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*Aust. J. Chem.* **2008**, *61*, 273–278

# Synthesis of Covalently-Linked Phthalocyanine–Phthalocyanine and Porphyrin–Phthalocyanine Dimers

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The synthesis of the dimeric homonuclear phthalocyanines (Pc) **4a**, **4b**, **5a** and **5b** and the dimeric heteronuclear Pc **4c** and **5c** is reported. The reactions are carried out by coupling the monomeric Pc **1a** and **1b** each containing a phenolic OH group in one of its substituents with the bromoalkyl-substituted Pc **2a**,**b** or **3a**,**b** respectively. From the spectral data of **4a**–**c** and **5a**–**c**, it can be concluded that in dichloromethane and toluene as solvents, these binuclear Pc are equilibrating between cofacial and open conformations with the open form predominating. Changing the solvent polarity, e.g. by adding methanol, the equilibrium is shifted towards a cofacial conformation. Treatment of the Pc **2a**,**b** and **3a**,**b** with 5-(4′-oxyphenyl)-10,15,20-triphenylporphin (**6**) in a basic solution gives the porphyrins (P)-Pc dimers **7a**,**b** and **8a**,**b** respectively. In dichloromethane, the open conformation is preferred for the P-Pc dimers.

Manuscript received: 28 December 2007.
Final version: 12 March 2008.

## Introduction

Multinuclear phthalocyanines (Pc) and porphyrins (P) have attracted much attention recently because of their potential applications as catalysts, semiconductors, and especially as non-linear optical materials.[1]

Dimeric Pc structures that are covalently linked by a spacer and in which the spacer length is systematically varied through a chain of one to five atoms were studied for the effect of the linkage length on the interaction between the two terminal Pc. After reaching a sufficient length of the spacer, a cofacial intramolecular association referred to as 'clamshell behaviour' is observed, with a dynamic equilibrium existing between open and closed arrangements.[2]

Covalently spacer-linked dimeric Pc have previously been reported by Lever,[3] Torres[4a–c] and our group.[4d] The spacers in these dimeric Pc can be bis-alkoxy groups (e.g. $–OCH_2C(CH_3)$-(R)$–CH_2O–$),[3a–c] catechols with oxygen as bridging atoms,[3d] methylene chains of different lengths (e.g. $–(CH_2)_n–$ with $n = 2, 4$),[3d] alkynyl chains of varying lengths (e.g. $–(C{\equiv}C)_m–$ with $m = 1, 2$),[4a,c] double alkynyl chains with $m = 2$[4b] or mixed alkyl-aryl spacers.[4d]

Similar dimeric systems have also been prepared with P taken as macrocycles instead.[5] Like the dimeric Pc, these P-based systems are covalently linked with alkyl or aryl groups through a *meso* carbon in a pillared cofacial configuration.

The combination of porphyrins with phthalocyanines (P-Pc) has been especially investigated as light harvesting systems because of their wider absorption spectrum with respect to the single macrocycles. As the Pc Q-band is very close to the fluorescence wavelength of P, an efficient energy transfer from the P to the Pc occurs after excitation in quite a few P-Pc dimers. P-Pc dimers that are connected via the *meso*- or the β-pyrrolic position of the P allow a close proximity of the two macrocycles.[6]

One method to synthesize dimeric Pc is a statistical condensation of bisphthalonitriles or bisdiiminoisoindolines already containing the spacer with other substituted phthalonitriles or diiminoisoindoline.[3,7] Using bisbenzaldehydes, bisporphyrins with different spacers were synthesized.[5] However, by using this method, only mononuclear bisphthalocyanines and bisporphyrins can be prepared.

Heteronuclear bisporphyrins and bisphthalocyanines can by synthesized by a step-by-step method. First, substituted phthalonitrile containing P or phthalocyanin is synthesized.[6a–d] The subsequent statistical condensation with another phthalonitrile gives dimeric mononuclear or heteronuclear Pc and P-Pc dimers. P-Pc dimers can be synthesized also from benzaldehyde containing the Pc-fragment by condensation with pyrrole and other benzaldehydes.[6e] However, in both cases, the last step results in low yields of the final products.

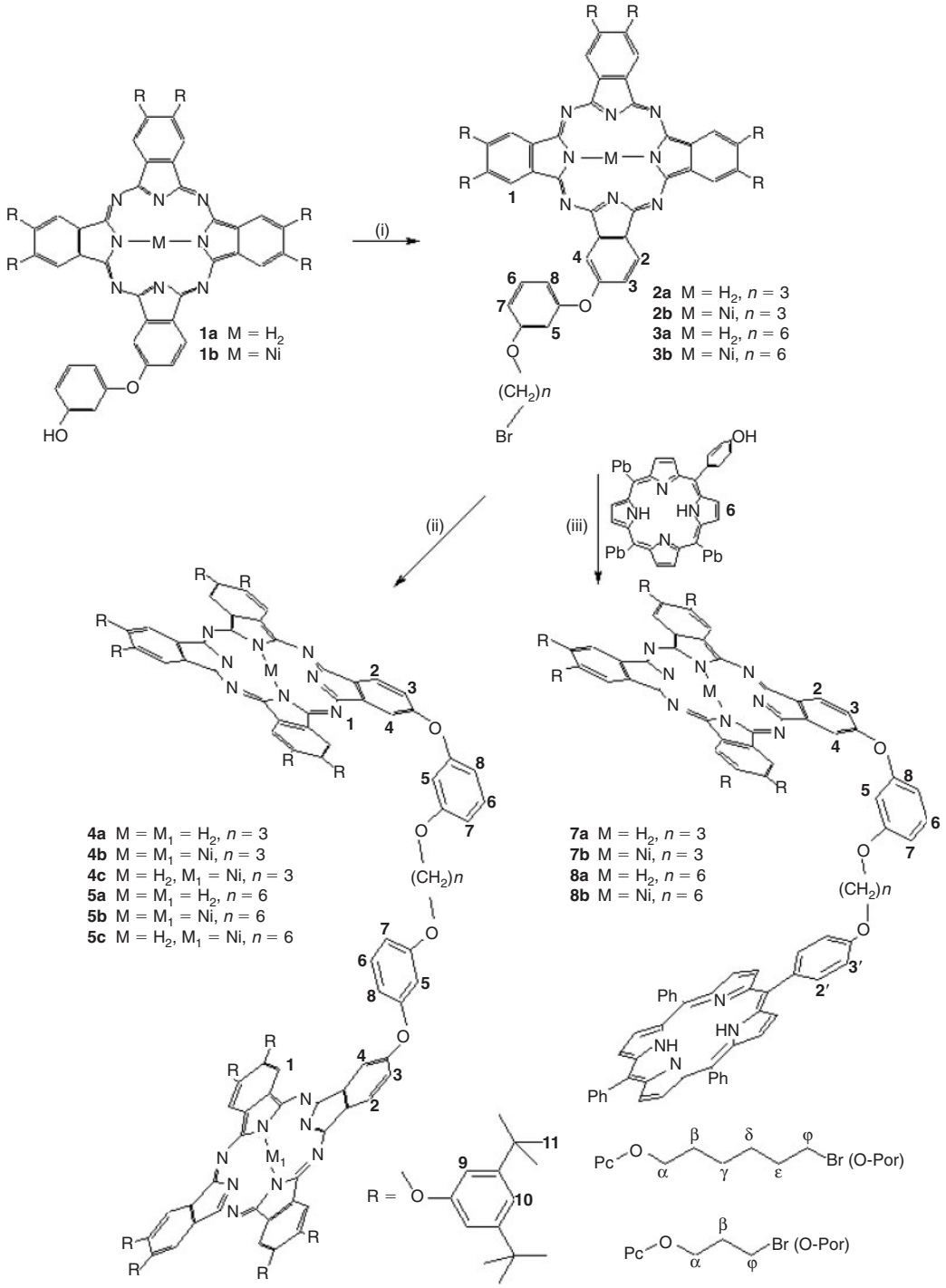
P or Pc containing a functional group such as OH, NH, or halogens can also be used directly for dimerization by applying a bifunctional spacer or by coupling two units.[4,6f,g] In our earlier work,[4d] we synthesized dimeric homo- and heteronuclear Pc, starting from unsymmetrical Pc **1a**,**b**, each containing a phenolic OH group in one of its substituents.

We report here the synthesis of Pc-Pc **4**, **5** and P-Pc **7**, **8** dimers linked through mixed alkyl-aryl spacers.

## Results and Discussion

The synthesis of Pc-Pc **4**, **5** and P-Pc **7**, **8** dimers is shown in Scheme 1. The preparation of the starting Pc **1** has been described by us earlier.[4d] Pc **3a** and **3b** were also prepared by us in

 10.1071/CH07449 0004-9425/08/040273




**Scheme 1.** (i) $Br(CH_2)_nBr$ ($n = 3$ or 6), DMF/THF, $K_2CO_3$, 75°C, 3 h; (ii) **1a** or **1b**, DMF/THF, $K_2CO_3$, 75°C, 6 h; (iii) DMF/THF, $K_2CO_3$, 75°C, 6 h.

the same publication. Treatment of **1a** and **1b** with excess 1,3-dibromopropane in the presence of potassium carbonate, either in DMF or in a DMF/THF mixture (1:1), resulted mainly in the formation of the corresponding bromopropyl derivatives **2a** and **2b**. As seen by TLC, **1a**,**b** were completely alkylated after a reaction time of 3 h; no starting material was present any more. The dimeric compounds **4a**,**b** and **5a**,**b** were also formed in small quantities under the synthesis conditions. They were separated by column chromatography as the first fraction.

The alkylation of the hydroxyl groups in **1a** and **1b** did not result in any significant change in the UV/visible spectra. All monomeric Pc **1**–**3** show the typical electronic spectra for metal-free Pc (**1a**, **2a**, **3a**) and metal-containing (**1b**, **2b**, **3b**). The tendency of aggregation in organic solvents (dichloromethane (DCM), toluene and mixture with methanol) in concentration in the regions $10^{-5}$–$10^{-7}$ mol $L^{-1}$ is relatively low.

The $^1H$ NMR spectra of Pc **2a**,**b** and **3a**,**b** exhibit no signals of hydroxyl protons. Two triplets at ~4.0 and 3.4 ppm correspond to four alkyl protons Hα and Hφ of the bromohexyl or bromopropyl fragments, and triplets near 2.3 ppm in the spectra of **2a** and **2b** correspond to two protons Hβ of the bromopropyl fragment, whereas the signals of the eight protons Hβ, Hγ, Hδ, and Hε

**Table 1. Absorption spectra of monomeric 2a,b and 3a,b and dimeric 4a–c and 5a–c phthalocyanines (Pc) in dichloromethane**
sh, shoulder

| Pc | $\lambda_{max}$ (log $\varepsilon$) | | | | | | |
|---|---|---|---|---|---|---|---|
| **2a** | 702 (5.26) | 668 (5.21) | 639 (4.76) | 606 (4.50) | 400 (sh) | 346 (5.00) | 292 (4.88) |
| **2b** | | 674 (5.40) | 645 (sh) | 607 (4.72) | 392 (sh) | 331 (sh) | 305 (5.11) |
| **3a** | 702 (5.27) | 668 (5.20) | 640 (4.75) | 607 (4.49) | 400 (sh) | 345 (4.99) | 292 (4.88) |
| **3b** | | 674 (5.41) | 646 (sh) | 607 (4.71) | 382 (sh) | 329 (sh) | 300 (5.12) |
| **4a** | 702 (5.40) | 668 (5.23) | 644 (5.23) | 610 (sh) | 400 (sh) | 343 (5.31) | 294 (5.18) |
| **4b** | | 671 (5.19) | 629 (5.10) | | 395 (sh) | | 301 (5.22) |
| **4c** | 700 (sh) | 672 (5.16) | 645 (5.04) | | 394 (sh) | 331 (sh) | 290 (5.20) |
| **5a** | 701 (5.16) | 668 (5.20) | 641 (5.02) | 611 (sh) | 393 (sh) | 340 (5.10) | 293 (5.00) |
| **5b** | | 671 (5.15) | 629 (5.11) | 577 (sh) | 383 (sh) | | 300 (5.26) |
| **5c** | 699 (sh) | 671 (5.18) | 644 (5.07) | | 392 (sh) | 331 (sh) | 301 (5.17) |

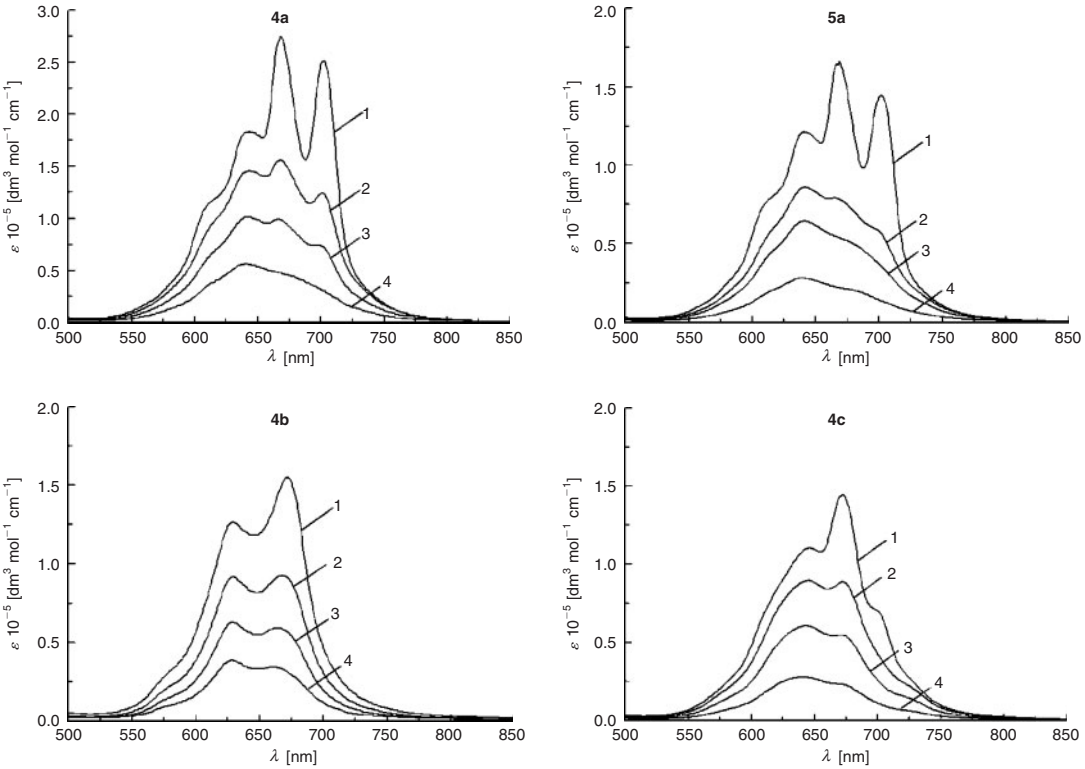



**Fig. 1.** UV/visible spectra of dimeric phthalocyanines **4a**–**c** and **5a** in dichloromethane with 0% (1), 25% (2), 50% (3) and 75% methanol (4).

of the bromohexyl fragment of Pc **3a** and **3b** are seen in the 1.88–1.25 ppm region and overlap with signals of the peripheral *tert*-butyl groups. In the spectra of **2a** and **3a**, the signals of the inner NH protons appear at approximately −0.47 ppm.

Dimeric homonuclear **4a**,**b** and **5a**,**b** and heteronuclear **4c** and **5c** Pc were synthesized by coupling the monomeric Pc **2a** and **2b** with Pc **1a** or **1b**, respectively.

The dimeric Pc **4a**–**c** and **5a**–**c** are more polar than the starting Pc **1a**,**b**, **2a**,**b** and **3a**,**b**, respectively, and were completely separated by column chromatography.

In the $^1$H NMR spectra of dimeric Pc **4** and **5**, signals of four protons Hα (Hφ) show a triplet at ∼4.3 ppm for dimers **4a**–**c** and at ∼4.0 ppm for dimers **5a**–**c**. Two alkyl protons of the propyl group Hβ in spectra Pc **4a**–**c** exhibit a triplet near 2.3 ppm.

The matrix-assisted laser desorption–ionization time of flight (MALDI-TOF) spectra of the synthesized dimers **4a**–**c** and **5a**–**c** show the expected molecular weight; no fragmentation was observed.

The dimeric Pc species may be open, with no interaction between Pc units, or closed, with Pc–Pc interaction. The mononuclear systems **1**, **2**, and **3** show visible spectra in organic solvents typical of monomeric Pc and can be used as models for the open form of the 'clamshell'.

The UV/visible spectra of binuclear Pc **4a** and **5a** in dichloromethane (Table 1, Fig. 1) show double π-π* bands near 700 and 670 nm, but the band near 640 nm exhibits enhanced intensities compared with the monomers **2a** and **3a**, typical for aggregation.[8] In addition, the Ni-Pc **4b** and **5b** exhibit bands at ∼670 and 630 nm in DCM, but the bands at 630 nm are blue-shifted and their intensity is greatly enhanced in comparison with absorption in monomeric metal-Pc **2b** and **3b**, also typical for aggregation. The aggregation is intramolecular rather than intermolecular as it is almost unaffected by dilution.

In the UV/visible spectra of heteronuclear dimers **4c** and **5c** in DCM, the Q-band near 700 nm is seen only as a shoulder

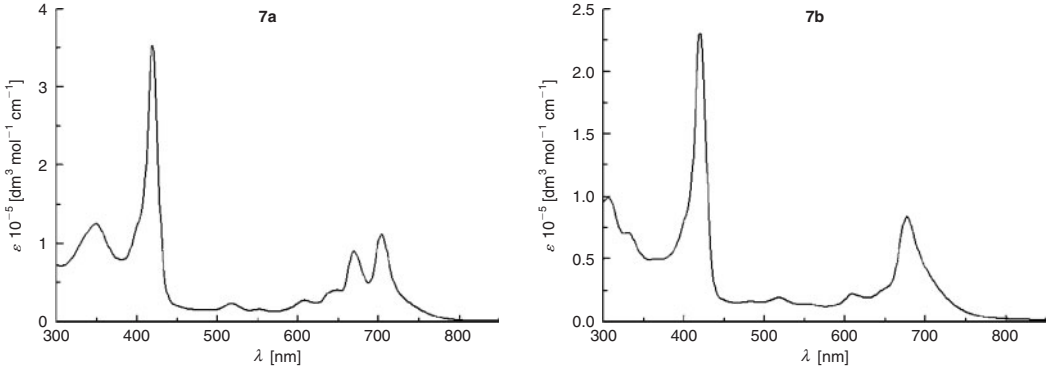



**Fig. 2.** UV/visible spectra of porphyrins-phthalocyanines dyads **7a** and **7b** in dichloromethane.

and the intense broad absorption can be seen between 600 and 650 nm (Table 1, Fig. 1).

In summary, the spectral data of dimeric Pc **4a**–**c** and **5a**–**c** show that in dichloromethane and toluene solution, these binuclear species are in an equilibrium between cofacial and non-cofacial conformations with the open form predominating.

We have studied the influence of solvent nature on the equilibrium between open and closed conformations of the Pc-Pc dyads **4a**–**c** and **5a**–**c**. We found that an addition of methanol to solutions of dimeric Pc **4**–**5** in dichloromethane changed the character of UV/visible spectra in the Q-band region. Figure 1 shows the changes of the UV/visible spectra after dilution of DCM solutions of Pc **4**–**5** with methanol. In all cases, the absorption between 670 and 700 nm decreases with increasing concentration of methanol, whereas the absorption at ~650 nm increases, which leads to the conclusion that addition of methanol shifts the equilibrium towards a cofacial conformation. Comparing the spectra of **5a** and **4a** (Fig. 1), a small dependence of the equilibrium on solvent that is greater for **5a** than **4a** containing the closed conformation can be seen. This effect is intramolecular because it is almost unaffected by dilution with the same solvent mixtures.

Treatment of Pc **2a**,**b** and **3a**,**b** with P **6** in DMF or a DMF/THF mixture using $K_2CO_3$ as base gave the P-Pc dimers **7a**,**b** and **8a**,**b** respectively. The separation of the dimers from excess P **6** was done by chromatography; no starting Pc **2a**,**b** and **3a**,**b** were detected any more by TLC and MALDI-TOF analysis. The $^1$H NMR spectra of P-Pc **7a**,**b** and **8a**,**b** exhibit proton signals of both the Pc and P units. Signals of four protons Hα and Hφ in the spectra of P-Pc dyads **7a** and **7b** show a multiplet near 4.5 ppm. In the spectra of the dimers **8a** and **8b**, these protons show two triplets at ~4.2 and 4.1 ppm because of the different electronic influence between Pc and P fragments.

The UV/visible spectra of all P-Pc dyads in DCM (Fig. 2) are combinations of the spectra of individual P and Pc units from which these have been derived. Addition of methanol to DCM solutions of **7a**,**b** and **8a**,**b** show only very small blue shifts of the Q-band. Hence for P-Pc dyads **7** and **8**, the open 'clamshell' is preferred.

## Conclusions

The dimeric homonuclear Pc **4a**,**b** and **5a**,**b** as well as the dimeric heteronuclear Pc **4c** and **5c** were synthesized by a simple coupling reaction between the monomeric Pc **1a** and **1b**, respectively, each containing a phenolic OH group in one of its substituents, with the bromoalkyl-substituted Pc **1a** or **1b**. In DCM or toluene as solvents, these binuclear Pc are in an equilibrium between a cofacial and an open conformation, with the open form predominating. The equilibrium between the conformations can be shifted towards the cofacial form by adding methanol to the DCM solution, changing the polarity of the solvent mixture.

In the P-Pc dimers **7a**,**b** and **8a**,**b**, the open conformation dominates. The synthesis of these P-Pc dimers was carried out by the reaction of the Pc **2a**,**b** and **3a**,**b** respectively with the P **6** containing a phenolic substituent.

## Experimental

### *General*

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. All solvents were dried by standard methods. $MgSO_4$ was used to dry all organic solutions during workup procedures. Analytical TLC was performed on Kieselgel F-254-percolated TLC plates. For flash chromatography, silica gel 60 (230–400 mesh) was used. $^1$H NMR spectra were recorded on Bruker AC 250 and 400 spectrometers. The UV/visible spectra were taken in $CH_2Cl_2$ with a Lambda 25 UV/visible spectrometer and IR spectra with a Nicolet 380 infrared spectroscopy (FT-IR). Mass spectra (FAB-MS, EI, MALDI-TOF) were obtained on a Finnigan TSQ 70 MAT and a Bruker Autoflex spectrometer.

### *Pc **2a** and **2b**. General Method*

Compound **1a** or **1b** (0.016 mmol) was mixed with excess dibromoalkane in DMF (2 mL; for **1b** in a 1:1 DMF/THF mixture) in the presence of $K_2CO_3$ (0.02 g, 0.145 mmol). The mixture was heated to 75°C for 3 h. After cooling, the reaction product was added to water/methanol (1:1, 20 mL), filtered off, washed thoroughly with methanol, dried, and subjected to column chromatography on silica gel with $CH_2Cl_2$/*n*-hexane (65:35) as eluent. Pc **2a** and **2b** were isolated as the largest chromatographic fractions (second).

*Pc **2a***: Yield: 0.022 g (69%). $^1$H NMR (400 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 9.20 (d, $^3J$ 8.2 Hz, 1 H, $H^2$), 9.07–9.00 (m, 6 H, $H^1$), 8.83 (d, $^4J$ 1.8 Hz, 1 H, $H^4$), 7.79 (dd, $^3J$ 8.4 Hz, $^4J$ 2.0 Hz, 1 H, $H^3$), 7.38–7.09 (m, 19 H, $H^6$, 12 $H^9$, 6 $H^{10}$), 6.98–6.74 (m, 3 H, $H^5$, $H^7$, $H^8$), 4.14 (t, $^3J$ 5.8 Hz, 2 H, Hα), 3.58 (t, $^3J$ 6.4 Hz, 2 H, Hφ), 2.31 (t, $^3J$ 5.8 Hz, 2 H, Hβ), 1.43–1.18 (m, 108 H, $H^{11}$), −0.46 (s, 2 H, $H_{NH}$). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 702.5 (5.26), 668.1 (5.21), 639.0 (4.76), 606.0 (4.50), 400 (sh), 345.5 (5.00), 292.0 (4.88). *m*/*z* (MALDI-TOF) 1970 $[M]^+$.

*Pc **2b***: Yield: 0.027 g (83%). $^1$H NMR (400 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 8.99 (d, $^3J$ 8.1 Hz, 1 H, $H^2$), 8.92–8.77 (m, 6 H, $H^1$), 8.63 (s, 1 H, $H^4$), 7.68 (d, $^3J$ 8.3 Hz, 1 H, $H^3$), 7.38–7.08 (m, 19 H, $H^6$, 12 $H^9$, 6 $H^{10}$), 6.94–6.74 (m, 3 H, $H^5$, $H^7$, $H^8$), 4.12 (t, $^3J$ 5.6 Hz, 2 H, Hα), 3.55 (t, $^3J$ 6.4 Hz, 2 H, Hφ), 2.29 (t, $^3J$ 6.1 Hz, 2 H, Hβ), 1.41–1.17 (m, 108 H, $H^{11}$). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 674.1 (5.40), 645.0 (sh), 607.1 (4.72), 392 (sh), 330.5 (sh), 304.8 (5.11). *m/z* (MALDI-TOF) 2026 $[M]^+$.

### *Homonuclear and Heteronuclear Dimeric Pc **4a**, **4b**, and **4c***

**4a**, **4b**, and **4c** were prepared using the method described by us earlier for the Pc dimers **5a**–**c** by reaction of alkylated Pc **2a** and **2b** with starting Pc **1a** and **1b**, respectively.[4d]

***4a***: Yield: 0.054 g (58%). $^1$H NMR (400 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 9.06 (d, $^3J$ 8.1 Hz, 2 H, $H^2$), 9.02–8.93 (m, 12 H, $H^1$), 8.71 (s, 2 H, $H^4$), 7.71 (d, $^3J$ 8.4 Hz, 2 H, $H^3$), 7.34–7.12 (m, 38 H, 2 $H^6$, 24 $H^9$, 12 $H^{10}$), 6.92 (s, 2 H, $H^5$), 6.87–6.80 (m, 4 H, 2 $H^7$, 2 $H^8$), 4.25 (t, $^3J$ 5.6 Hz, 4 H, 2 Hα and 2 Hφ), 2.30 (t, $^3J$ 6.1 Hz, 2 H, Hβ), 1.40–1.15 (m, 216 H, $H^{11}$), −0.84 (s, 4 H, $H_{NH}$). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 702.2 (5.40), 668.1 (5.42), 644.0 (5.23), 610.0 (sh), 400.0 (sh), 343.0 (5.31), 294.0 (5.18). *m/z* (MALDI-TOF) 3740 $[M]^+$.

***4b***: Yield: 0.071 g (74%). $^1$H NMR (400 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 8.82–8.58 (m, 14 H, 2 $H^2$, 12 $H^1$), 8.57 (s, 2 H, $H^4$), 7.51 (d, $^3J$ 8.1 Hz, 2 H, $H^3$), 7.30–7.10 (m, 38 H, 2 $H^6$, 24 $H^9$, 12 $H^{10}$), 6.99 (s, 2 H, $H^5$), 6.83–6.77 (m, 4 H, 2 $H^7$, 2 $H^8$), 4.26 (t, $^3J$ 5.9 Hz, 4 H, 2 Hα and 2 Hφ), 2.27 (t, $^3J$ 5.9 Hz, 2 H, Hβ), 1.36–1.16 (m, 216 H, $H^{11}$). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 671.6 (5.19), 629.0 (5.10), 395.0 (sh), 301.3 (5.22). *m/z* (MALDI-TOF) 3852 $[M]^+$.

***4c***: Yield: 0.064 g (67%). $^1$H NMR (400 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 9.01–8.57 (m, 14 H, 2 $H^2$, 12 $H^1$), 8.51 (s, 2 H, $H^4$), 7.66–7.57 (m, 2 H, $H^3$), 7.35–7.03 (m, 38 H, 2 $H^6$, 24 $H^9$, 12 $H^{10}$), 6.93 (s, 2 H, $H^5$), 6.84–6.77 (m, 4 H, 2 $H^7$, 2 $H^8$), 4.24 (t, $^3J$ 5.9 Hz, 4 H, 2 Hα and 2 Hφ), 2.28 (t, $^3J$ 6.1 Hz, 2 H, Hβ), 1.37–1.25 (m, 216 H, $H^{11}$), −1.01 (s, 2 H, $H_{NH}$). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 700 (sh), 672.3 (5.16), 645.0 (5.04), 394.0 (sh), 331.2 (sh), 290.0 (5.20). *m/z* (MALDI-TOF) 3796 $[M]^+$.

### *P–Phthalocyanin Dimers **7a**,**b** and **8a**,**b***

Pc **2a**,**b** or **3a**,**b** (0.025 mmol) and 5-(4′-oxyphenyl)-10,15,20-triphenylporphin (**6**) (0.05 mmol) were mixed with $K_2CO_3$ (0.1 mmol) in DMF (2 mL, or DMF/THF 1:1). The mixture was heated to 75°C for 6 h. After cooling, the product was added to methanol (20 mL), filtered off, washed thoroughly with methanol, dried, and subjected to column chromatography on silica gel with $CH_2Cl_2$/*n*-hexane (65:35) as eluent.

Dimers **7a** and **7b** were obtained by reaction of Pc **2a** and **2b** with P **6**, respectively.

***7a***: Yield: 0.047 g (74%). $^1$H NMR (250 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 9.13 (d, $^3J$ 8.3 Hz, 1 H, $H^2$), 9.01–8.90 (m, 6 H, $H^1$), 8.67 (d, $^4J$ 2.2 Hz, 1 H, $H^4$), 8.54–8.44 (m, 8 H, Hβ), 8.28–8.22 (m, 6 H, $H_o$), 8.12 (d, $^3J$ 8.6 Hz, 2 H, H2′), 7.80 (dd, $^3J$ 8.3 Hz, $^4J$ 2.2 Hz, 1 H, $H^3$), 7.74–7.61 (m, 9 H, $H_{m,p}$), 7.46–7.10 (m, 21 H, $H^6$, 12 $H^9$, 6 $H^{10}$, H3′), 7.00–6.86 (m, 3 H, $H^5$, $H^7$, $H^8$), 4.51–4.42 (m, 4 H, Hα and Hφ), 2.46 (t, $^3J$ 5.9 Hz, 2 H, Hβ), 1.41–1.30 (m, 108 H, $H^{11}$), −1.69 (s, 2 H, $H_{NH}$(Pc)), −3.96 (s, 2 H, $H_{NH}$(porphyrin)). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 703.4 (4.99), 668.9 (4.90), 647.5 (4.55), 607.5 (4.36), 551.8 (4.10), 517.0 (4.29), 482 (sh), 418.8 (5.55), 348.7 (5.10), 291.6 (4.89). *m/z* (MALDI-TOF) 2518 $[M]^+$.

***7b***: Yield: 0.050 g (77%). $^1$H NMR (250 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 8.97–8.75 (m, 7 H, $H^2$, 6 $H^1$), 8.41 (d, $^4J$ 2.2 Hz, 1 H, $H^4$), 8.39–8.14 (m, 16 H, 8 Hβ, 6 $H_o$, 2 H2′), 7.75–7.54 (m, 10 H, $H^3$, 9 $H_{m,p}$), 7.46–7.07 (m, 21 H, $H^6$, 12 $H^9$, 6 $H^{10}$, H3′), 7.02–6.81 (m, 3 H, $H^5$, $H^7$, $H^8$), 4.62–4.42 (m, 4 H, Hα and Hφ), 2.44 (t, $^3J$ 6.2 Hz, 2 H, Hβ), 1.46–1.27 (m, 108 H, $H^{11}$), −3.89 (s, 2 H, $H_{NH}$(porphyrin)). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 677.0 (4.92), 648.2 (sh), 608.4 (4.32), 551.0 (4.11), 517.5 (4.26), 482.6 (sh), 419.7 (5.37), 329.9 (4.85), 305.6 (4.99). *m/z* (MALDI-TOF) 2574 $[M]^+$.

Dimers **8a** and **8b** were obtained by reaction of Pc **3a** and **3b** with P **6**, respectively.

***8a***: Yield: 0.047 g (73%). $^1$H NMR (250 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 9.17 (d, $^3J$ 8.3 Hz, 1 H, $H^2$), 9.05–8.96 (m, 6 H, $H^1$), 8.81 (d, $^4J$ 1.8 Hz, 1 H, $H^4$), 8.70–8.62 (m, 8 H, Hβ), 8.25–8.18 (m, 6 H, $H_o$), 8.09 (d, $^3J$ 8.5 Hz, 2 H, H2′), 7.79 (dd, $^3J$ 8.5 Hz, $^4J$ 2.2 Hz, 1 H, $H^3$), 7.76–7.64 (m, 9 H, $H_{m,p}$), 7.41–7.11 (m, 21 H, $H^6$, 12 $H^9$, 6 $H^{10}$, H3′), 6.95–6.83 (m, 3 H, $H^5$, $H^7$, $H^8$), 4.24 (t, $^3J$ 6.3 Hz, 2 H, Hφ), 4.12 (t, $^3J$ 6.3 Hz, 2 H, Hα), 2.05–1.30 (m, 116 H, 108 $H^{11}$, 2 Hβ, 2 Hγ, 2 Hδ, 2 Hε), −1.01 (s, 2 H, $H_{NH}$(Pc)), −3.36 (s, 2 H, $H_{NH}$(porphyrin)). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 701.0 (5.09), 670.4 (5.07), 644.4 (4.61), 607.4 (4.40), 550.0 (4.05), 514.8 (4.26), 480 (sh), 418.5 (5.59). *m/z* (MALDI-TOF) 2557 $[M]^+$.

***8b***: Yield: 0.052 g (79%). $^1$H NMR (250 MHz, $CDCl_3$, numbering according to Scheme 1): $\delta$ 9.00 (d, $^3J$ 8.5 Hz, 1 H, $H^2$), 8.92–8.80 (m, 6 H, $H^1$), 8.64 (d, $^4J$ 2.2 Hz, 1 H, $H^4$), 8.57–8.47 (m, 8 H, Hβ), 8.30–8.20 (m, 6 H, $H_o$), 8.12 (d, $^3J$ 8.5 Hz, 2 H, H2′), 7.74–7.61 (m, 10 H, $H^3$, 9 $H_{m,p}$), 7.40–7.08 (m, 21 H, $H^6$, 12 $H^9$, 6 $H^{10}$, H3′), 6.94 (t, t, $^4J$ 2.2 Hz, 1 H, $H^5$), 6.88–6.79 (m, 2 H, $H^7$, $H^8$), 4.24 (t, $^3J$ 6.3 Hz, 2 H, Hφ), 4.14 (t, $^3J$ 5.9 Hz, 2 H, Hα), 2.06–1.31 (m, 116 H, 108 $H^{11}$, 2 Hβ, 2 Hγ, 2 Hδ, 2 Hε), −3.73 (s, 2 H, $H_{NH}$(porphyrin)). UV/vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 675.9 (5.11), 646.3 (sh), 607.4 (4.45), 550.0 (4.15), 514.8 (4.29), 479.5 (sh), 418.5 (5.40). *m/z* (MALDI-TOF) 2616 $[M]^+$.

## Acknowledgement

Zafar Iqbal thanks the Deutsche Akademische Austauchdienst (DAAD) for financial support.

## References

[1] (a) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435. doi:10.1021/CR00011A005
(b) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40. doi:10.1021/AR9801301
(c) M. Calvete, M. Hanack, *Eur. J. Org. Chem.* **2003**, 2080. doi:10.1002/EJOC.200300090
(d) D. M. Guldi, *Pure Appl. Chem.* **2003**, *75*, 1069. doi:10.1351/PAC200375081069
(e) G. De La Torre, P. Vázquez, F. Agulló-López, T. Torres, *Chem. Rev.* **2004**, *104*, 3723. doi:10.1021/CR030206T
(f) D. Dini, M. Hanack, in *The Porphyrin Handbook* (Eds K. M. Kadish, K. M. Smith, R. Guilard) **2003**, Vol. 16, Ch. 107 (Academic Press: New York, NY).
(g) D. Wöhrle, D. Meissner, *Adv. Mater.* **1991**, *3*, 129. doi:10.1002/ADMA.19910030303
[2] E. S. Dodsworth, A. B. P. Lever, P. Seymour, C. C. Leznoff, *J. Phys. Chem.* **1985**, *89*, 5698. doi:10.1021/J100272A025
[3] (a) C. C. Leznoff, S. Greenberg, S. M. Marcuccio, P. C. Minor, P. Seymour, A. B. P. Lever, *Inorg. Chim. Acta* **1984**, *89*, L35. doi:10.1016/S0020-1693(00)82337-3

(b) C. C. Leznoff, S. M. Marcuccio, S. Greenberg, A. B. P. Lever, *Can. J. Chem.* **1985**, *63*, 623. doi:10.1139/V85-102
(c) S. M. Marcuccio, P. I. Svirskaya, S. Greenberg, A. B. P. Lever, C. C. Leznoff, *Can. J. Chem.* **1985**, *63*, 3057. doi:10.1139/V85-507
(d) 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. doi:10.1039/C39870000699
(e) C. C. Leznoff, P. I. Svirskaya, B. Knouw, R. L. Cerny, P. Seymour, A. B. Lever, *J. Org. Chem.* **1991**, *56*, 82. doi:10.1021/JO00001A019

[4] (a) E. M. Garcia-Frutos, S. M. O'Flaherty, E. M. Maya, G. De La Torre, W. Blau, P. Vazquez, T. Torres, *J. Mater. Chem.* **2003**, *13*, 749. doi:10.1039/B210707D
(b) E. M. Garcia-Frutos, F. Fernandez-Lazaro, E. M. Maya, P. Vazquez, T. Torres, *J. Org. Chem.* **2000**, *65*, 6841. doi:10.1021/JO0006019
(c) E. M. Maya, P. Vazquez, T. Torres, L. Gobbi, F. Diederich, S. Pyo, L. Echegoyen, *J. Org. Chem.* **2000**, *65*, 823. doi:10.1021/JO991505E
(d) A. Lyubimtsev, S. Vagin, S. Syrbu, M. Hanack, *Eur. J. Org. Chem.* **2007**, 2000. doi:10.1002/EJOC.200600733

[5] (a) C. J. Chang, Y. Deng, A. F. Heyduk, C. K. Chang, D. Nocera, *Inorg. Chem.* **2000**, *39*, 959. doi:10.1021/IC990987+
(b) C. J. Chang, Z. H. Loh, Y. Deng, D. G. Nocera, *Inorg. Chem.* **2003**, *42*, 8262. doi:10.1021/IC034750W
(c) D. Jokic, C. Boudon, G. Pognon, M. Bonin, K. J. Schenk, M. Gross, J. Weis, *Chem. Eur. J.* **2005**, *11*, 4199. doi:10.1002/CHEM.200401225

[6] (a) S. Gaspard, C. Giannotti, P. Maillard, C. Schaeffer, T.-H. Tran-Thi, *J. Chem. Soc. Chem. Commun.* **1986**, 1239. doi:10.1039/C39860001239
(b) H.-J. Tian, Q.-F. Zhou, S.-Y. Shen, H.-J. Xu, *Chin. J. Chem.* **1998**, *16*, 97.
(c) Z. Zhao, A. O. Oqusipe, M. D. Maree, T. Nyokong, *J. Porphyrins Phthalocyanines* **2005**, *9*, 186.
(d) J. P. C. Tomé, A. M. V. M. Pereira, C. M. A. Alonso, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, M. V. Martínez-Díaz, T. Torres, G. M. Aminur Rahman, J. Ramey, D. M. Guldi, *Eur. J. Org. Chem.* **2006**, 257. doi:10.1002/EJOC.200500558
(e) K. Kameyama, A. Satake, Y. Kobuke, *Tetrahedron Lett.* **2004**, *45*, 7617. doi:10.1016/J.TETLET.2004.08.101
(f) J. M. Sutton, R. W. Boyle, *Chem. Commun.* **2001**, 2014. doi:10.1039/B105840C
(g) A. R. M. Soares, M. V. Martinez-Diaz, A. Bruckner, A. M. V. M. Pereira, J. P. C. Tome, C. M. A. Alonso, M. A. F. Faustino, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, T. Torres, D. M. Guldi, *Org. Lett.* **2007**, *9*, 1557. doi:10.1021/OL0703635

[7] (a) A. Tolbin, A. Ivanov, L. Tomilova, N. Zefirov, *J. Porphyrins Phthalocyanines* **2003**, *7*, 162.
(b) I. Seotsanyana-Mokhosi, S. Maree, M. David Maree, T. Nyokong, *J. Porphyrins Phthalocyanines* **2003**, *7*, 167.

[8] (a) A. W. Snow, N. L. Jarvis, *J. Am. Chem. Soc.* **1984**, *106*, 4706. doi:10.1021/JA00329A012
(b) R. D. Farina, D. J. Halko, J. H. Swinehart, *J. Phys. Chem.* **1972**, *76*, 2343. doi:10.1021/J100661A001
(c) H. Sigel, P. Waldmeier, B. Prus, *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 161. doi:10.1016/0020-1650(71)80145-9
(d) K. Bernauer, S. Fallab, *Helv. Chim. Acta* **1961**, *44*, 1287. doi:10.1002/HLCA.19610440516