One-pot electrochemical generation of a porphyrin dimer with a bis(diphenylphosphonium)acetylene bridge

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The electrochemical oxidation of zinc tetraphenylporphyrin in the presence of bis(diphenylphosphino)acetylene leads to the formation of a β-bridged dimer using 0.5 equiv. of Lewis base per mole of [Zn(tpp)]; a mixture of monomer and dimer is observed when stoichiometric amounts or an excess of diphosphine was used.

Covalently linked porphyrin dimers are of major importance for understanding processes of photosynthesis.[1] Since the building of porphyrin oligomers often requires several synthetic steps,[2] the direct assembling of porphyrins has been investigated. We described recently an alternative pathway for obtaining conveniently dimeric porphyrins through electrochemical oxidation of porphyrins in the presence of 4,4′-bipyridine.[3] However, this electrochemical synthesis required two steps: first, the formation of the monomeric β- or *meso*-substituted porphyrin subunit followed by a second oxidation step to obtain the dimer.

Here, we report the introduction of a new type of spacer which allowed us to obtain a dimeric porphyrin with a diphosphonium bridge in a direct one-pot reaction. The starting point for the synthesis was the electrochemical oxidation of the zinc *meso*-tetraphenylporphyrin [Zn(tpp)] in the presence of bis(diphenylphosphino)acetylene.

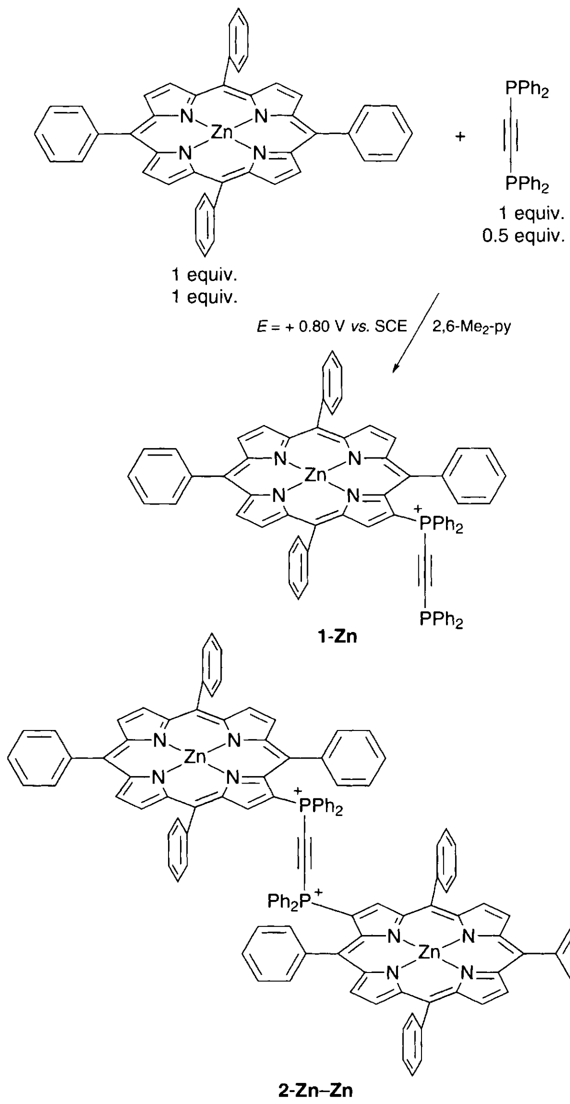
The exhaustive electrochemical oxidations were performed under standard conditions previously reported.[3] A solution of the metalloporphyrin [Zn(tpp)] (1 equiv.) and bis(diphenylphosphino)acetylene (1 equiv.) was oxidized in the presence of 2,6-dimethylpyridine (2,6Me_2-py). 2,6Me_2-py was used to trap protons which were liberated in the course of porphyrin oxidation. After maintaining the working potential at +0.80 V *vs.* SCE for 3 h, the initially violet solution turned green and the electrolysis current decreased to the initial background current value. This electrolysis gave a mixture of two products. The minor product was identified and characterized as the β-monosubstituted porphyrin **1-Zn**,[†] and the major product as the dimeric porphyrin **2-Zn–Zn**.[†] The complete separation of the mono- and di-meric forms could not be achieved with the metallated porphyrin. Pure monomer and dimer could only be obtained by demetallation to give the corresponding free bases [**1-H_2**, (22%) and **2-H_2–H_2**, (66%)].

By using 0.5 mol equiv. of bis(diphenylphosphino)acetylene only the selecting dimer **2-Zn–Zn** is produced in good yield (72%). Dimer formation in one electrochemical oxidation step is particularly significant when considering that only the monomer was generated in the case of the pyridine nucleophiles[3] under similar experimental conditions. The reactions are presented in the Scheme 1.

UV-VIS absorption spectra (Fig. 1) showed that all the porphyrins synthesized exhibited a red shift of the Soret (B) and visible (Q) bands compared to the corresponding unsubstituted porphyrins. This bathochromic shift results from the electron-withdrawing effect of the positive charge on the phosphonium cation(s). The Soret band of the dimer showed a significant broadening and its absorption coefficient was approximately half that expected. This result indicated excitonic interactions[4] between the two porphyrins rings in the dimer.

The ^1H NMR spectra are consistent with the structure assigned; the pyrrolic protons all appear downfield from those of the phenyl ring, thus demonstrating that the aromaticity of the porphyrin ring was not interrupted[5] and the typical adjacent β-H proton signals appeared at low field as characterizing the β-substitution.

In the symmetrical bis(diphenylphosphino)acetylene Lewis base, the two phosphorus atoms were equivalents and resonated as one singlet at high field (δ −33) in the ^{31}P NMR spectrum. As expected the two phosphoniums of the bis(diphenylphosphonium)acetylene bridge in the dimers **2-Zn–Zn** and **2-H_2–H_2** gave signals at lower field.[6] Two signals are



Scheme 1 Yield of **1-Zn** = 22, 0% and of **2-Zn–Zu** = 66, 72% using 1, 0.5 equiv. of $Ph_2PC{\equiv}CPPh_2$, respectively

Table 1 Electrochemical data for the studied porphyrins and diporphyrins. All potentials are given in V *vs.* SCE and were obtained from stationary (RDE) voltammetry or by cyclic voltammetry (CV) in MeCN–1,2-$C_2H_4Cl_2$ (1 : 4)–0.1 mol dm^{-3} NEt_4PF_6; working electrode is Pt

Porphyrin	Ring oxidation			Phosphonium reduction	Ring reduction	
	$E_{1/2}^{III}$	$E_{1/2}^{II}$	$E_{1/2}^{I}$		$E_{1/2}^{I}$	$E_{1/2}^{II}$
1-H$_2$			1.11(2e,irr.)	−0.93	−1.18	
2-H$_2$–H$_2$			1.32(4e,irr.)	−0.73 −1.02	−1.30(2e)	−1.52(2e)
1-Zn		1.18	0.89	−1.03	−1.22	
2-Zn–Zn	1.35(1e)	1.25(1e)	1.03(2e)	−0.73 −1.12	−1.30(2e)	

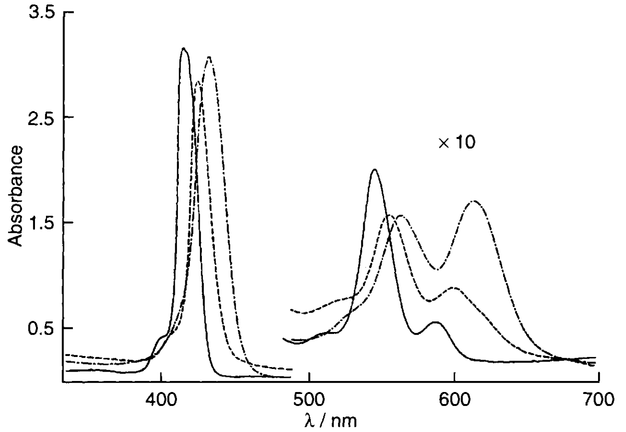


Fig. 1 UV–VIS spectra of [Zn(tpp)] (—), the monomer **1-Zn** (---) and the diporphyrin **2-Zn–Zn** (–·–) in CH_2Cl_2

observed indicating that the two cations are not equivalent and therefore that the diporphyrins are not symmetrical. In the monomer **1-H$_2$** the phosphonium and the neutral phosphorus atom are clearly discriminated with signals respectively at δ 18.95 and 3.51. The phosphorus atoms of the **1-Zn** resonated at δ 4.64 and 3.61. These two signals appeared at intermediate field compared respectively to those of the neutral and doubly charged spacer. This suggests that the single positive charge is not located only at the phosphorus atom bearing the porphyrin ring, but is partially delocalized onto the second phosphorus atom, through the acetylene triple bond.

Redox studies of the substituted monomers have shown that, in addition to the typical oxidations and reductions of the porphyrin,[3,7] a one-electron transfer corresponding to the reduction of the PPh_2^+ substituent was observed. The dimers exhibited three distinct electroactive sites, namely the diphosphonium spacer and the two adjacent porphyrins. The reduction signal of the two phosphoniums gave two distinct peaks, each corresponding to a reversible one-electron transfer. The irreversible electron transfer observed with the free bases may be explained by the instability and high reactivity of their radical cations. All electrochemical data are gathered in Table 1.

In conclusion, the bis(diphenylphosphino)acetylene ligand acts as a nucleophile allowing diporphyrins with a diphosphonium spacer bridged directly on to the *meso*-tetraphenylporphyrin rings to be obtained in one oxidation step. The strong reactivity of this unusual type of spacer and the good yield of the reaction suggest that diphosphines are promising candidates for ready and convenient coupling porphyrins. We are now testing various diphosphines which are expected to exhibit a reactivity toward porphyrin π-cation radicals that is higher than that of pyridinic nucleophiles.

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Footnote

† *Spectroscopic data*: **1-Zn**, mp > 300 °C; ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]; δ 8.84 [d, J_{cis}(HH) 4.8 Hz, 1 H, β-H], 8.800 [d, J_{cis}(HH) 4.8 Hz, 1 H, β-H], 8.798 (s, 1 H, β-H adj. to PPh_2^+), 8.77 [d, J_{cis}(HH) 4.8 Hz, 1 H, β-H], 8.768 [d, J_{cis}(HH) 4.8 Hz, 1 H, β-H], 8.63 [d, J_{cis}(HH) 4.8 Hz, 1 H, β-H], 8.17 [d, J_{cis}(HH) 4.8 Hz, 1 H, β-H], 8.11 [dd, J_o(HH) 8.8, J_m(HH) 1.8 Hz, 4 H, *o*-H of PPh_2^+], 8.01 [dd, J_o(HH) 8.1 Hz, J_m(HH) 1.5 Hz, 2 H, *o*-H of Ph adj. to PPh_2^+], 7.94–7.55 (m, 26 H, *o*- and *m*-H of Ph), 7.49 [t, J_o(HH) 7.4 Hz, 2 H, *p*-H of PPh_2], 7.41 [t, J_o(HH) 7.4 Hz, 3 H, *p*-H of Ph], 7.31 [t, J_o(HH) 7.4 Hz, 1 H, *p*-H of Ph adj. to PPh_2^+], 7.03 [t, J_o(HH) 7.4 Hz, 2 H, *p*-H of PPh_2^+]; ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C)]; δ 4.64 (s, PPh_2^+), 3.51 (s, PPh_2^+), −145.44 [spt, ^1J(PF) 700.8 Hz, PF_6^-]; UV–VIS (CH_2Cl_2): $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1}) 428 (209 200), 560 (9400), 603 (5000). Anal. Calc. for $C_{70}H_{47}F_6N_4P_3Zn$: C, 69.12, H, 3.89, N, 4.61, P, 7.64; Zn 5.37. Found: C, 69.41; H, 4.25, N, 4.74, P, 7.95, Zn, 5.56%.

2-Zn–Zn, mp > 300 °C; ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]; δ 8.87 [d, J_{cis}(HH) 4.8 Hz, 2 H, β-H], 8.82 [d, J_{cis}(HH) 4.8 Hz, 4 H, β-H], 8.80 (s, 1 H, β-H adj. to PPh_2^+), 8.79 (s, 1 H, β-H adj. to PPh_2^+), 8.78 [d, J_{cis}(HH) 4.8 Hz, 2 H, β-H], 8.65 [d, J_{cis}(HH) 4.8 Hz, 2 H, β-H], 8.18 [d, J_{cis}(HH) 4.8 Hz, 2 H, β-H], 8.16 [d, J_o(HH) 7.7 Hz, 4 H, *o*-H of PPh_2^+], 8.12 [d, J_o(HH) 7.7 Hz, 4 H, *o*-H of PPh_2^+], 8.03 [d, J_o(HH) 7.7 Hz, 4 H, *o*-H of Ph adj. to PPh_2^+], 7.90–7.10 (m, 48 H, H of Ph); ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C], δ 14.03 (s, PPh_2^+), 13.62 (s, PPh_2^+), −145.44 [spt, ^1J(PF) 700.8 Hz, PF_6^-]; UV–VIS (CH_2Cl_2): $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1}) 438 (215 600), 569 (10 600), 623 (11 800). Anal. Calc. for $C_{114}H_{74}F_{12}N_8P_4Zn_2$: C, 67.17; H, 3.66; N, 5.50; P, 6.08; Zn, 6.41. Found: C, 67.32; H, 3.94; N, 5.42; P, 6.32; Zn, 6.52%.

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