Synthesis of vinylated 5,10,15,20-tetraphenylporphyrins *via* Heck-type coupling reaction and their photophysical properties

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The direct coupling reaction between substituted olefins and 5,10,15,20-tetrakis(4-bromophenyl)porphyrin, *via* a Heck-type reaction, constitutes a versatile method for the vinylation of 5,10,15,20-tetrakis(4-bromophenyl)porphyrin to yield new vinylated tetraphenylporphyrins quantitatively. Another strategy for the vinylporphyrin synthesis has been developed. A phosphapalladacycle has been used as catalyst for the coupling reaction between 4-bromoaryl aldehydes and olefins to yield vinyl aldehydes quantitatively. These aldehydes have been condensed with pyrrole, by the one-step nitrobenzene method, to give the corresponding vinylated tetraphenylporphyrins. Photophysical studies of these new porphyrins are also reported.

Introduction

The development of new strategies to improve the synthesis of functionalized *meso*-arylporphyrins[1] has been extensively studied in recent years due to the multiple applications of porphyrins and metalloporphyrins in various areas such as photodynamic therapy,[2–4] molecular electronics,[5] sensors[6] and oxidation catalysis.[7–9] *meso*-Arylporphyrins have been the compounds of choice in the great majority of these applications mainly due to their ease of synthesis. Extension of the *one-pot* Rothemund[10] synthesis by Adler *et al.*[11] using propionic acid instead of pyridine, and by Gonsalves and Pereira[12,13] using acetic acid–nitrobenzene opened the way for large scale synthesis of several *meso*-arylporphyrins. The attachment of unusual organic groups to such porphyrins is of considerable interest, since slight changes in the substituents can significantly change the fundamental properties of the macrocycle.

The application of the Heck reaction to promote the coupling of halogenated aromatic compounds with several substituted olefins is an established method reckoned as a powerful synthetic strategy to functionalize aromatic compounds.[14,15] The usual catalyst for the classic Heck reaction is palladium acetate, palladium chloride or preformed (triarylphosphine)-palladium complexes.[16] Recently, other catalytic systems have been explored, using different palladium ligands namely, diphosphine,[17] phosphite,[18,19] sulfur–phosphine[20] and the very active phosphapalladacycles.[21–23]

Palladium-catalysed coupling reactions have often been employed to functionalize the porphyrin periphery and have recently been reviewed.[24] In previously described methods only the coupling of β-halogenated porphyrins with the desired unsaturated compounds has been studied.[25–29]

Furthermore, the coupling of 5,15-diiodo-10,20-diphenylporphyrins with alkynes[30] and aromatic iodides with the vinyl group of protoporphyrin-IX,[31] *via* Heck reaction, has also been described.

To the best of our knowledge the Heck-type reaction has never been used in direct functionalization of *meso*-substituted halogenated phenylporphyrins. In this paper we report the synthesis of new *meso*-vinylphenylporphyrins by direct coupling of substituted olefins **1a**–**f** and 5,10,15,20-tetrakis(4-bromophenyl)porphyrin **2**, *via* Heck reaction and also by the condensation reaction between vinyl aldehydes **3** and **4** with pyrrole. Comparative studies of the catalytic efficiency of the palladacycles **5** and the classic catalytic system palladium(II) acetate–triphenylphosphine are discussed. Fluorescence, phosphorescence, flash photolysis and photoacoustic calorimetry were employed to characterise the photophysics of the new porphyrins **6**–**8**.

Experimental

Reagents were used as received: 4-bromobenzaldehyde (Aldrich), 4-methoxystyrene (Janssen Chimica), butyl acrylate (Fluka), methyl vinyl ketone (Fluka), cinnamyl acetate (Aldrich), 2-methylbut-3-en-1-ol (Aldrich), vinyl acetate (Fluka), dimethylformamide (Fluka), 4-bromobenzaldehyde (Aldrich), pyrrole (Aldrich).

All solvents and reagents were purified and dried using standard procedures. Except where noted, all the solutions were carefully de-aerated with N_2-saturated in toluene before the photophysical measurements were made. In order to obtain an appropriate glass, at liquid nitrogen temperature, the toluene solutions were frozen very quickly.

Instrumentation

^{1}H NMR spectra were recorded on a 300 MHz Bruker AMX spectrometer. Mass spectra were obtained through the MS services of the University of Swansea. Elemental analysis was carried out using Fisons Instruments EA1108-CHNS-0 apparatus. Absorption and luminescence spectra were recorded with Shimadzu UV-2100 and SPEX Fluorolog 3.22 spectrophotometers, respectively. Low-temperature phosphorescence spectra and lifetimes were obtained with the same SPEX Fluorolog 3.22 with 1934D phosphorimeter.

Methods

Luminescence measurements. Fluorescence measurements were made in 1 cm quartz cuvettes on toluene solutions, carefully deaerated with N_2. Fluorescence quantum yields (Φ_F) were

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measured with carefully diluted solutions of the desired porphyrin in deaerated toluene, with absorbance 0.02 at an excitation wavelength of 417 nm. Using $\Phi_F = 0.10$ for tetraphenylporphyrin (TPP) as reference,[32] the Φ_F values for the new porphyrins were obtained as previously described.[33] The phosphorescence studies were carried out in toluene solution at liquid nitrogen temperature with excitation at the maximum of the Soret band. Fluorescence excitation spectra for all the porphyrins are in agreement with the corresponding absorption spectra, confirming the purity of the samples.

Flash photolysis measurements. Flash photolysis employed an Applied Photophysics LKS.60 spectrometer, with a Spectra-Physics Quanta-Ray GCR-130 Nd–YAG laser and a Hewlett-Packard Infinium Oscilloscope (1 GS s^{-1}; GS = Giga Sample); the samples were irradiated with the third harmonic of the laser (355 nm), the monitoring light was produced by a 150 W pulsed Xe lamp and the detection of the transient spectra in the 300–900 nm range was made with Hamamatsu 1P28 and R928 photomultipliers. Experiments were carried out both in aerated and N_2-saturated toluene solutions.

Time-resolved photoacoustic measurements. Time-resolved photoacoustic (PAC) measurements were carried out with a front-face cell using a dielectric mirror.[34] This PAC apparatus and the procedure employed in the measurements was recently described in detail.[35,36] In short, the sample and reference solutions, and the solvent were allowed to flow separately at a rate of 1 ml min^{-1} (SSI chromatographic pump) through a 0.11 mm thick cell. They were irradiated at 421 nm with an unfocused PTI dye laser (model PL2300), pumped by an N_2 laser working at a frequency of 2 Hz. A small fraction of the laser beam was reflected on to a photodiode that was used to trigger the transient recorder (Tektronix DSA 601, 1 GS s^{-1}). The photoacoustic waves, detected with a 2.25 MHz Panametrics transducer (model 5676) and captured by the transient recorder, were transferred to a PC for data analysis. In a typical PAC experiment 100 waves of the sample, reference and pure solvent are recorded and averaged under the same experimental conditions. Four sets of averaged sample, reference and solvent waves were used for the data analysis at a given laser intensity, and four laser intensities were employed in each experiment. The different laser intensities were obtained by interposing neutral density filters with transmissions between 25 and 100%. All the measurements were made in toluene using all-*trans*-β-carotene as the photoacoustic reference.

Synthesis

Synthesis of *anti*-[Pd(μ-Ac){(2-$C_6H_4CH_2$)PBzPh}]$_2$ (5). To a solution of palladium acetate (1.50 g, 6.7×10^{-3} mol) in toluene (150 ml) was added dibenzylphenylphosphine (2.55 g, 8.8×10^{-3} mol); the resulting mixture was stirred for 16 hours at 50 °C. Then, the solution was cooled to room temperature and concentrated. Addition of hexane caused the precipitation of **5** as a yellow solid that was filtered off and dried under vacuum. Yield: 2.59 g (85%). ^1H NMR (250 MHz, $CDCl_3$) δ 2.23 (s, 6H, CH_3), 2.60–3.20 (m, 8H, CH_2), 6.00–7.70 (m, 28H, aromatics); $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$) δ 53.45 (s), 44.98 (d, J = 4.2 Hz); $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$) δ 24.5 (s, CH_3), 33.6–37.2 (m, CH_2), 180 (s, COO). Anal. calcd. for $C_{44}H_{42}O_4P_2Pd_2$: C, 58.10; H, 4.65; found: C, 57.61; H, 4.54%. IR (KBr) 1559, 1409, 1096, 698 cm^{-1}.

General catalytic conditions for the synthesis of aldehydes

Complex **5** (10.0 mg, 1×10^{-5} mol) was dissolved in dimethylformamide (5 ml) under a nitrogen atmosphere in a Schlenk tube. In another Schlenk tube, 4-bromobenzaldehyde (27.0×10^{-3} mol), the desired olefin (35.1×10^{-3} mol) and sodium acetate (2.50 g, 30.5×10^{-3} mol) were dissolved in dimethylformamide (15 ml), also under a nitrogen atmosphere. Both solutions were heated to 120 °C, and then the catalyst solution was transferred by cannula to the Schlenk tube containing the reagents. After 16 hours the reaction was stopped, and the mixture was cooled to room temperature and quenched by adding 10 ml of HCl (5%). The crude product was purified by extraction with dichloromethane and water. The organic phase was dried with Na_2SO_4 and concentrated to dryness.

(*E*)-4-(2-Butoxycarbonylethenyl)benzaldehyde (3)

5.20 g of (*E*)-4-(2-butoxycarbonylethenyl)benzaldehyde were obtained as a yellow oil (yield: 83%). ^1H NMR ($CDCl_3$, 250 MHz) δ 0.91 (t, J = 7.3 Hz, 3H), 1.37 (m, 2H), 1.63 (m, 2H), 4.17 (d, J = 6.6 Hz, 2H), 6.48 (d, J = 16.0 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 16.0 Hz, 1H), 7.84 (d, J = 8.3 Hz, 2H), 9.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 13.56, 19.01, 30.56, 64.54, 121.33, 128.33, 129.96, 136.91, 139.96, 142.60, 166.22, 191.22. MS-EI m/z = 232 (M^+).

(*E*)-4-[2-(4-Methoxyphenyl)ethenyl]benzaldehyde (4)

1.27 g of (*E*)-4-[2-(4-methoxyphenyl)ethenyl]benzaldehyde were obtained as a yellow powder (yield: 89%). ^1H NMR ($CDCl_3$, 200 MHz) δ 3.85 (s, 3H, Me), 6.93 (d, J = 8.2 Hz, 2H, *ortho* MeO), 7.50 (d, J = 8.2 Hz, 2H, *meta* MeO), 7.63 (d, J = 8.6 Hz, 2H, *ortho* CHO), 7.86 (d, J = 8.6 Hz, 2H, *meta* CHO), 7.01 (d, J = 16.4 Hz, 1H, vinyl), 7.23 (d, J = 16.4 Hz, 1H, vinyl), 9.98 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 53.35 (OMe), 114.20 (*ortho* OMe), 125.07 (vinyl), 126.52, 128.17, 129.23 (*para* OMe), 130.19, 131.70 (vinyl), 134.87 (*ipso* CHO), 143.75 (*para* CHO), 159.87 (*ipso* OMe), 191.51 (CHO). MS-EI m/z = 238 (M^+).

General conditions for porphyrin synthesis *via* Heck reaction

5,10,15,20-Tetrakis(4-bromophenyl)porphyrin **2** (0.1×10^{-3} g, 1.07×10^{-4} mol) was dissolved in dimethylformamide (15 ml) under a nitrogen atmosphere. The desired olefin (7.00×10^{-3} mol), sodium acetate (45.0×10^{-3} g, 5.50×10^{-4} mol) and phosphapalladacycle **5** (5.5×10^{-3} g, 6.05×10^{-6} mol) or palladium acetate (2.80×10^{-3} g, 1.25×10^{-5} mol) and triphenylphosphine (10.0×10^{-3} g, 3.80×10^{-5} mol) were then added. The temperature was raised to 120 °C for the desired time. The evolution of the reaction was followed by TLC using hexane–dichloromethane (1 : 1) as eluent. The crude product was extracted with dichloromethane and washed with water. After standard work-up and evaporation of the solvents the residue was washed with methanol to remove the triphenylphosphine oxide. The product was purified by silica gel column chromatography using hexane–dichloromethane (1 : 1) as eluent.

(all-*E*)-5,10,15,20-Tetrakis[4-(2-butoxycarbonylethenyl)phenyl]porphyrin (6)

Isolated yield: 80 mg (67%). ^1H NMR ($CDCl_3$, 200 MHz) δ −2.79 (2H, br s, NH), 1.01 (12H, t, CH_3, J = 7.3 Hz), 1.54 (8H, m, CH_2), 1.77 (8H, m, CH_2), 4.30 (8H, t, CH_2, J = 6.6 Hz), 6.73 (4H, d, vinyl, J = 16.0 Hz), 7.91 (8H, d, *meta*, J = 8.1 Hz), 8.00 (4H, d, vinyl, J = 16.0 Hz), 8.22 (8H, d, *ortho*, J = 8.1 Hz), 8.84 (8H, s, Hβ). MS-FAB m/z 1118 (M^+). Anal. calcd. for $C_{72}H_{70}N_4O_8$: C, 77.28; H, 6.26; N, 5.0; found: C, 76.93; H, 6.50; N, 4.97%.

(all-*E*)-5,10,15,20-Tetrakis[4-(3-oxobut-1-enyl)phenyl]porphyrin (7)

Isolated yield: 76 mg (80%). ^1H NMR ($CDCl_3$, 200 MHz) δ −2.77 (2H, br s, NH), 2.54 (12H, s, CH_3), 7.04 (4H, d, vinyl, J = 16.3 Hz), 7.87 (4H, d, vinyl, J = 16.3 Hz), 7.96 (8H, d, *meta*, J = 8.0 Hz), 8.27 (8H, d, *ortho*, J = 8.0 Hz), 8.87 (8H, s, Hβ).

MS-FAB *m/z* 887 (M^+). Anal. calcd. for $C_{60}H_{46}O_4N_4$: C, 81.26; H, 5.19; N, 6.32; found: C, 81.71; H, 4.96; N, 6.10%.

General porphyrin synthesis *via* the nitrobenzene method

The desired vinyl aldehyde, **3** or **4** (0.40×10^{-3} mol), was dissolved in a mixture of glacial acetic acid (140 ml, 2.45 mol) and nitrobenzene (70.0 ml, 0.68 mol), and the temperature was raised to 120 °C. Pyrrole (0.40×10^{-3} mol) was then added. The evolution of the reaction was followed by UV–visible absorption spectroscopy until the Soret band reached its maximum. The reaction was left at room temperature during 12 hours. If the porphyrin crystallized directly from the reaction medium, it was filtered off. If it did not precipitate, the solvent was evaporated and the crude product was purified by column chromatography. The purple fraction was collected and porphyrins were recrystallized from dichloromethane–methanol.

(all-*E*)-5,10,15,20-Tetrakis[4-(2-butoxycarbonylethenyl)phenyl]porphyrin (6)

Isolated yield: 7%. The porphyrin exhibits the same spectroscopic and analytic data as those described above.

(all-*E*)-5,10,15,20-Tetrakis{4-[2-(4-methoxyphenyl)ethenyl]phenyl}porphyrin (8)

The required porphyrin was obtained from 200 mg (5.40×10^{-3} mol) of (*E*)-4-[2-(4-methoxyphenyl)ethenyl]benzaldehyde and pyrrole (0.35 ml, 5.40×10^{-3} mol). Isolated yield: 18.1 mg (7.5%). ^1H NMR ($CDCl_3$, 300 MHz) δ −2.7 (2H, br s, NH), 3.89 (12H, s, OCH_3), 7.01 (8H, d, J = 9 Hz, phenyl), 7.35 (4H, d, J = 12 Hz, H-vinyl), 8.19–8.26 (20H, 16-phenyl-porphyrin, 4H-vinyl), 7.88 (8H, d, J = 9 Hz, phenyl), 8.92 (8H, s, H_β); MS-FAB *m/z* 1143 (M^+). Anal. calcd. for $C_{80}H_{62}N_4O_4 \cdot 4\ H_2O$: C, 79.07, H, 5.76, N, 4.61; found: C, 79.09, H, 5.08, N, 4.67%.

5,10,15,20-Tetrakis(4-bromophenyl)porphyrin (2)

The required porphyrin was obtained from 4-bromobenzaldehyde (1.2×10^{-3} mol) and an equivalent amount of pyrrole. Isolated yield: 93 mg (25%). ^1H NMR δ −1.8 (2H, br s, NH), 7.89 (8H, d, *meta*, J = 9.0 Hz), 8.05 (8H, d, *ortho*, J = 9.0 Hz), 8.8 (8H, s, Hβ). MS-FAB *m/z* 930 (M^+). Anal. calcd. for $C_{44}H_{26}N_4Br_4$: C, 56.79; H, 2.79; N, 6.02; found: C, 56.81; H, 2.90; N, 5.91%.

Results and discussion

Palladacyclic complexes are structurally defined catalysts for the Heck vinylation of haloaromatic compounds, and are easy to handle and thermally more stable than conventional ones.[21] A new phosphapalladacycle has been synthesized by reaction between palladium acetate and the appropriate phosphine to give **5** (Scheme 1).

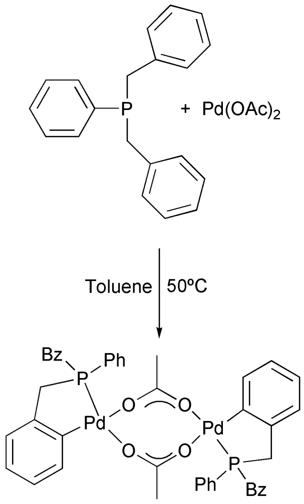
The halo derivative 5,10,15,20-tetrakis(4-bromophenyl)porphyrin **2** was prepared using the nitrobenzene method[12] by mixing equimolar amounts of pyrrole and 4-bromobenzaldehyde in a mixture of acetic acid–nitrobenzene (2 : 1) at 120 °C during 1 hour. The pure compound, without any chlorin contamination, was obtained in 25% yield by direct filtration of the crystals from the reaction medium.

In order to study the effect of the olefin in the Heck reaction, the reaction of brominated porphyrin **2** with olefins **1a**–**f** (Fig. 1) in the presence of palladacycle **5** and with the classic Heck catalytic system, palladium acetate–triphenylphosphine, were investigated.

Table 1 Comparative studies of the coupling reaction between brominated porphyrin, **2**, and different olefins, using the palladacycle, **5**, or palladium acetate–triphenylphosphine as catalyst

Entry	Substrate	Catalyst	Time	Conversion[a] (%)
1	**1a**	**5**	7 days	70[b]
2	**1b**	**5**	7 days	—[c]
3	**1c**	**5**	10 days	—[c]
4	**1a**	$Pd(OAc)_2$–PPh_3	24 hours	100
5	**1d**	$Pd(OAc)_2$–PPh_3	24 hours	100
6	**1e**	$Pd(OAc)_2$–PPh_3	7 days	80[b]
7	**1f**	$Pd(OAc)_2$–PPh_3	7 days	—[c]

[a] Conversion obtained by ^1H NMR by comparison between the new olefinic protons and the aromatic porphyrin signals. [b] Mixture of mono-, di-, tri- and tetra-substituted vinylporphyrins. [c] Only signals due to the starting material were observed.



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Scheme 1

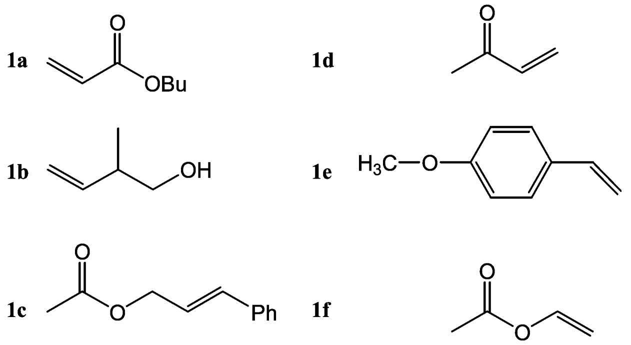
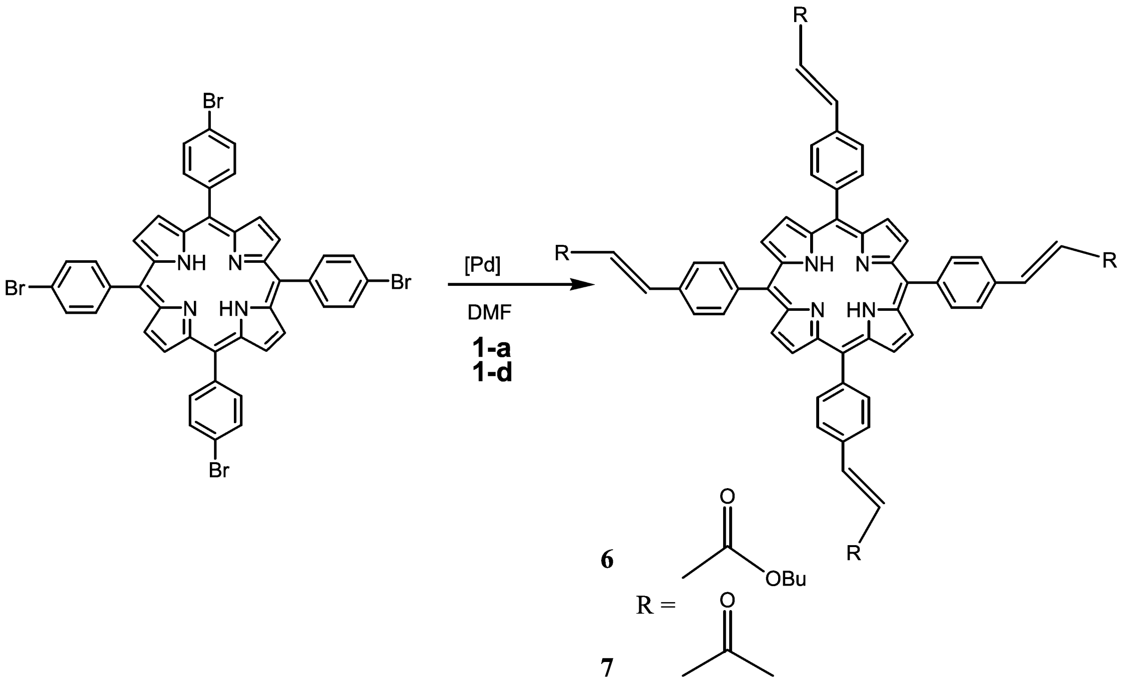


Fig. 1 Structures of the olefins studied.

In the catalytic coupling reaction, porphyrin **2** was dissolved in dimethylformamide and the olefin **1a**–**c**, sodium acetate, and the palladium complex **5** were subsequently added and the reaction mixture maintained at 120 °C. The evolution of the reaction was monitored by TLC and the final conversions were evaluated by ^1H NMR. The results are presented in Table 1. A great excess of olefin is used to force the coupling reaction with the four porphyrin bromine groups. This catalytic system is not very active (entries 1–3), and showed a significant dependence on the structure of the olefin. Only with the activated terminal electron-poor olefin **1a** was an overall yield of 70% obtained, after 7 days, but as a complicated mixture of substituted vinylated porphyrins. The porphyrins from the reaction mixture were isolated by preparative thin layer chromatography giving mainly porphyrins with four, and two olefin groups, as shown by NMR and FAB mass spectra, with peaks centered at 1118 and 1025, respectively. With the electron-rich, disubstituted deactivated olefins **1b**,**c** no reaction was observed after 7 days.

In order to compare the palladacycle **5** with conventional catalysts[14] the coupling of olefins **1a**, **1d**–**f** with **2**, in the



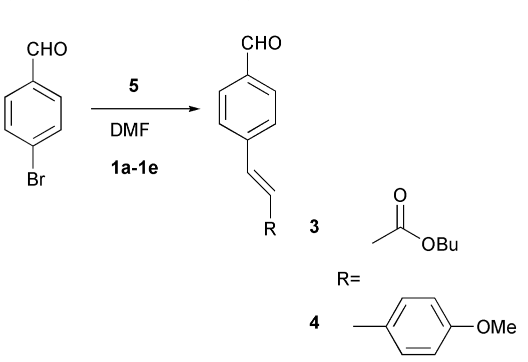
Scheme 2

presence of $Pd(OAc)_2$–PPh_3 and sodium acetate was attempted (Scheme 2). The results are collected in Table 1 (entries 4–7).

In the coupling reactions using electron-poor olefins **1a** and **1d**, complete transformation of the porphyrin **2** to the corresponding tetravinylporphyrins was observed after 24 hours, while with electron-rich olefins either no reaction or a complex mixture of products was observed after 7 days. It is noteworthy that vinylation gave only the (*E*)-isomer with 100% regioselectivity for the terminal olefinic carbon. We were surprised to find that the catalytic activity for the palladacycle **5** was significantly lower, even for the activated olefin **1a**.

In light of the results presented in Table 1, it is likely that the standard Heck catalytic system is efficient for the vinylation of 5,10,15,20-tetrakis(4-bromophenyl)porphyrin with electron-withdrawing olefins, but the catalyst palladacycle **5** only permits very specific applications.

Another approach to the synthesis of the desired vinylporphyrins is prior functionalization of the aldehyde, *via* Heck reaction, followed by condensation with pyrrole. The palladacycle **5** was able to catalyse the coupling reaction of the activated 4-bromobenzaldehyde with the olefins **1a** and **1e** to give (*E*)-4-(2-butoxycarbonylethenyl)benzaldehyde **3** (83%) in 16 hours and (*E*)-4-[2-(4-methoxyphenyl)ethenyl]benzaldehyde **4** (89%) in 16 hours (Scheme 3).



Scheme 3

Then, the one-step porphyrin synthesis using the direct condensation–cyclization reaction between the new aldehydes **3** or **4** and an equivalent amount of pyrrole was carried out in a mixture of glacial acetic acid–nitrobenzene.[12] After evaporation of the nitrobenzene and purification of the product by silica gel column chromatography using chloroform as eluent, the purple fraction was collected, yielding 7 and 7.5% of the corresponding porphyrins **6** and **8** (Scheme 4) without any contamination from the corresponding chlorin.

The catalytic system using the palladacycle **5** allows the transformation of brominated aldehydes into the corresponding vinyl ketones, using either electron-rich or electron-poor olefins which are good precursors for the synthesis of the corresponding *meso*-*p*-vinylphenylporphyrins, using the simple one-step nitrobenzene methodology.[12,13]

Photophysical results

The photophysical properties of the three new porphyrins **6**–**8** studied in this work are presented in Table 2. The UV–visible absorption spectra were interpreted in terms of the nomenclature of the four-orbital model of Gouterman[37–39] for the D_{2h} symmetry expected for these free-base porphyrins. The absorption and fluorescence features shown in Fig. 2 closely resemble those of TPP, also included in the Table 2 for comparison. The excitation and absorption spectra are in excellent agreement, also confirming the purity of the compounds.

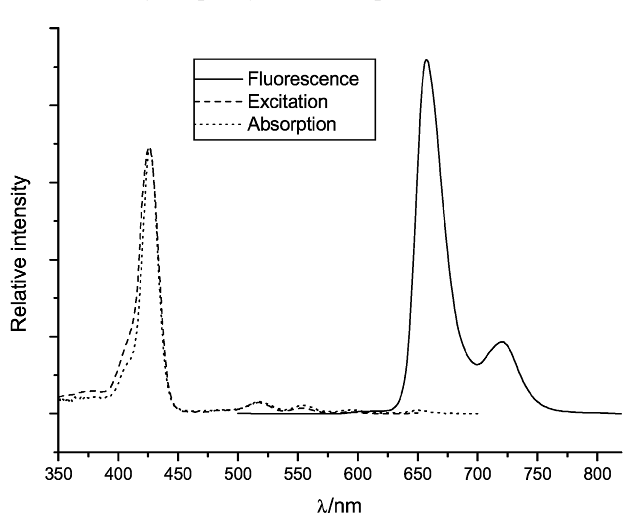
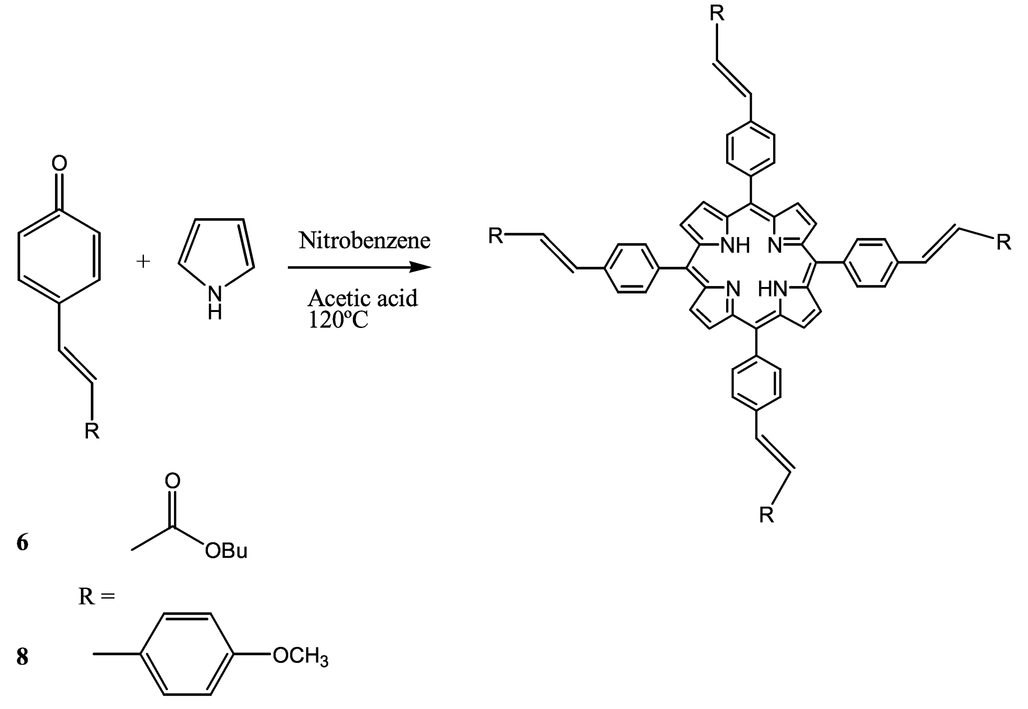


Fig. 2 Absorption, fluorescence, and excitation spectra of porphyrin **6** (5.7×10^{-7} M), in toluene solution at room temperature.

Table 2 Absorption and luminescence data of the porphyrins in toluene solution

Porphyrin	Absorption λ_{max}/nm (ε/M^{-1} cm^{-1}) Q$_x$(0–0)	Q$_x$(1–0)	Q$_y$(0–0)	Q$_y$(1–0)	B(0–0)	Fluorescence λ_{max}/nm (RT) Q(0–0)	Q(0–1)	E_S/kJ mol^{-1}	Φ_F (N_2)
6	651.0 (3.8×10^3)	594.0 (4.1×10^3)	554.5 (9.3×10^3)	518.0 (1.3×10^4)	426.5 (3.3×10^5)	657	720	182.9	0.17
7	651.0 (2.8×10^3)	594.0 (3.2×10^3)	555.0 (7.4×10^3)	518.5 (1.0×10^4)	427.0 (3.1×10^5)	656	719	183.0	0.15
8	654.0 (9.6×10^3)	597.0 (8.2×10^3)	558.0 (2.2×10^4)	520.0 (2.4×10^4)	431.0 (5.6×10^5)	659	722	182.3	0.27
H_2TPP[a]	649.8 (9.6×10^3)	592.0 (1.0×10^4)	548.0 (1.2×10^4)	514.6 (1.8×10^4)	418.0 (2.7×10^5)	652	719	183.9	0.11

[a] Refs. 33 and 40.



Scheme 4

However, quite unexpectedly, phosphorescence was observed with bands at 691–697 and 764–773 nm, with a lifetime of *ca.* 1.4 ms. The phosphorescence of free-base porphyrins is much more difficult to detect, occurs at much lower energy and is longer lived.[40]

The palladium complex of porphyrin **6** was synthesised by refluxing porphyrin **6** in dimethylformamide with an excess of palladium(II) acetate and phosphorescence studies were carried out. The position of the phosphorescence bands and lifetimes are, within experimental error, identical to those observed for the vinylporphyrins. This strongly suggests that the observed phosphorescence originates from the residual palladium that remains in the materials even after repeated purification.

The singlet state energies (E_S) were obtained from the intersection of the normalised absorption and fluorescence spectra (Fig. 2).

We further investigated the nature of the triplet state of the porphyrins **6**–**8** using flash photolysis and PAC. The transient spectrum observed in flash photolysis is typical of tetraphenylporphyrins (Fig. 3). The lifetime in N_2-saturated toluene solutions measured at all wavelengths (350, 460, and 650 nm) is *ca.* 70 μs, which is comparable with the lifetimes measured for tetraphenylporphyrins subjected to the deoxygenation procedure followed. The isosbestic points at 403 and 443 nm, associated with the bleaching of the ground state, indicate that the triplet state decays directly to the ground state. The emissive triplet state is not observed in room-temperature flash photolysis.

PAC measures the fraction of light energy released as heat in each of the radiationless processes following electronic excitation. The transient heat released may be due to internal conversion, intersystem crossing, energy transfer or some other photoinduced reaction. The experimental conditions employed in this work, associated with the deconvolution of reference and sample waves, allow us to distinguish sequential heat releases that occur in the 10 ns to 5 μs time range. All the heat released in less than 10 ns appears as prompt heat (a faster process that includes the internal conversion from higher excited states, the intersystem crossing to the triplet manifold and the relaxation

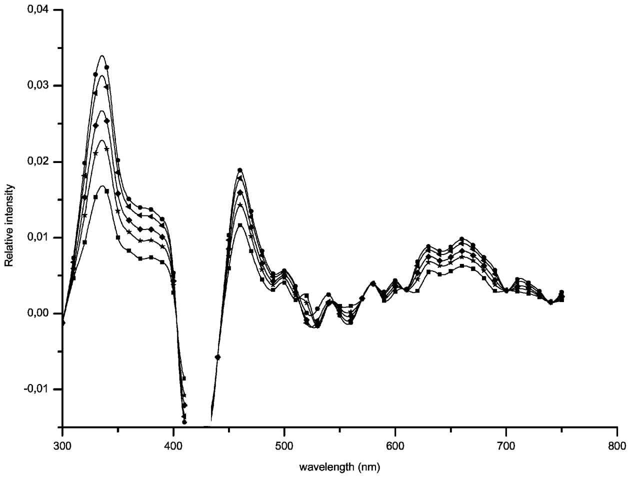


Fig. 3 Laser flash photolysis of porphyrin **8** (6×10^{-6} M), in toluene solution at room temperature. Triplet–triplet absorption spectrum.

of the spectroscopically formed ground state species). Processes occurring with lifetimes longer than 5 μs are not detected and the sum of their enthalpies is the fraction of energy not released in the PAC experiment.

The fraction of heat released in the formation of an intermediate is the product of the quantum yield and the enthalpy of its formation. We cannot determine Φ_T because E_T is not accurately known for the porphyrins **6**–**8**. Thus, we focussed the PAC studies on the measurement of the singlet oxygen quantum yield, Φ_Δ.

Deconvolution of the photoacoustic waves of porphyrin **8** in toluene solution in air revealed that 72 ± 2% of the light energy absorbed is lost as heat in the time window of the experiment. This energy comes from the formation of the S_1 state with unity quantum yield, the formation of singlet oxygen with a quantum yield Φ_Δ, and the radiationless decay to the ground state,[33]

$$E_{h\nu}\Phi_1 = (E_{h\nu} - E_{S1}) + (E_{S1} - E_\Delta)\Phi_\Delta + E_{S1}\Phi_{ic} \qquad (1)$$

where $E_\Delta = 94$ kJ mol^{-1} is the electronic energy of singlet oxygen.

This equation neglects the relaxation of the ground state produced by fluorescence at the excited-state nuclear configuration, because these molecules have small Stokes shifts. The sum of the quantum yields of the processes available to the S_1 state must be unity: $\Phi_F + \Phi_\Delta + \Phi_{ic} = 1$. This equation assumes that all the triplet states quantitatively transfer their energy to singlet oxygen in the time window of the experiment. Furthermore, $\Phi_F = 0.20$ in air-saturated solutions and $E_{S1} = 182.3$ kJ mol^{-1}, and, thus, a value of $\Phi_\Delta \approx 0.46$ was calculated.

It is interesting to note that this porphyrin has a much larger Φ_F and a significantly lower Φ_Δ than TPP. The deactivation of the S_1 state of porphyrin **8** by radiative and non-radiative channels is more efficient than that of TPP.

Conclusion

This paper describes the application of a new phosphapalladacycle **5** as a catalyst for Heck-type reactions using 5,10,15,20-tetrakis(4-bromophenyl)porphyrin **2** or 4-substituted aldehydes as substrates. However, in the direct vinylation of 5,10,15,20-etrakis(4-bromophenyl)porphyrin **2** the standard Heck catalytic system proved to be more active.

This is the first time that the standard Heck coupling reaction has been conducted successfully with a tetra-halogenated porphyrin to give new *tetra*vinylporphyrins with yields up of to 70%. In this work we present an almost general method for the synthesis of vinylporphyrin using two different methodologies: i) direct coupling of 4-brominated porphyrin **2** with electron-poor olefins catalysed by palladium acetate, yielding **6** and **7**; ii) coupling of 4-bromobenzaldehyde with either electron-rich or electron-poor olefins, catalysed by phosphapalladacycle **5**, giving the corresponding vinyl aldehydes **3** and **4**, followed by condensation with pyrrole to yield **6** and **8**.

The luminescent properties of the new extended conjugated *meso*-phenylvinylporphyrins have been studied. They have proved to be more fluorescent than TPP and their efficiency in singlet-oxygen sensitisation is lower.

The synthesis of new free-base porphyrins with other vinyl groups is currently being developed.

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References

1 K. M. Kadish and R. Guilard, *The Porphyrin Handbook*, Academic Press, New York, 2000, Vol. 1, p. 46.
2 T. J. Dougherty, *Photochemistry in the Treatment of Cancer*, Wiley & Sons, New York, 1992, p. 275.
3 H. Honigsmann, G. Jori and A. R. Young, *The Fundamental Bases of Phototherapy*, OEMF SPA, Milan, 1996, p. 181.
4 R. Bonnett, *Chemical Aspects of Photodynamic Therapy*, Gordon and Breach, Science, Amsterdam, 2000, Vol. 1.
5 T. E. O. Screen, I. M. Blake, L. H. Rees, W. Clegg, S. J. Borwick and H. L. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 2002, **3**, 320.
6 X. Lu, I. Manners and M. A. Winnik, *Macromolecules*, 2001, **34**, 1917.
7 A. M. d'A. Rocha Gonsalves and M. M. Pereira, *J. Mol. Catal. A: Chem.*, 1996, **113**, 209.
8 C.-C. Guo, G. Huang, Z.-P. Li and J.-X. Song, *J. Mol. Catal. A: Chem.*, 2001, **170**, 43.
9 J. T. Groves, *J. Porphyrins Phthalocyanines*, 2000, **4**, 350.
10 P. Rothemund, *J. Am. Chem. Soc.*, 1935, **57**, 2010.
11 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
12 A. M. d'A. Rocha Gonsalves, M. M. Pereira and J. M. T. B. Varejão, *J. Heterocycl. Chem.*, 1991, **28**, 635.
13 R. A. W. Johnstone, M. L. Nunes, M. M. Pereira, A. M. d'A. Rocha Gonsalves and A. C. Serra, *Heterocycles*, 1996, **43**, 1423.
14 R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146.
15 N. J. Whitcombe, K. K. Hii and S. E. Gibson, *Tetrahedron*, 2001, **57**, 7449.
16 A. de Meijere and F. E. Meyer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2379.
17 M. Portnoy, Y. Ben-David and D. Milstein, *Organometallics*, 1993, **12**, 4734.
18 M. Beller and A. Zapf, *Synlett*, 1998, 792.
19 D. A. Albisson, R. B. Bedford and P. N. Scully, *Tetrahedron Lett.*, 1998, **39**, 9793.
20 M. Casey, J. Lawless and C. Shirran, *Polyhedron*, 2000, **19**, 517.
21 W. A. Herrmann, C. Brossmer, K. Ofele, C.-P. Reisinger, T. Priermeier, M. Beller and H. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1844.
22 W. A. Herrmann, C. Brossmer, K. Ofele, C.-P. Reisinger, T. H. Riermeier, K. Ofele and M. Beller, *Chem. Eur. J.*, 1997, **3**, 1357.
23 R. B. Bedford and S. L. Welch, *Chem. Commun.*, 2001, 129.
24 W. M. Sharman and J. E. van Lier, *J. Porphyrins Phthalocyanines*, 2000, **4**, 441.
25 N. Risch, R. Gauler and R. Keuper, *Tetrahedron Lett.*, 1999, **40**, 2925.
26 H. Ali and J. E. van Lier, *Tetrahedron*, 1994, **50**, 11933.
27 K. S. Chan, X. Zhou, B. S. Luo and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1994, 271.
28 R. Gauler and N. Risch, *Eur. J. Org. Chem.*, 1998, 1193.
29 C. M. A. Alonso, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva and J. A. S. Cavaleiro, *Tetrahedron Lett.*, 2000, **41**, 5679.
30 R. W. Boyle, C. K. Johnson and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, 1995, 527.
31 M. Castella, F. Calahorra, D. Sainz and D. Velasco, *Org. Lett.*, 2001, **3**, 541.
32 D. J. Quimby and F. R. Longo, *J. Am. Chem. Soc.*, 1975, **97**, 5111.
33 M. Pineiro, A. L. Carvalho, M. M. Pereira, A. M. d' A. Rocha Gonsalves, L. G. Arnaut and S. J. Formosinho, *Chem. Eur. J.*, 1998, **4**, 2299.
34 L. G. Arnaut, R. A. Caldwell, J. E. Elbert and L. A. Melton, *Rev. Sci. Instrum.*, 1999, **63**, 5381.
35 C. Serpa and L. G. Arnaut, *J. Phys. Chem. A*, 2000, **104**, 11075.
36 M. Pineiro, M. M. Pereira, A. M. d A. Rocha Gonsalves, L. G. Arnaut and S. J. Formosinho, *J. Photochem. Photobiol., A*, 2001, **138**, 147.
37 M. Gouterman, *J. Mol. Spectrosc.*, 1961, **6**, 138.
38 M. Gouterman and H. Wagneriére, *J. Mol. Spectrosc.*, 1963, **11**, 108.
39 M. Gouterman, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, Vol. 3, p. 1.
40 A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1978.