# NMR characterisation of five isomeric β,β′-diformyl-*meso*-tetraphenylporphyrins

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Five isomeric β,β′-diformyl-*meso*-tetraphenylporphyrins, and the corresponding nickel complexes, were synthesised, separated and fully characterised by NMR.

## Introduction

Formylporphyrins in general, and β-formylporphyrins in particular, are valuable precursors in the synthesis of porphyrin derivatives with important applications in biomedical and natural sciences.[1–3] The introduction of formyl groups into a porphyrin macrocycle is, thus, an important goal for a further functionalization of the macrocycle. The Vilsmeier formylation of nickel complexes of porphyrins is a conventional method for the preparation of these compounds. Porphyrins with *meso*-unsubstituted positions give *meso*-formyl derivatives while *meso*-tetrasubstituted-β-free porphyrins yield β-formyl compounds.[4–7] For instance, formylation of (*meso*-tetraphenylporphyrinato)nickel(II) (**1**) using $POCl_3$–DMF in refluxing 1,2-dichloroethane gives (β-formyl-*meso*-tetraphenylporphyrinato)-nickel(II) (**2a**) as the main product[4–6] and a small amount (less than 4%) of a mixture of five nickel complexes of β,β′-diformyl-*meso*-tetraphenylporphyrins (**3a**–**7a**). Column chromatography allows an easy separation of the monoformyl derivative from the diformyl ones, which are usually discharged.

During the last years we have been involved in the structural modification of β-formyl-*meso*-tetraphenylporphyrin derivatives.[8,9] It was clear for us that each time we were preparing **2a**, with the concomitant discharge of the diformyl derivatives, we were wasting potentially useful compounds for further structural modifications. We then decided to set up a project to look for applications of such diformyl compounds as precursors of novel porphyrinic structures. The success of this project depends on how easily the following matters could be solved: a) improvement of the synthesis of the diformyl derivatives, b) the separation of the five isomers and c) their unequivocal structural characterisation. All these questions were successfully approached; we have also shown that these diformyl compounds can be transformed into novel dipyrrolo-porphyrins.[10]

In this paper we describe the full details for the synthesis, separation and structural characterisation of the five isomeric β,β′-diformyl-*meso*-tetraphenylporphyrin derivatives **3a**–**7a** and **3b**–**7b**.

## Results and discussion

### 1 Synthesis, separation and nuclear magnetic resonance characterisation of compounds 3a–7a

The diformyl compounds **3a**–**7a** were obtained from **1** by a modification of the standard conditions of the Vilsmeier formylation: a bigger excess of $POCl_3$–DMF and longer reaction times were used. In this way, the diformyl derivatives can be obtained in reasonable amounts. After the hydrolysis of the iminium salts, which are intermediates in the Vilsmeier formylation, and the usual work up, porphyrin **2a** (57%) and a mixture of the diformylporphyrins **3a**–**7a** (31%) were obtained. Porphyrin **2a** was separated from that mixture by column chromatography; the latter compounds were further separated and purified by preparative thin layer chromatography affording four fractions (these fractions were numbered in order of decreasing $R_f$). The mass spectra ($FAB^+$) of all fractions exhibited the same parent ion at *m*/*z* 727. A detailed NMR analysis of reddish fractions 2, 3 and 4 allowed us to identify, respectively, the compounds **3a**, **6a** and **7a**. Fraction 1 (the one with higher $R_f$ and a greenish colour) was shown to be a 1 : 1 mixture of **4a** and **5a** (*vide infra*).

The five diformyl derivatives **3a**–**7a** (Scheme 1) were also obtained, in 71% yield, by direct formylation of the mono-β-formyl derivative **2a**.

The $^1$H NMR spectrum of compound **3a** suggests the presence of a symmetric molecule: the resonances of the two formyl protons and the adjacent β-protons appear as two singlets ($\delta$ 9.12 and 9.29); the remaining β-protons appear as two doublets ($\delta$ 8.66 and 8.74). The HETCOR spectrum of this compound revealed a correlation of the resonance at $\delta$ 9.12 with that of the carbon at $\delta$ 187.8, and was attributed to the formyl protons. The region corresponding to the *ortho* protons of the *meso*-phenyl rings revealed three resonances ($\delta$ 7.93, 7.96 and 8.00), the latter corresponding to four protons (two equivalent phenyl rings). In the NOESY spectra of **3a** the proton resonance of the CHO groups showed a NOE cross peak with the *ortho* protons of the two equivalent phenyl rings ($\delta$ 8.00), whereas the singlet corresponding to the β-protons resonance ($\delta$ 9.29) showed NOE cross peak with the signals of the protons of another phenyl ring ($\delta$ 7.93) (**I**, Fig. 1). All these data are only compatible with the structure of (2,8-diformyl-*meso*-tetraphenylporphyrinato)nickel(II) **3a**. The NOESY spectrum also showed a NOE cross peak between the resonance of the *ortho* protons of 10,20-phenyl rings and the signal at $\delta$ 8.74 and this allowed us to assign it to the resonance of H-12 and H-18 (**I**, Fig. 1).

The $^1$H NMR spectrum of compound **7a** is similar to that of **3a**, suggesting the presence of another symmetric diformyl-porphyrin. The NOESY spectrum of **7a** revealed a close proximity between the CHO protons ($\delta$ 8.99) and the *ortho* protons (2 H) of only one phenyl ring ($\delta$ 8.07) (**III**, Fig. 1). These data support the structure of the (2,18-diformyl-*meso*-tetraphenylporphyrinato)nickel(II).

The $^1$H NMR spectrum of compound **6a** showed four singlets ($\delta$ 9.10, 9.14, 9.24 and 9.32) and four doublets ($\delta$ 8.65,

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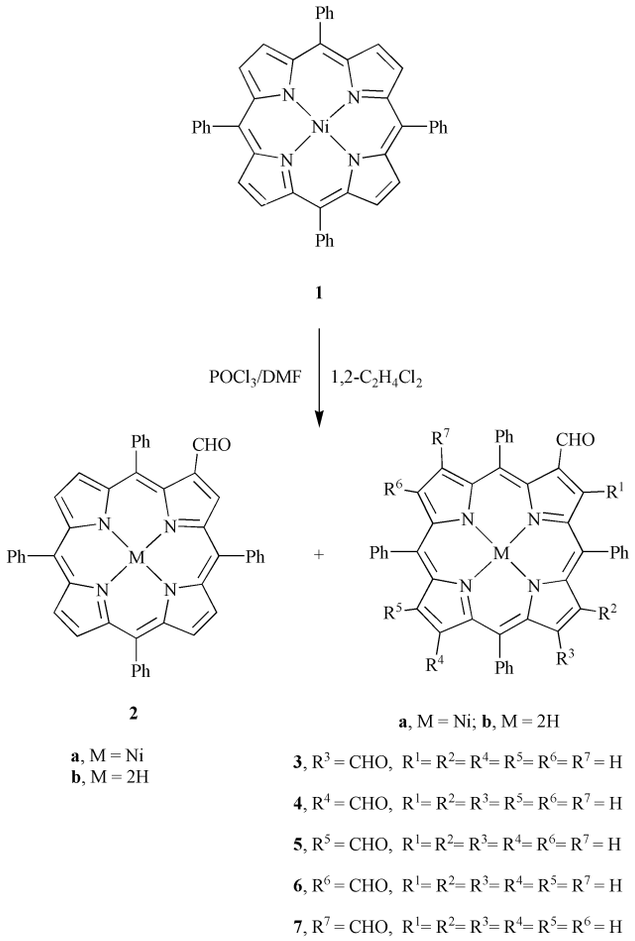


**Scheme 1**

8.68, 8.71 and 8.73) corresponding to the resonances of the two CHO groups and six β-protons of a porphyrin ring. The HETCOR spectrum of this compound showed correlations between the singlets at $\delta$ 9.10 and 9.14 with the carbon resonances at $\delta$ 187.7 and 187.8, being assigned to the CHO protons. These NMR data indicate the presence of an asymmetric structure. The NOESY spectra showed close proximities: i) between the *ortho* protons ($\delta$ 7.99) of one phenyl ring (5-Ph) and a β-proton (H-3; $\delta$ 9.32) and a formyl proton (7-CHO; $\delta$ 9.10); ii) between another β-proton (H-8; $\delta$ 9.24) and the *ortho* protons ($\delta$ 7.93) of another phenyl ring (10-Ph); and also iii) between the other formyl group (2-CHO; $\delta$ 9.14) and the *ortho* protons ($\delta$ 7.96) of a third phenyl ring (20-Ph) (**II**, Fig. 1). These data are only compatible with the structure of (2,7-diformyl-*meso*-tetraphenylporphyrinato)nickel(II) **6a**. The analysis of the HMBC spectrum of **6a** showed connectivities between H-3 and the carbon resonance at $\delta$ 187.8 and also between H-8 and that at $\delta$ 187.7, confirming the assignment of those carbon resonances to, respectively, the 2-CHO and 7-CHO groups.

The characterisation of the compound in the first TLC fraction (the one with a greenish colour) was more difficult. Since five isomeric diformyl derivatives were expected and only three of them (**3a**, **6a** and **7a**) were already found and characterised, the other two expected isomers (**4a** and **5a**) could be anticipated to be present in this fraction. However, only one spot could be observed in the TLC. Its $^1$H NMR spectrum showed four singlets ($\delta$ 9.12, 9.14, 9.28 and 9.29) of identical intensities, the former two being assigned to the resonance of CHO protons (confirmed with the correlations found in their HETCOR spectrum). Our conclusion was that we could have a 1 : 1 mixture of the two possible isomers **4a** and **5a**. Attempts for their separation by preparative TLC and HPLC were

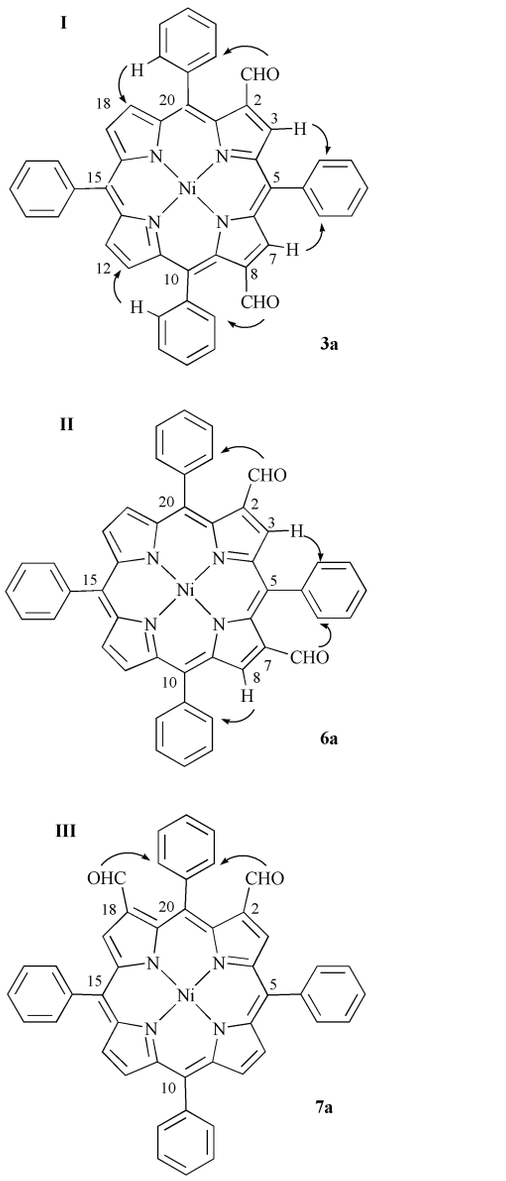


**Fig. 1** Important NOE cross peaks observed in the NOESY spectra of the diformyl derivatives **3a**, **6a** and **7a**.

unsuccessful. Later, we were able to confirm (indirectly) the structures of these two compounds using their free bases **4b** and **5b** (*vide infra*).

## 2 Synthesis, separation and nuclear magnetic resonance characterisation of compounds 3b–7b

The metal-free forms of the diformyl derivatives **3**–**7** are, obviously, synthetic targets. Direct acidic demetallation of compounds **3a**–**7a** is not possible due to intramolecular cyclizations which occur during such processes.[6,11] We were able to promote the demetallation of the intermediate iminium salts resulted from the Vilsmeier formylation of **1** before performing their hydrolysis. The monoformylporphyrin **2b** was separated from the diformyl derivatives **3b**–**7b** by column chromatography. A preparative thin layer chromatography of the diformyl derivatives afforded fractions 1–4 (in order of decreasing $R_f$). Fractions 2, 3 and 4 were identified, respectively, as compounds **3b**, **6b** and **7b** (the same order as in the nickel complexes). Both the $^1$H NMR and the HPLC of fraction 1 showed that it is a mixture of two diformylporphyrins in a proportion of *ca.* 1 : 1. Careful successive separations of these compounds by preparative TLC afforded small amounts of two fractions consisting of single compounds (confirmed by HPLC). The upper band was identified as **4b** and the lower

band as **5b**. The $^1$H NMR spectrum of the first one (**4b**) indicated the presence of a symmetric structure, since: i) the two formyl groups appear as one singlet ($\delta$ 9.18, confirmed by the HETCOR spectrum); ii) the β-protons appear as one singlet ($\delta$ 9.38, 2 H) and two doublets ($\delta$ 8.93 and 8.96, 2 H each); and iii) the *ortho* protons of the *meso*-phenyl rings also appear as two doublets ($\delta$ 8.21 and 8.24, 4 H each). The NOESY spectra of compound **4b** revealed a close proximity between the formyl groups and the *ortho* protons of two phenyl rings (10,20-Ph) appearing at $\delta$ 8.24 and also between the β-protons ($\delta$ 9.38, H-3 and H-13) with those of the *ortho* protons of the other two phenyl rings ($\delta$ 8.21, 5,15-Ph) (**IV**, Fig. 2). These data support the structure of 2,12-diformyl-*meso*-tetraphenylporphyrin **4b**.

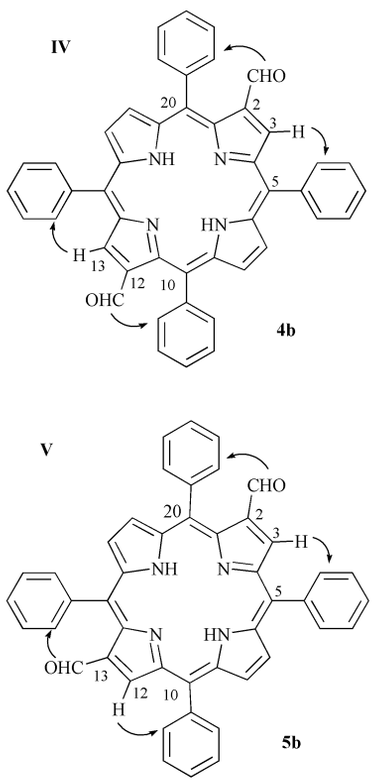


**Fig. 2** Important NOE cross peaks observed in the NOESY spectra of the diformyl derivatives **4b** and **5b**.

The $^1$H NMR spectrum of compound **5b** is similar to that of **4b**, however, in this case, the signals corresponding to the CHO and H-β protons resonances appear as four singlets [$\delta$ 8.93 (2 H), 8.97 (2 H), 9.17 (2 × CHO) and 9.38 (2 H)], which indicate the presence of the more symmetric diformylporphyrin derivative. The close proximities found in the NOESY spectrum of **5b** (**V**, Fig. 2) confirm the structure of the expected 2,13-diformyl-*meso*-tetraphenylporphyrin **5b**.

The characterisation of the diformylporphyrins **3b**, **6b** and **7b** was made by comparison of their $^1$H NMR spectra with those of the corresponding nickel complexes **3a**, **6a** and **7a**.

## Experimental

### General

$^1$H and $^{13}$C NMR spectra were recorded in deuteriochloroform using Bruker AMX 300 and DRX 300 spectrometers operating at 300.13 and 75.47 MHz, respectively; the spectra of compounds **4b** and **5b** were recorded on a Bruker DRX 500 spectrometer operating at 500.13 and 126.76 MHz, respectively. The chemical shifts are expressed in $\delta$ (ppm) values relative to TMS as internal reference and the coupling constants ($J$) are expressed in Hz. $^1$H assignments were made using 2D COSY and NOESY (mixing time of 800 ms) experiments, while $^{13}$C assignments were made using 2D HETCOR and HMBC experiments (long range C/H coupling constants were optimised to 7 Hz). Mass spectra and HRMS were recorded on VG AutoSpec Q and M mass spectrometers using $CHCl_3$ as solvent and 3-nitrobenzyl alcohol (NBA) as matrix. Elemental analyses were performed with a Leco CNHS 932 analyzer. The UV–Vis spectra were recorded on a Uvikon spectrophotometer using $CH_2Cl_2$ as solvent. Column chromatography was carried out using Silica gel (Merck, 35–70 mesh). Preparative thin-layer chromatography was carried out on 20 × 20 cm glass plates coated with Merck 60 silica gel (1 mm thick). Analytical TLC was carried out on precoated sheets with silica gel (Merck 60, 0.2 mm thick).

The HPLC analysis of compounds **4b** and **5b** (retention time 10.2 and 11.0 min, respectively) was carried out in a Gilson Model 305 equipped with a Gilson Model 118 UV–Vis detector and a Spherisorb S5W column using a mixture of ethyl acetate–chloroform–hexane (80 : 18 : 2) as eluent.

### Synthesis of (diformyl-*meso*-tetraphenylporphyrinato)nickel(II) 3a–7a

**Method A.** A 1,2-dichloroethane (15 ml) solution of **1** (38.6 mg, 0.058 mmol), *N,N*-dimethylformamide (1.2 ml, 15.8 mmol) and phosphorus oxychloride (0.8 ml, 8.2 mmol) was refluxed for 48 h under a nitrogen atmosphere. The chromatographic analysis (TLC) of the reaction mixture has shown a small amount of the mixture of diformyl compounds (**3a**–**7a**). Further portions of *N,N*-dimethylformamide (1.2 ml) and phosphorus oxychloride (0.8 ml) were added and the resulting mixture was further refluxed for 16 h. The solution was cooled and worked up as described to give **2a** (23.0 mg, 57%). The mixture of diformyl compounds was further separated by preparative thin layer chromatography using a (7 : 3) mixture of dichloromethane–light petroleum as eluent and afforded, in order of increasing polarity, a mixture of greenish compounds **4a** and **5a** (5.6 mg, 13%), and also the red ones **3a** (2.1 mg, 5%), **6a** (4.2 mg, 10%) and **7a** (1.2 mg, 3%).

**Method B.** A 1,2-dichloroethane (20 ml) solution of **2a** (52.7 mg, 0.076 mmol), *N,N*-dimethylformamide (1.6 ml, 20.7 mmol) and phosphorus oxychloride (1 ml, 10.7 mmol) was refluxed for 24 h under a nitrogen atmosphere. The solution was cooled and worked up to give the starting material **2a** (7.5 mg, 14%), and a mixture of green products **4a** and **5a** (14.1 mg, 26%), and the red ones **3a** (6.9 mg, 13%), **6a** (13.9 mg, 25%) and **7a** (4.0 mg, 7%).

### Synthesis of diformyl-*meso*-tetraphenylporphyrins 3b–7b

*N,N*-Dimethylformamide (1.2 ml, 15.8 mmol) and phosphorus oxychloride (0.8 ml, 8.2 mmol) were added to a 1,2-dichloroethane (15 ml) solution of **1** (38.6 mg, 0.058 mmol). The reaction mixture was refluxed for 48 h under a nitrogen atmosphere. Further portions of *N,N*-dimethylformamide (1.2 ml) and phosphorus oxychloride (0.8 ml) were added and the resulting mixture was refluxed for another 16 h period. After cooling to room temperature, concentrated $H_2SO_4$ (6 ml) was added to the reaction mixture, which was stirred for about 10 min at room temperature. The resulting green mixture was washed with water and then with a saturated aqueous solution of sodium carbonate and stirred at room temperature for about 14 h. The organic phase was separated and worked up as described to give **2b** (19.3 mg, 52%), a mixture of green compounds **4b** and **5b** (2.6 mg, 7%) and the red ones **3b** (1.2 mg, 3%), **6b** (2.8 mg, 7%) and **7b** (0.6 mg, 2%).

**(2,8-Diformyl-*meso*-tetraphenylporphyrinato)nickel(II) 3a.** $^1$H NMR $\delta$ 7.66–7.76 (m, 12 H, $H_{meta,para}$-Ph), 7.93 (dd, 2 H, $J$ 1.5 and 7.8, $H_{ortho}$-Ph-5), 7.96 (dd, 2 H, $J$ 2.5 and 6.2, $H_{ortho}$-Ph-15), 8.00 (dd, 4 H, $J$ 1.4 and 7.9, $H_{ortho}$-Ph-10,20), 8.66 (d, 2 H, $J$ 5.1,

H-13 and H-17), 8.74 (d, 2 H, *J* 5.1, H-12 and H-18), 9.12 (s, 2 H, 2 × C*H*O), 9.29 (s, 2 H, H-3 and H-7). $^{13}$C NMR $\delta$ 118.7, 119.3, 124.7, 125.1; 127.25 and 127.28 ($C_{meta}$-Ph-5,15), 127.7 ($C_{meta}$-Ph-10,20); 128.2, 128.6 and 129.2 ($C_{para}$-Ph); 133.3 (C-13 and C-17), 133.7 ($C_{ortho}$-Ph-5,15), 133.8 ($C_{ortho}$-Ph-10,20), 134.1 (C-12 and C-18), 136.9 (C-3 and C-7); 139.0, 139.1, 139.6, 140.4, 141.8, 142.1, 144.3, 145.1; 187.8 (2 × *C*HO); *m*/*z* (LSIMS) 727 (M + H)$^+$.

**2,8-Diformyl-*meso*-tetraphenylporphyrin 3b.** $^1$H NMR $\delta$ −2.15 (s, 2 H, 2 × N*H*), 7.74–7.85 (m, 12 H, $H_{meta,para}$-Ph), 8.15 (dd, 2 H, *J* 1.5 and 8.0, $H_{ortho}$-Ph-5), 8.19 (dd, 2 H, *J* 1.9 and 6.0, $H_{ortho}$-Ph-15), 8.22 (dd, 4 H, *J* 1.7 and 6.5, $H_{ortho}$-Ph-10,20), 8.77 (d, 2 H, *J* 4.9, H-13 and H-17), 8.83 (d, 2 H, *J* 4.9, H-12 and H-18), 9.24 (s, 2 H, 2 × C*H*O), 9.40 (s, 2 H, H-3 and H-7); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 120.2, 120.5, 125.3, 126.97 and 126.99 ($C_{meta}$-Ph-5, 15), 127.6 ($C_{meta}$-Ph-10, 20), 128.1, 128.6 and 129.2 ($C_{para}$-Ph), 132.2 (C-13, 17), 132.9 (C-12, 18), 134.6 ($C_{ortho}$-Ph-5), 134.7 ($C_{ortho}$-Ph-15), 135.8 ($C_{ortho}$-Ph-10, 20), 136.2 (C-3, 7), 140.4 (C-2, 8), 141.0, 141.3, 141.9, 188.8 (2 × CHO); *m*/*z* (LSIMS) 671 (M + H)$^+$, 670 (M$^{+\bullet}$); calc. for $C_{46}H_{30}N_4O_2 \cdot H_2O$: C, 80.21; N, 8.13; H, 4.68; found: C, 80.07; N, 8.11; H, 4.54%; $\lambda_{max}$ ($CH_2Cl_2$)/nm (log $\varepsilon$): 671 (3.76), 612 (3.79), 575 (4.05), 535 (4.22), 436 (5.47).

**(2,12-Diformyl-*meso*-tetraphenylporphyrinato)nickel(II) 4a and (2,13-diformyl-*meso*-tetraphenylporphyrinato)nickel(II) 5a (1 : 1 mixture).** $^1$H NMR $\delta$ 7.65–7.76 (m, 2 × 12 H, $H_{meta\ +\ para}$-Ph), 7.92–7.96 (m, 8 H, $H_{ortho}$-Ph), 7.98–8.02 (m, 2 × 8 H, $H_{ortho}$-Ph), 8.68, 8.70, 8.72 (3 s, 2 × 4 H, H-β), 9.12 (s, 2 H, C*H*O), 9.14 (s, 2 H, C*H*O), 9.28 (s, 2 H, H-β), 9.29 (s, 2 H, H-β). $^{13}$C NMR $\delta$ 118.6, 118.9, 121.8, 122.2; 127.2, 127.68 and 127.71 ($C_{meta}$-Ph); 128.4 and 129.2 ($C_{para}$-Ph); 133.5, 133.57, 133.62 and 133.66 (C-β); 133.66, 133.7, 133.83 and 133.9 ($C_{ortho}$-Ph); 136.6 and 136.9 (C-β); 139.4, 140.0, 140.3, 140.4, 141.1, 141.4, 142.3, 142.5, 143.7, 143.9, 144.8, 144.9; 187.78 and 187.82 (2 × *C*HO); *m*/*z* (LSIMS) 727 (M + H)$^+$.

**2,12-Diformyl-*meso*-tetraphenylporphyrin 4b.** $^1$H NMR $\delta$ −2.53 (s, 2 H, N*H*), 7.76–7.87 (m, 12 H, $H_{meta,para}$-Ph), 8.21 (d, 4 H, *J* 6.6, $H_{ortho}$-Ph-5,15), 8.24 (d, 4 H, *J* 6.6, $H_{ortho}$-Ph-10,20), 8.93 (d, 2 H, *J* 4.8, H-7 and H-17), 8.96 (d, 2 H, *J* 4.8, H-8 and H-18), 9.18 (s, 2 H, 2 × C*H*O), 9.38 (s, 2 H, H-3 and H-13). $^{13}$C NMR $\delta$ 120.4, 122.9; 127.0 and 127.6 ($C_{meta}$-Ph); 128.4 and 129.2 ($C_{para}$-Ph); 134.8 and 135.1 ($C_{ortho}$-Ph); 139.5 (C-3 and C-13); 141.2, 141.9; 189.0 (2 × *C*HO) (because of the small amount of sample available these are the only observable $^{13}$C signals). HRMS (FAB) *m*/*z* for $C_{46}H_{31}N_4O_2$ (M + H)$^+$: calculated 671.2447, found 671.2419; $\lambda_{max}$ ($CH_2Cl_2$)/nm (log $\varepsilon$): 679 (4.02), 619 (3.64), 575 (3.74), 532 (4.17), 432 (5.42).

**2,13-Diformyl-*meso*-tetraphenylporphyrin 5b.** $^1$H NMR $\delta$ −2.54 (s, 2 H, N*H*), 7.75–7.87 (m, 12 H, $H_{meta,para}$-Ph), 8.19 (d, 4 H, *J* 6.9, $H_{ortho}$-Ph-5,10), 8.26 (d, 4 H, *J* 7.0, $H_{ortho}$-Ph-15,20), 8.93 (s, 2 H, H-7 and H-8), 8.97 (s, 2 H, H-17 and H-18), 9.17 (s, 2 H, 2 × C*H*O), 9.38 (s, 2 H, H-3 and H-12). $^{13}$C NMR $\delta$ 120.4, 122.9; 127.0 and 127.6 ($C_{meta}$-Ph); 128.4 and 129.3 ($C_{para}$-Ph); 130.9 (C-7,8 and C-17,18); 134.7 and 135.3 ($C_{ortho}$-Ph); 140.2 (C-3 and C-12); 141.0, 142.1; 188.9 (2 × *C*HO) (because of the small amount of sample available these are the only observable $^{13}$C signals). HRMS (FAB) *m*/*z* for $C_{46}H_{31}N_4O_2$ (M + H)$^+$: calculated 671.2447, found 671.2427; $\lambda_{max}$ ($CH_2Cl_2$)/nm (log $\varepsilon$): 679 (4.01), 619 (3.66), 574 (3.71), 532 (4.19), 436 (5.50).

**(2,7-Diformyl-*meso*-tetraphenylporphyrinato)nickel(II) 6a.** $^1$H NMR $\delta$ 7.65–7.79 (m, 12 H, $H_{meta,para}$-Ph), 7.93 (dd, 2 H, *J* 2.0 and 7.8, $H_{ortho}$-Ph-10), 7.96 (dd, 2 H, *J* 1.4 and 7.4, $H_{ortho}$-Ph-20), 7.99 (d, 2 H, *J* 6.8, $H_{ortho}$-Ph-5), 8.01 (dd, 2 H, *J* 1.1 and 6.9, $H_{ortho}$-Ph-15), 8.65 (d, 1 H, *J* 5.1, H-β), 8.68 (d, 1 H, *J* 5.2, H-β), 8.71 (d, 1 H, *J* 5.2, H-β), 8.73 (d, 1 H, *J* 5.1, H-β), 9.10 (s, 1 H, 7-C*H*O), 9.14 (s, 1 H, 2-C*H*O), 9.24 (s, 1 H, H-8), 9.32 (s, 1 H, H-3). $^{13}$C NMR $\delta$ 118.5, 119.7, 121.2, 122.9; 127.3 and 127.7 ($C_{meta}$-Ph); 128.2, 128.4, 129.2 and 129.4 ($C_{para}$-Ph); 133.2, 133.6, 133.8 and 134.0 (C-β); 133.7 and 133.9 ($C_{ortho}$-Ph); 136.2 (C-8), 136.9 (C-3); 139.3, 139.6, 140.05, 140.08, 140.3, 140.4, 140.7, 141.6, 142.2, 142.5, 143.3, 144.6, 144.7, 145.2; 187.7 (7-*C*HO), 187.8 (2-*C*HO); *m*/*z* (LSIMS) 727 (M + H)$^+$.

**2,7-Diformyl-*meso*-tetraphenylporphyrin 6b.** $^1$H NMR $\delta$ −2.24 (s, 2 H, 2 × N*H*), 7.74–7.88 (m, 12 H, $H_{meta,para}$-Ph), 8.17 (dd, 2 H, *J* 1.6 and 6.4, $H_{ortho}$-Ph-10), 8.19 (dd, 2 H, *J* 2.0 and 7.9, $H_{ortho}$-Ph-20), 8.22 (dd, 2 H, *J* 1.7 and 7.1, $H_{ortho}$-Ph-5), 8.24 (dd, 2 H, *J* 1.4 and 6.1, $H_{ortho}$-Ph-10), 8.78 (d, 2 H, *J* 3.8, H-β), 8.82 (d, 1 H, *J* 3.8, H-β), 8.84 (d, 1 H, *J* 3.8, H-β), 9.18 (s, 1 H, 7-C*H*O), 9.23 (s, 1 H, 2-C*H*O), 9.37 (s, 1 H, H-8), 9.42 (s, 1 H, H-3); *m*/*z* (LSIMS) 671 (M + H)$^+$, 670 (M$^{+\bullet}$); HRMS (FAB) *m*/*z* for $C_{46}H_{31}N_4O_2$ (M + H)$^+$: calculated 671.2447, found 671.2424; $\lambda_{max}$ ($CH_2Cl_2$)/nm (log $\varepsilon$): 674 (3.75), 613 (3.85), 577 (4.08), 537 (4.27), 444 (5.50).

**(2,18-Diformyl-*meso*-tetraphenylporphyrinato)nickel(II) 7a.** $^1$H NMR $\delta$ 7.66–7.85 (m, 12 H, $H_{meta,para}$-Ph), 7.96 (dd, 6 H, *J* 1.6 and 7.4, $H_{ortho}$-Ph-5,10,15), 8.07 (dd, 2 H, *J* 1.4 and 7.6, $H_{ortho}$-Ph-20), 8.66 (d, 2 H, *J* 5.1, H-7,13 or H-8,12), 8.74 (d, 2 H, *J* 5.1, H-8,12 or H-7,13), 8.99 (s, 2 H, 2 × C*H*O), 9.25 (s, 2 H, H-3 and H-17). $^{13}$C NMR $\delta$ 117.6, 120.0, 121.7; 127.2 and 127.3 ($C_{meta}$-Ph); 128.2, 128.3 and 128.4 ($C_{para}$-Ph); 130.4; 133.3 and 133.7 (C-7,13 and C-8,12); 133.6 ($C_{ortho}$-Ph-15), 133.8 ($C_{ortho}$-Ph-10,20), 134.7 ($C_{ortho}$-Ph-15); 136.2 (C-3 and C-17); 139.4, 139.7, 140.5, 141.2, 141.3, 143.0, 143.8, 145.0; 187.5 (2 × *C*HO); *m*/*z* (LSIMS) 727 (M + H)$^+$.

**2,18-Diformyl-*meso*-tetraphenylporphyrin 7b.** $^1$H NMR $\delta$ −2.28 (s, 2 H, 2 × N*H*), 7.68–7.92 (m, 12 H, $H_{meta,para}$-Ph), 8.18 (dd, 6 H, *J* 1.5 and 7.5, $H_{ortho}$-Ph-5,10,15), 8.28 (d, 2 H, *J* 7.5, $H_{ortho}$-Ph-20), 8.80 (d, 2 H, *J* 4.8, H-7,13 or H-8,12), 8.82 (d, 2 H, *J* 4.8, H-8,12 or H-7,13), 9.10 (s, 2 H, 2 × C*H*O), 9.36 (s, 2 H, H-3 and H-17); *m*/*z* (LSIMS) 671 (M + H)$^+$, 670 (M$^{+\bullet}$); calc. for $C_{46}H_{30}N_4O_2 \cdot ½\ H_2O$: C, 81.28; N, 8.24; H, 4.60; found: C, 81.10; N, 8.67; H, 4.51%; $\lambda_{max}$($CH_2Cl_2$)/nm (log $\varepsilon$): 670 (3.94), 613 (3.82), 578 (4.11), 537 (4.19), 442 (5.44).

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