were then dried under vacuum (10^{-2} mbar) at 60 °C.

2,3,9,10,16,17,23,24-Octakis(2,6-dimethylphenoxy)phthalocyanine (**3**): Green crystals; yield: 0.36 g (24 %); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.18$ (s, 8 H), 7.30–7.41 (br m, 24 H), 2.43 (s, 48 H), −0.76 ppm (br s, 2 H); IR (KBr): $\tilde{\nu} = 3296$ (N−H), 3024, 2952, 2922, 2854, 1612, 1588, 1442, 1396, 1328, 1276, 1222, 1188, 1092, 1016, 920, 878, 834, 800, 762, 708, 696 cm^{-1}; UV/Vis: see Table 2; MS (ESI, positive mode): m/z: 1475 [M^++H], 1497 [M^++Na]; MS (ESI, negative mode): m/z: 1473 [M^-−H].

Compound **4**: Green powder; yield: 0.15 g (11 %); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 11.14$ (s, 2 H), 9.06 (s, 4 H), 8.29 (s, 4 H), 8.15 (s, 4 H), 7.32–7.44 (br m, 36 H), 2.62 (s, 24 H), 2.48 (s, 24 H), 2.38 (s, 24 H), −0.04 ppm (br s, 4 H); IR (KBr): $\tilde{\nu} = 3296$ (N−H), 3024, 2952, 2922, 2854, 1612, 1588, 1470, 1446, 1398, 1352, 1328, 1274, 1222, 1186, 1092, 1058, 1012, 880, 764, 706, 694 cm^{-1}; UV/Vis: see Table 2; MS (ESI, positive mode): m/z: 2390 [$M^{+\bullet}$]; MS (ESI, negative mode): m/z: 2389 [M^-−H].

Compound **5**: Green powder, yield: 2.0 mg (0.2 %); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 11.12$ (s, 4 H), 9.15 (s, 4 H), 9.06 (s, 4 H), 8.29 (s, 4 H), 8.16 (s, 4 H), 7.48–7.53 (br m, 12 H), 7.32–7.44 (br m, 36 H), 2.64 (s, 24 H), 2.60 (s, 24 H), 2.49 (s, 24 H), 2.37 (s, 24 H), 0.65 (br s, 2 H), 0.01 ppm (br s, 4 H); UV/Vis (THF): λ_{max} (ε) = 944 (300 000), 890 (73 000), 836 (88 000), 754 (69 000), 661 (40 000), 608 (36 000), 355 nm (177 000 M^{-1} cm^{-1}) (see Table 2); MS (MALDI-TOF): m/z: 3306 [$M^{+\bullet}$].

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[1] 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.

[2] K.-Y. Law, *Chem. Rev.* **1993**, *93*, 449–486.

[3] a) E. Ben-Hur in *The Porphyrin Handbook, Vol. 19* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, California, **2003**, pp. 1–36; b) I. Rosenthal in *Phthalocyanine—Properties and Applications, Vol. 4* (Eds.: C. C.: Leznoff, A. B. P. Lever), VCH, New York, **1996**, pp. 481–514; c) *Photodynamic Tumor Therapy* (Ed.: G. Moser), Harwood Academic Publishers, Amsterdam, **1998**.

[4] a) D. Wöhrle, O. Suvorova, R. Gerdes, O. Bartels, Łapok, N. Baziakina, S. Makarov, A. Słodek, *J. Porphyrins Phthalocyanines* **2004**, *8*, 1020–1041; b) R. Gerdes, O. Bartels, G. Schneider, D. Wöhrle, G. Schulz-Ekloff, *Polym. Adv. Technol.* **2001**, *12*, 152–160.

[5] a) D. Wöhrle, L. Kreienhoop, D. Schlettwein in *Phthalocyanine—Properties and Applications, Vol. 4* (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, New York, **1996**, pp. 219–284; b) M. D. K. Nazeeruddin, R. Humpfry-Baker, M. Grätzel, D. Wöhrle, G. Schnurpfeil, G. Schneider, A. Hirth, N. Trombach, *J. Porphyrins Phthalocyanines* **1999**, *3*, 230–237; c) T. Yoshida, M. Iwaya, D. Komatsu, T. Oekermann, K. Nonomura, D. Schlettwein, D. Wöhrle, H. Minoura, *Chem. Commun.* **2004**, 400–401.

[6] J. Fabian, H. Nakazumi, M. Matsuoka, *Chem. Rev.* **1992**, *92*, 1197–1226.

[7] a) E. A. Lukyanets, *Electronic Spectra of Phthalocyanines and Related Compounds*, NIOPIK, Moscow, **1989**; b) M. J. Stillman, T. Nyokong in *Phthalocyanine—Properties and Applications* (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, New York, **1989**, pp. 291–341; c) M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson, K. J. Harrison, *J. Chem. Soc. Perkin Trans. 1* **1988**, 2453–2458.

[8] a) W. Fryer, Q. Minh, *J. Prakt. Chem.* **1987**, 329, 365; W. Fryer, Q. Minh, *Monatsh. Chem.* **1986**, *117*, 475; b) N. Kobayashi, S. Nakajima, H. Ogata, T. Fukuda, *Chem. Eur. J.* **2004**, *10*, 6294–6312.

[9] 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) I. M. Blake, A. Krivokapic, M. Katterle, H. L. Anderson, *Chem. Commun.* **2002**, 1662–1663; 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.

[10] a) N. Kobayashi, H. Ogata, *Eur. J. Inorg. Chem.* **2004**, 906–914; b) K. Ishi, N. Kobayashi, Y. Higashi, T. Osa, D. Lelievre, J. Simon, S. Yamauchi, *Chem. Commun.* **1999**, 969–970; c) N. Kobayashi, T. Fukuda, D. Lelievre, *Inorg. Chem.* **2000**, *39*, 3632–3637; d) 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; e) M.

Calvete, M. Hanack, *Eur. J. Inorg. Chem.* **2003**, 2080–2083; f) N. Kobayashi, *Coord. Chem. Rev.* **2002**, *227*, 129–152; g) D. Lelievre, L. Bosio, J. Simon, J.-J. Andre, F. Benesbaa, *J. Am. Chem. Soc.* **1992**, *114*, 4475.

[11] D. Wöhrle, M. Eskes, K. Shigehara, A. Yamada, *Synthesis* **1993**, 194–196.

[12] C. C. Leznoff, S. M. Marcuccio, S. Greenberg, A. B. P. Lever, *Can. J. Chem.* **1985**, *63*, 623–631.

[13] D. Wöhrle, V. Schmidt, *J. Chem. Soc. Dalton Trans.* **1988**, 549–551.

[14] W. M. Sharman, J. E. van Lier in *The Porphyrin Handbook, Vol. 15* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, California, **2003**, pp. 1–60.

[15] a) C. C. Leznoff, H. Lam, S. M. Marcuccio, W. A. Nevin, P. Janda, N. Kobayashi, A. B. P. Lever, *J. Chem. Soc. Chem. Commun.* **1987**, 699–701; b) D. Lelievre, O. Damette, J. Simon, *J. Chem. Soc. Chem. Commun.* **1993**, 939–940.

[16] A. G. Montalban, W. Jarrell, E. Rignet, Q. J. McCubbin, M. E. Anderson, A. J. P. White, D. J. Williams, A. G. M. Barrett, B. M. Hoffmann, *J. Org. Chem.* **2000**, *65*, 2472–2478.

[17] G. Schnurpfeil, A. K. Sobbi, W. Spiller, H. Kliesch, D. Wöhrle, *J. Porphyrins Phthalocyanines* **1997**, *1*, 159–167.

[18] a) N. B. McKeown, *J. Mater. Chem.* **2000**, *10*, 1979–1995; b) T. Fukuda, J. R. Stork, R. J. Potucek, M. M. Olmstead, B. C. Noll, N. Kobayashi, W. S. Durfee, *Angew. Chem.* **2002**, *114*, 2677–2680; *Angew. Chem. Int. Ed.* **2002**, *41*, 2565–2568.

[19] C. G. Claessens, T. Torres, *Angew. Chem.* **2002**, *114*, 2673–2677; *Angew. Chem. Int. Ed.* **2002**, *41*, 2561–2565.

[20] G. de la Torre, M. V. Martinez-Diaz, T. Torres, *J. Porphyrins Phthalocyanines* **1999**, *3*, 560–568.

[21] a) M. J. Cook, M. J. Heeney, *Chem. Eur. J.* **2000**, *6*, 3958–3964; b) E. M. Garcia-Frutos, F. Fernandez-Lazaro, E. M. Maya, P. Vazquez, T. Torres, *J. Org. Chem.* **2000**, *65*, 6841–6846.

[22] N. Kobayashi, H. Ogata, N. Nonaka, E. A. Luk'yanets, *Chem. Eur. J.* **2003**, *9*, 5123–5134.

[23] a) 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; b) N. Kobayashi, Y. Higashi, T. Osa, *Chem. Lett.* **1994**, 1813.

[24] E. A. Lissi, M.V. Encinas, E. Lemp, M. A. Rubio, *Chem. Rev.* **1993**, *93*, 699.

[25] J. R. Darwent, P. Douglas, A. Harriman, G. Porter, M.-C. Richoux, *Coord. Chem. Rev.* **1982**, *44*, 83.

[26] W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Röder, G. Schnurpfeil, *J. Porphyrins Phthalocyanines* **1998**, *2*, 145–158.

[27] E. Zenkevich,, E. Sagun, V. Knyukshto, A. Shulga, A. Mironow, O. Efremova, R. Bonnett, S. P. Songea, M. Kassem, *J. Photochem. Photobiol. B* **1997**, *33*, 171–180.

[28] O. Korth, T. Hanke, I. Rückmann, B. Röder, *Exp. Tech. Phys.* **1995**, *41*, 25–36.

[29] B. Röder, Th. Hanke, St. Oelckers, St. Hackbarth, Ch. Symietz, *J. Porphyrins Phthalocyanines* **2000**, *4*, 37–44.

[30] M. Leduc, C. Weisbuch, *Opt. Commun.* **1978**, *26*, 78–80.

[31] O. Korth, T. Hanke, B. Röder, *Thin Solid Films* **1998**, *320*, 305–315.

[32] D. Wöhrle, U. Marose, R. Knoop, *Makromol. Chem.* **1985**, *186*, 2209–2228.

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