A First Series of Dimeric Porphyrins Electrochemically Linked with Diphosphonium Bridges

Laurent Ruhlmann[b] and Alain Giraudeau*[a]

Keywords: Electrochemistry / Oxidation / Phosphorus / Synthetic methods / Porphyrins

The synthesis of dimeric porphyrins with a diphosphonium bridge in a direct one-pot electrochemical reaction is reported. The variation in the yields of this coupling reaction depends on the conditions of the electrolysis, and was examined mainly with respect to the detected by-products. An interpretation of this selective formation of dimers is proposed. Monomers and trimers were also obtained. These new compounds were characterized by ^{1}H NMR, ^{31}P NMR, UV/Vis spectroscopy and microanalysis. Important excitonic interactions were observed when the two porphyrin chromophores were linked with a short diphosphonium bridge. The NMR-spectroscopic data suggest that isomers are present in solution. Electrochemical data indicate that the two phosphonium groups of the bridge are not electrochemically independent in the zinc dimers.

Introduction

The synthesis of porphyrin dimers is being extensively pursued as these compounds provide models for the study of electron-transfer processes. Over the years, many models with various extended porphyrin structures have been prepared and studied with a particular interest in the dependence of the geometric factors on their physical properties.[1−8] The structural flexibility of the models is largely determined by the nature of the bridge. The totally rigid, covalently linked bis(porphyrins)[9−13] have chromophores fixed at well-defined distances and orientations, whereas conformational effects can be observed with less rigid systems.[14−16] To observe efficient interactions between the different chromophores, a large variety of bridging chains have been used as spacers in the building of dimers, but only a few reports[17−20] have been devoted to phosphanylporphyrins. Electrochemistry has been shown to be an appropriate synthetic tool in the coupling of porphyrins.[21−25] Recently, we reported a dimeric porphyrin,[23] with a diphosphonium bridge, which was synthesized by controlled potential electrolysis, a method that readily provides a convenient access to a large variety of new homometallated porphyrin dimers and trimers in a direct one-pot electrochemical reaction. This paper demonstrates the power of this approach and describes the efficient synthesis of various diphosphonium-bridged porphyrins using more or less rigid diphosphanes with variable length (Figure 1).

[a] Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, U.M.R. C.N.R.S. no. 7512, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France
[b] Laboratoire de Chimie Physique, Equipe d'Electrochimie et de Photoélectrochimie, U.M.R. C.N.R.S. no. 8000, Université Paris-Sud
Bâtiment 420, 91405 Orsay Cedex, France

Physical characteristics of the synthesized porphyrins have been analyzed to identify the interactions between the different moieties in the dimers and the trimers.

Results

Electrosynthesis

The starting point for the synthesis is the electrochemical oxidation of (*meso*-tetraphenylporphyrin)zinc (ZnTPP) in the presence of various di- and triphosphanes. The oxidation waves of ZnTPP are reversible one-electron reactions in CH_3CN/1,2-$Cl_2C_2H_4$ (1:4).[26−28] In the presence of diphosphanes or ARPHOS, the second oxidation step became irreversible (Figure 2) and a new cathodic peak appeared, as observed in the reduction of electrochemically generated isoporphyrins.[28−31] Only the first oxidation step of ZnTPP was taken into account in this work.

In a typical experiment, a solution of the metalloporphyrin ZnTPP (1 equiv.) and bis(diphenylphosphanyl)methane (0.5 equiv.) was oxidized in the presence of 2,6-lutidine (2,6-Lut). 2,6-Lut was used to trap protons liberated during the course of porphyrin oxidation[23] and to prevent diphosphane-induced demetallation of ZnTPP before electrolysis. After maintaining the working potential at +0.85 V vs. SCE for 3 h, the initial violet solution turned green. The decrease in the oxidation current was not exponential with time. When this current reached the residual current measured in the absence of electroactive moieties, the electrolysis was stopped. The number of Coulombs consumed calculated from the recorded current−time curve $i = f(t)$ indicated that 2 Faradays per mol of ZnTPP were consumed in the reaction. After extraction and purification (see Exp. Sect.) the dimer **1-Zn-Zn** was characterized as the only new bis(porphyrin), obtained in 81% yield.

Increasing the diphosphane concentration caused a drastic decrease in the yield of the dimer, even in the presence

  1434−1948/01/0303−0659 $ 17.50+.50/0

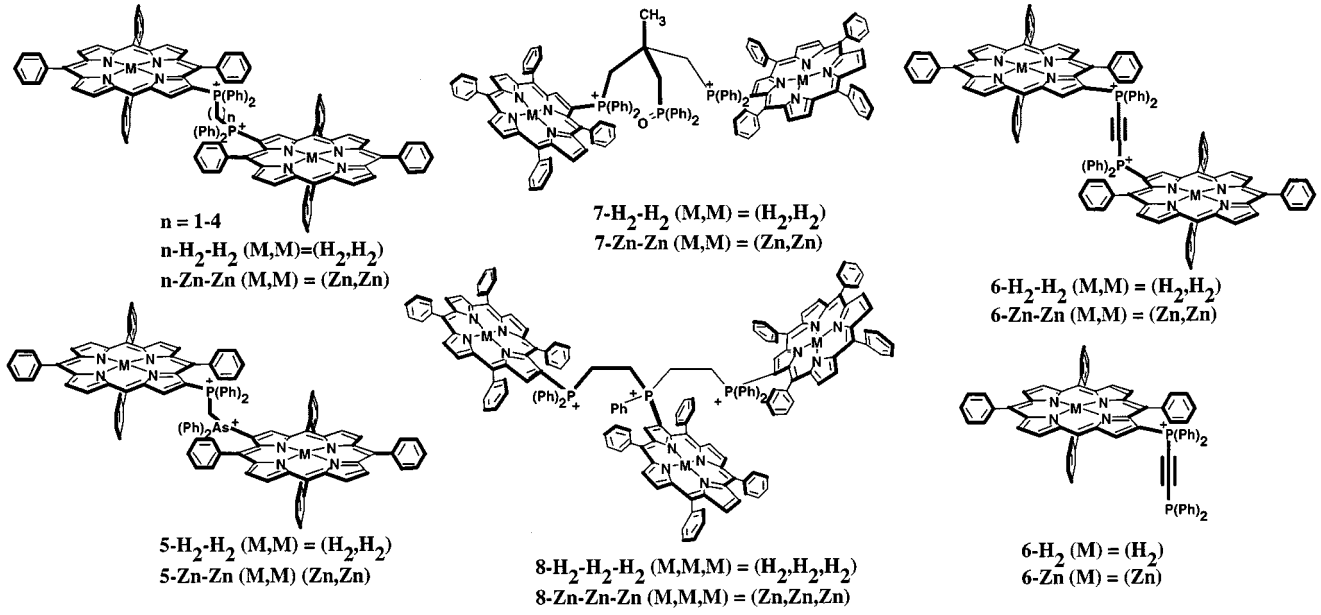

Figure 1. Porphyrins synthesized in this study

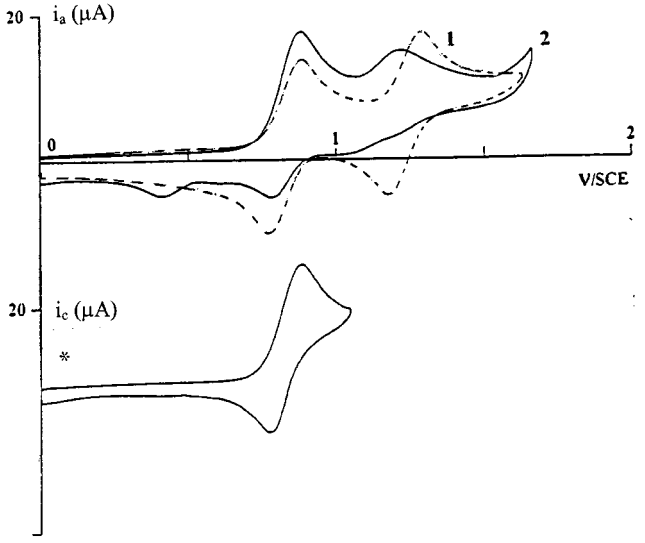

Figure 2. Cyclic voltammetry of ZnTPP in the absence of [1) dotted line] and in the presence of [2) full line] 1,2-bis(diphenylphosphanyl-ethane) (10 equiv.); *: first oxidation step only, in both cases; $CH_3CN/1,2\text{-}Cl_2C_2H_4$ (1:4) + T.E.A.PF_6 (0.1 M); working electrode Pt (v = 100 mV·s^{-1})

of a large excess of 2,6-Lut. No dimer was obtained when more than 10 equiv. of diphosphanes were used. This unexpected feature is interpreted in the discussion on the analysis of the side-products of the reaction. Diphosphane oxide and/or violin were recovered in these experiments; the overall yields of these compounds were high when using high concentrations of diphosphane and 2,6-lutidine.

By using 0.5 mol-equiv. of diphosphane (0.33 mol-equiv. of triphosphane in the case of the trimer **8-Zn-Zn-Zn**), only the desired dimers (or trimer) were produced in good yield.

In the present electrosynthesis, the formation of the dimers is described by Equation (1).

$$2\ P + Nu\text{-}\square\text{-}Nu \xrightarrow{E^1_{ox}} (P\text{-}\beta\text{-}Nu\text{-}\square\text{-}Nu\text{-}\beta\text{-}P)^{2+} + 4\ e^- + 2\ H^+ \quad (1)$$

(P = ZnTPP, Nu-□-Nu = diphosphane)

β-Monosubstituted porphyrin was also formed during the synthesis of the dimer **6-Zn-Zn**, in the presence of more than 0.5 equiv. of bis(diphenylphosphanyl)acetylene, as already described.[23]

UV/Vis Absorption Spectra

All the synthesized porphyrins exhibit a red shift of the Soret (B) and visible (Q) bands relative to the porphyrin subunits ZnTPP and H_2TPP. Complete UV/Vis data are reported in the Exp. Sect. for the electrosynthesized porphyrins. This bathochromic shift results from the electron-withdrawing effect of the positive charge located on the phosphonium cation(s). In the case of the metallated dimers, the Soret band shows significant broadening and its extinction coefficient is less intense than expected. These results suggest the presence of excitonic interactions between the two porphyrin rings in the dimers. These effects are greatly enhanced in the short-bridged **1-M-M** dimers (M = Zn and Cu) as shown in Figure 3 by the large red shift and by the splitting of the Q bands associated with a broad Soret band, with an extinction coefficient that is the lowest of those observed in the case of the **1-Zn-Zn** dimer.

This is clearly the result of exciton coupling which has been reported to become important when two porphyrin moieties are brought into close proximity[32−34] and/or when going from the nonmetallated porphyrin to the metallated parent.[34]

^{1}H NMR Spectra

The ^{1}H NMR spectra of the monomers, dimers and trimers show the well-known downfield shift of the aro-

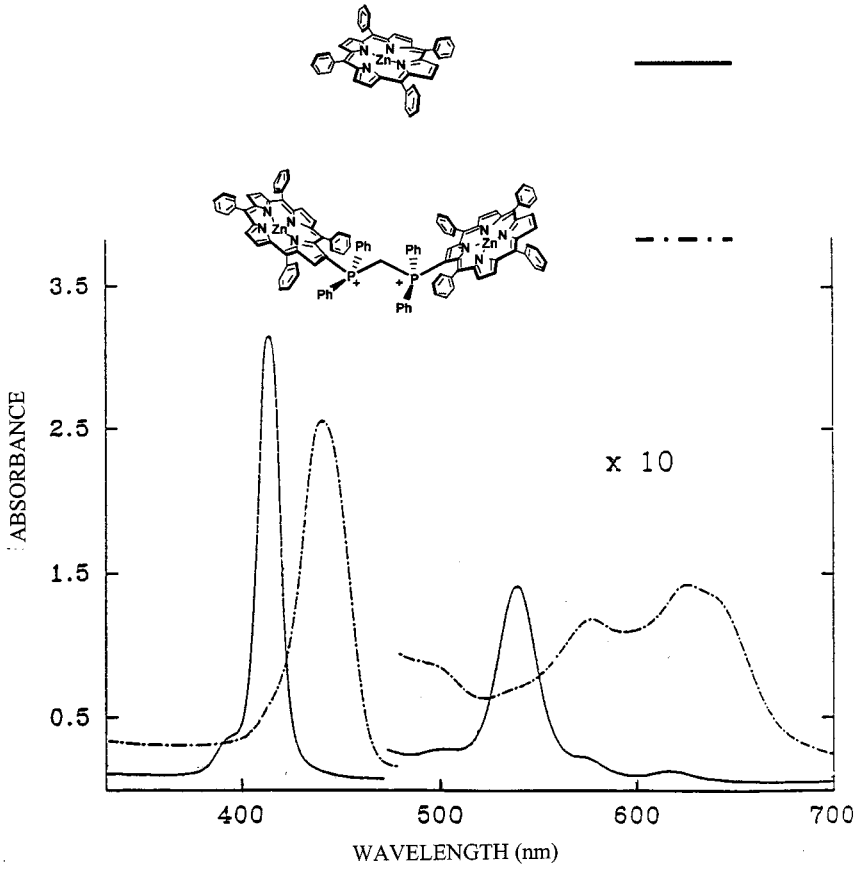

Figure 3. UV/Vis absorption spectra of the bis(porphyrin) **1-Zn-Zn** and of its monomeric subunit in CH_2Cl_2

matic proton signals of the porphyrin ring which characterizes the β-substitutions.[35] In the porphyrin rings of the dimers, the two β-H protons adjacent to the spacer give two distinct well-separated singlets, whereas the other β-proton signals appear as six doublets. The signals for the alkyl protons of the spacers are further downfield than those of the neutral ligands as owing to the presence of a positive charge on the phosphonium group. (For a full assignment, see Exp. Sect.) These protons coalesce into broadened signals or complex multiplets, with a splitting of the signal for the protons of the $-CH_2-$ groups bearing the phosphonium cations. A typical spectrum,[36] illustrated for the dimer **3-H_2-H_2** (Figure 4) shows a broad peak at $\delta \approx 2.42$, corresponding to the internal $-CH_2-$ of the linker and two distinct multiplets at $\delta = 2.80$ and 3.00, corresponding to the external $-CH_2-$ groups.

Such a distinct pair of multiplets is not observed in the corresponding neutral diphosphane which gives a triplet at $\delta = 2.25$. The appearance of two sets of resonances for the protons of the CH_2 groups bearing the phosphorus atoms as well as for the adjacent β-H protons, whose corresponding resonance signals are separated by $\Delta\delta = 0.03$ in the synthesized dimers and trimers, indicates the presence of a mixture of two isomers (Table 1). This is in agreement with previous studies of dimeric porphyrin systems[32,37–39] which connect two rings through their β-pyrrole positions. In particular, conformational analysis predicts a great conformational freedom when the two phenyl groups of the porphyrin unit are not substituted.[39] Furthermore, one of the β-H resonance doublets is shifted significantly downfield from the others. This could suggest that it experiences more shielding than the others, and may indicate the position of the phosphorus-linked phenyl groups.

The signals for the inner N−H protons of all the free-base porphyrins appear upfield as singlets and ruled out a cofacial conformation of the dimers which would induce a large upfield shift of the internal N−H protons[40] that is not observed.

^{31}P NMR Spectra

In the different neutral diphosphanes, the two phosphorus atoms are equivalent and their signals appear upfield as a singlet. In the bis(2-diphenylphosphanylethyl)-phenylphosphane, the signals of the two lateral phosphorus atoms appear as a doublet at $\delta = -13.15$, whereas the central atom gives a triplet at $\delta = -17.15$.

As expected, the two phosphonium cations of the dimers give rise to signals further downfield. Two well-separated signals are observed. A clear-cut evolution of these signals is depicted by the increase in the relative chemical shift $\Delta\delta$ (Table 1) between the two phosphonium groups which correlates with the increase in the length of the bridge linking the porphyrin subunits. These two signals indicate that the two phosphonium cations are in different environments. This result is not surprising because it is energetically not

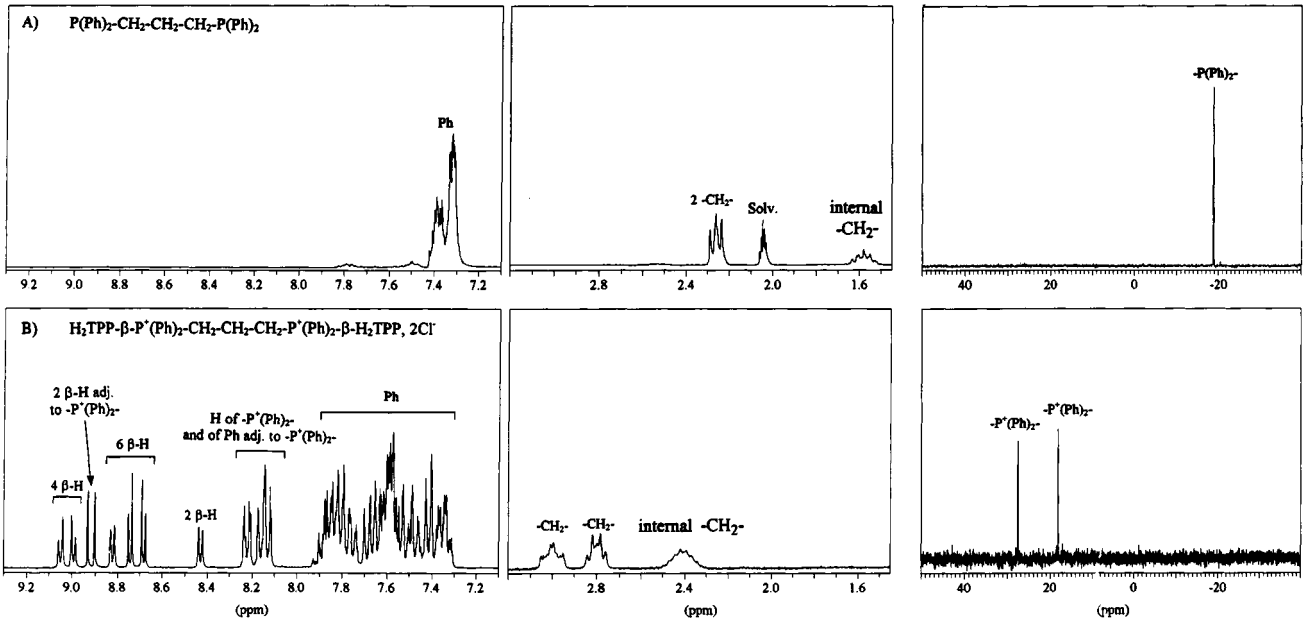

Figure 4. ^{1}H NMR and ^{31}P NMR spectra of A) 1,3-bis(diphenylphosphanyl)propane in [D_6]acetone; B) the bis(porphyrin) **3-H_2-H_2** in [D_6]acetone; for the region $\delta = 3.2-1.5$, see ref.[36]

Table 1. ^{31}P NMR: chemical shifts ($\Delta\delta$) of the phosphonium and phosphane* in the series; ^{1}H NMR: chemical shifts ($\Delta\delta$) of the β-H protons adjacent to the phosphonium in the series

Porphyrins	δ $P^+(Ph)_2$	or δ $P(Ph)_2$	$\Delta\delta$	δ β-H adj.		$\Delta\delta$
1-Zn-Zn	20.02	18.64	1.38	9.08	9.05	0.03
2-Zn-Zn	31.55	25.11	6.44	8.82	8.79	0.03
3-Zn-Zn	28.19	18.68	9.51	8.91	8.88	0.03
4-Zn-Zn	29.67	18.52	11.15	8.94	8.91	0.03
5-Zn-Zn	23.03		–	9.10	9.07	0.03
6-Zn	4.64	3.51*	–	7.80		–
6-Zn-Zn	14.03	13.62	0.41	8.80	8.79	0.01
7-Zn-Zn	26.43	15.88	10.55	9.71	9.68	0.03
1-H_2-H_2	19.83	18.08	1.75	9.08	9.04	0.04
2-H_2-H_2	29.70	26.81	2.89	8.76	8.73	0.03
3-H_2-H_2	27.66	18.08	9.58	8.96	8.93	0.03
4-H_2-H_2	30.02	21.02	9.00	9.01	8.98	0.03
5-H_2-H_2	23.54		–	9.13	9.10	0.03
6-H_2	18.95	3.81*	–	8.93		–
6-H_2-H_2	24.80	16.51	8.29	9.06	9.02	0.04
7-H_2-H_2	25.87	15.61	10.24	9.82	9.79	0.03

favorable to have a dimer when the two phosphorus atoms are in identical environments.

There is clear evidence that this is the case: Both the $(Ph)_2P(CH_2)P(Ph)_2$ and $(Ph)_2P(CH_2)_2P(Ph)_2$ linkages show doublets in the ^{31}P spectra (see Exp. Sect.) indicating the coupling of the phosphorus atoms in different environments. It is quite likely that this is true for the longer congeners, but that the coupling is too small to show it.

Electrochemistry

All electrochemical data are collated in Table 2. Owing to adsorption phenomena that occurred at the Pt electrode and inhibited the reduction signals, the cathode redox behavior of the different synthesized porphyrins was examined on an Hg electrode. The number of exchanged electrons for each system was determined by exhaustive coulometry, and by comparing the limiting currents of the different waves characterizing a given system.

The observed electron transfers were assigned to the π-systems of the porphyrins[41–42] or to the phosphonium cations,[43] based on their known general redox characteristics. This assignment was also achieved by the use of the recorded spectroelectrochemical data. All the spectra show typical features of porphyrin π-cation or π-anion radical complexes: broad α,β bands and a Soret band with decreased intensity as illustrated in Figure 5.

Redox behavior of the substituted monomers has previously been reported.[23] The dimers and trimers exhibit three distinct electroactive sites, namely the spacer and the two or three lateral porphyrin units. The electrochemical ring oxidations and reductions of the porphyrin subunits occur on both sides of the electroactivity range of the spacer. The oxidation potentials of the porphyrins in the dimers and trimers are more positive than the corresponding ones in the unsubstituted subunits. This positive shift may be ascribed to the electron-withdrawing effect of the positively charged spacer.[44] The close values observed between the reduction potentials of the dimers and trimers, and those of the corresponding porphyrin subunits were expected because this reduction occurred in neutral molecules,

Table 2. All potentials in V/SCE obtained from stationary (RDE) or cyclic voltammetry in $CH_3CN/1,2\text{-}Cl_2C_2H_4$ (1:4), T.E.A.PF_6 (0.1 M) medium; transfers are reversible one-electron steps, except when noted; working electrode: Pt

Porphyrins	Ring oxidation			Reduction of $P(Ph)_2^+$ and/or $As(Ph)_2^+$		Ring reduction		
	$E^{II}_{1/2}$		$E^{I}_{1/2}$	$E^{II}_{1/2}$	$E^{I}_{1/2}$	$E^{I}_{1/2}$		$E^{II}_{1/2}$
H_2TPP	1.34		1.10			−1.10		−1.48
ZnTPP	1.16		0.80			−1.37		−1.75
CuTPP	1.33		1.06			−1.22		−1.68
Violine	1.52^{irr}		1.08^{irr}			−0.82		-1.30^{irr}
1-H_2-H_2			$1.22^{2e,irr}$	$-0.74^{2e\ [a]}$		$-1.10^{2e[a]}$		$-1.55^{2e[a]}$
1-Zn-Zn	1.17^{2e}		0.97^{2e}	$-1.04^{[a]}$	$-1.16^{[a]}$	$-1.42^{2e[a]}$		$-1.77^{2e[a]}$
1-Cu-Cu	1.22^{2e}		0.98^{2e}	$-0.97^{[a]}$	$-1.14^{[a]}$	−		$-1.72^{2e[a]}$
2-H_2-H_2			$1.28^{2e,irr}$	$-0.74^{2e[a]}$		$-1.10^{2e[a]}$		$-1.55^{2e[a]}$
2-Zn-Zn	1.23^{2e}		1.02^{2e}	$-0.99^{[a]}$	$-1.17^{[a]}$	$-1.38^{2e[a]}$		$-1.76^{2e[a]}$
3-H_2-H_2			$1.32^{2e,irr}$	$-0.73^{2e[a]}$		$-1.08^{2e[a]}$		
3-Zn-Zn	1.40^{2e}		1.10^{2e}	$-1.00^{[a]}$	$-1.11^{[a]}$	$-1.37^{2e[a]}$		$-1.75^{2e[a]}$
4-H_2-H_2			$1.31^{2e,irr}$	$-0.70^{2e[a]}$		$-1.05^{2e[a]}$		$-1.73^{2e[a]}$
4-Zn-Zn	1.19^{2e}		0.90^{2e}	$-0.94^{[a]}$	$-1.10^{[a]}$	$-1.35^{2e[a]}$		$-1.68^{2e[a]}$
5-H_2-H_2			$1.34^{2e,irr}$	$-0.63^{2e[a]}$		$-0.98^{2e[a]}$		$-1.38^{2e[a]}$
5-Zn-Zn	1.32^{2e}		1.07^{2e}	$-0.97^{[a]}$	$-1.12^{[a]}$	$-1.34^{[a]}$	$-1.66^{[a]}$	$-2.08^{2e[a]}$
6-H_2			1.11^{irr}	$-0.93^{[a]}$		$-1.18^{[a]}$		
6-Zn	1.18		0.89	$-1.04^{[a]}$		$-1.22^{[a]}$		$-1.41^{[a]}$
6-H_2-H_2			$1.32^{2e,irr}$	$-0.73^{[a]}$	$-1.02^{[a]}$	$-1.30^{2e[a]}$		$-1.52^{2e[a]}$
6-Zn-Zn	1.35	1.25	1.03^{2e}	$-0.73^{[a]}$	$-1.12^{[a]}$	$-1.30^{2e[a]}$		
7-H_2-H_2			$1.34^{2e,irr}$	$-0.62^{2e[a]}$		$-1.01^{2e[a]}$		
7-Zn-Zn	1.29^{2e}		1.00^{2e}	$-0.92^{[a]}$	$-1.10^{[a]}$	$-1.38^{2e[a]}$		$-1.68^{2e[a]}$
8-H_2-H_2-H_2			$1.27^{3e,irr}$	$-0.67^{3e[a]}$		$-0.94^{3e[a]}$		
8-Zn-Zn-Zn	$1.37^{3e,irr}$		1.02^{3e}	$-0.93^{3e[a]}$		$-1.27^{3e[a]}$		$-1.65^{3e[a]}$

[a] Potentials obtained by polarography (dropping mercury electrode).

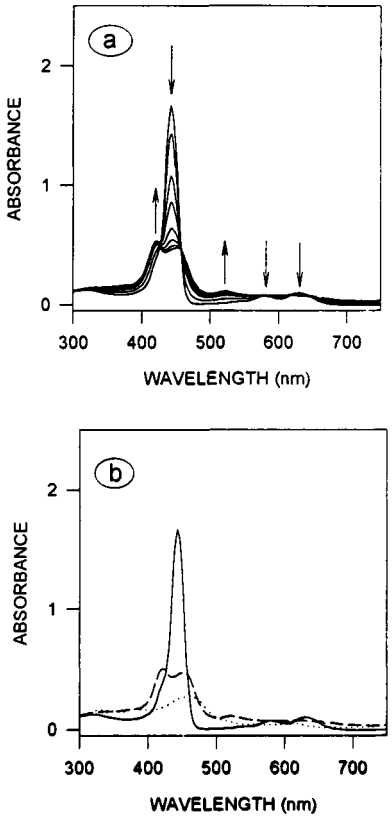

Figure 5. a) UV/Vis absorption spectra recorded during the oxidation of **4-Zn-Zn** in $CH_3CN/1,2\text{-}Cl_2C_2H_4$ (1:4) + T.E.A.PF_6 (0.1 M) at 1.0 V vs. SCE; b) UV/Vis absorption spectra of **4-Zn-Zn**: (− − − −) unoxidized form, (------) two-electron oxidized species (first wave, 1.00 V), and (·····) four-electron oxidized species (second wave, 1.27 V)

and the positively charged spacers become neutral before the reduction of the side porphyrin rings. In the synthesized porphyrins, each of the different oxidation and reduction steps observed appears as reversible or quasi-reversible, with an exchange of one electron per porphyrin subunit, except for the oxidation step of the nonmetallated complexes. The irreversible two-electron transfer observed in the free-base porphyrins may be explained by the instability of the radical cation.[24]

The reduction signal of the phosphonium cations appeared in CV at −0.70 V vs. SCE for the free bases and −1.1 V vs. SCE for the zinc complexes. This cathode signal corresponds to a two-electron reduction step. Two distinct reduction peaks are observed in all the zinc dimers and in the **6-H_2-H_2** dimer, each corresponding to a reversible electron transfer. This feature indicates that the two phosphonium cations are not independent.

By analyzing both the redox and UV/Vis results of the synthesized dimers, a common behavior appeared that depended on the nature (metallated or not) of these compounds. While the free-base dimers showed only minimal excitonic effects, the corresponding metallated dimers showed significant interactions between the chromophores. Similarly, the two phosphonium cations appeared as independent electroactive centers in the free-base dimers, but showed an interaction in their metallated homologs. This behavior could be analyzed as a consequence of δ−π interactions present in the metalloporphyrins. These interactions would thus favor a coupling between the different subunits (spacer, porphyrin). Consequences of these δ−π interactions have already been reported with the redox behavior of substituted metalloporphyrins.[44]

Discussion

Previous results on the electrochemical preparation of porphyrin dimers with a viologen as a spacer have established that the synthesis is achieved by means of a two-electron reaction per mol of porphyrin.[24] This sequence was also validated in the synthesis of the above porphyrins.

Nevertheless, a large increase in the diphosphane present in solution somewhat limits the range of the experiments. When a large excess of diphosphanes is added, the concentration of the 2,6-lutidine has to be increased to prevent the diphosphane-induced demetallation of ZnTPP. Owing to the lengthy electrolysis and the hygroscopic nature of 2,6-lutidine, an increase in its concentration leads to the introduction of significant amounts of water in the coulometric solution. Thus, if the hydroxide ions become the main nucleophile present in solution and if they react with the generated π-cation radical of the porphyrin, then, hydroxyisotetraphenylporphyrin is produced. Further α-attack of the OH^- ions would lead to violin formation, as already described by Dolphin et al.[45] The final purple complex isolated as a by-product exhibited electronic and ^1H NMR spectra similar to violins, in which only three of the pyrrole rings are conjugated. When phosphanes are the main nucleophiles in solution, phosphonium isoporphyrin would be formed before further α-attack of the OH^- ions would take place. This α-attack would give betaine and a four-membered ring transition state[46] (intermediate in the Wittig reaction), leading to the formation of (*meso*-tetraphenylporphyrin)zinc and phosphane oxide. This reaction would explain the drastic decrease in the yield of the dimers and of the characterized side-products collected when the concentration of 2,6-lutidine and/or of the diphosphanes was increased.

The most intriguing feature in this synthesis is the selective formation of dimers even with excess nucleophile. This was not observed with the rigid linear 4,4′-bipyridine linker. This result may be explained if one considers that the phosphorous atoms act as more efficient nucleophiles than the nitrogen atoms in these experiments, and that the phosphorus ligands used as linkers are flexible chains. The fact that both monomers and dimers are formed when the more rigid acetylene chain is used agrees with this hypothesis. This is also supported by the higher yield of desired dimer observed in the case of the long flexible diphosphane: 1,4-bis(diphenylphosphanyl)butane chain. Steric hindrance is most probably the reason why only two porphyrin units are linked with 1,1,1-tris(diphenylphosphanylmethyl)ethane, while the trimer **8-Zn-Zn-Zn** is formed when using the stretched bis(2-diphenylphosphanylethyl)phenylphosphane chain.

Conclusion

The results presented in this paper clearly illustrate that phosphorus ligands act as powerful nucleophiles which allow electrochemical β-substitutions on *meso*-tetraphenylporphyrins. When 0.5 mol-equiv. of diphosphanes is used, only the dimers are produced in good yields (> 60%). Selective dimer formation in a one-pot electrochemical step is particularly noteworthy when considering that only the monomer was generated in the case of the 4,4′-bipyridine nucleophiles.

Evidence for excitonic coupling is observed in the dimers. This effect is particularly enhanced in the metallated **1-M-M** dimers and demonstrates that bridging with the short 1,2-bis(diphenylphosphonium)methane chain keeps the two porphyrin chromophores in an interactive proximity. Isomers are therefore possible because of the two different electrophilic β-sites. Both ^1H NMR and ^{31}P NMR spectroscopy results suggest that geometric factors modulate the mutual interactions of the two porphyrin units in the dimers. The preparation of the trimer further validates this electrochemical method as a direct route to oligomeric porphyrins linked by phosphonium bridges.

Experimental Section

I. Materials: All solvents and chemicals were of reagent-grade quality, purchased commercially and used without further purification unless otherwise stated. CH_2Cl_2, for use in exhaustive electrolysis or UV/Vis spectrophotometry, was heated at reflux in the presence of CaH_2 and then distilled off. The supporting electrolyte tetraethylammonium hexafluorophosphate (T.E.A.PF_6) was used without further purification. All the diphosphanes and triphosphanes were purchased from Strem Chemical Inc. Thin-layer chromatography (TLC) was performed on commercially prepared alumina or silica gel plates purchased from Roth Sochiel.

II. Apparatus: All electrochemical measurements were carried out under argon at 25 °C on a dropping mercury electrode or on a disk electrode. Voltammetric data were obtained with a standard three-electrode system using a Bruker E 130 M potentiostat and a high-impedance millivoltmeter (minisis 6000, Tacussel). Current−potential curves were obtained from an Ifelec If 3802 X-Y recorder. The working electrode was a platinum disk (E.D.I. type, Solea Tacussel) with a surface area of 3.14 mm^2. A platinum wire was used as the auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE) that was electrically connected to the studied solution by a junction bridge filled with the corresponding solvent/supporting electrolyte solution. − For polarographic and differential pulse polarographic experiments, a signal generator (GSATP from Solea-Tacussel) was associated with a potentiostatic device (Solea-Tacussel), comprising of a potentiostat (PRT 20−2X) and a voltage pilot unit (Servovit 2). − Coulometric measurements and quantitative electrochemical synthesis were performed either in a standard 50-mL cell or in a large 300-mL cell. In the standard cell, the working electrode was a platinum wire (Ø = 0.8 mm) with a length of 60 cm. In the large cell, the working electrode was a cylindrical platinum grid (Ø = 5 cm, h = 7 cm). For the controlled-potential electrolysis, the anodic and cathodic compartments were separated by a fritted glass disk to prevent diffusion of the electrogenerated species. − The spectrophotometric analyses were performed with a Hewlett−Packard 8452 A diode array spectrometer. The thin-layer spectroelectrochemical cell has been described previously.[47] − UV/Vis spectra were recorded with a Shimazu UV-260 spectrophotometer and a Hewlett−Packard 8452 A diode array spectrometer. − ^1H and ^{31}P NMR spectra were

obtained in [D_6]acetone with a Bruker AC 300 spectrometer (300 MHz and 120 MHz, respectively). − Elemental analyses were performed by the microanalysis services of the Chemical Department of I.U.T. Sud (Strasbourg).

III. Synthesis: Compounds H_2TPP, ZnTPP and CuTPP were prepared and purified by known procedures.[48,49]

Electrochemical Synthesis. − General Procedure: Prior to electrolysis, the corresponding mixtures were stirred and degassed by bubbling argon through the solution for 10 min. The desired working potential was then applied. During anodic oxidation, the electrolyzed solution was continuously stirred and maintained under argon. The course of the reaction was monitored by TLC (silica gel/1% CH_3OH in CH_2Cl_2) and UV/Vis spectrophotometry. Electrolysis was stopped when the current reached the residual current measured in the absence of electroactive material (i.e., 0.1 M solution of T.E.A.PF_6). After electrolysis, the solvents were removed in a rotary evaporator. The residue was dissolved in a minimum amount of CH_2Cl_2; the mixture was then poured into water, and the organic layer was washed three times. The organic solution was dried with $CaSO_4$, concentrated (to 5 mL), and then purified by chromatography. Typical preparation and characterization of a dimer **1-Zn-Zn**, **1-H_2-H_2** and **1-Cu-Cu** are reported below.

1-Zn-Zn: ZnTPP (200 mg, 2.95×10^{-4} mol), 2,6-Lut (50 μL, 4.30 10^{-4} mol) and $(Ph)_2P-CH_2-P(Ph)_2$ (57 mg, 1.475×10^{-4} mol) were dissolved in a solution of T.E.A.PF_6 (0.1 M, 300 mL) in 1,2-$Cl_2C_2H_4$/CH_3CN (4:1). The electrolysis was carried out for 6 h at +0.85 V vs. SCE. After the workup, as described above, the organic extract (5 mL) was purified by chromatography on silica gel. The first fraction (eluted with CH_2Cl_2) was unchanged ZnTPP (32 mg, 0.47×10^{-4} mol). The desired product was eluted with a mixture of CH_2Cl_2/CH_3OH (99:1). After evaporation of the solvent, **1-Zn-Zn** was recrystallized from CH_2Cl_2/*n*-hexane to afford the product as green crystals (242 mg, 1.19×10^{-4} mol, 81%). − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$): = 442 (186900), 580 (9100), 624 (10800), 644 nm (10700). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 9.08 [s, 1 H, β-H adj. to $-P(Ph)_2-^+$], 9.05 [s, 1 H, β-H adj. to $-P(Ph)_2-^+$], 8.85 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.83 (d, J_{cis} = 4.80 Hz, 4 H, β-H), 8.79 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.64 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.17 [dt, J_o = 7.71 Hz, J_m= 1.47 Hz, 4 H, *o*-H of $-P(Ph)_2-^+$], 8.15 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.13 [dt, J_o= 7.71 Hz, J_m = 1.47 Hz, 4 H, *o*-H of $-P(Ph)_2-^+$], 8.02 [dt, J_o = 7.71 Hz, J_m = 1.47 Hz, 4 H, *o*-H of Ph adj. to $-P(Ph)_2^+$], 7.84−7.49 (m, 36 H, H of Ph), 7.40 (t, J_o = 7.71 Hz, 3 H, *p*-H of Ph), 7.39 [t, J_o = 7.71 Hz, 3 H, *p*-H of Ph], 7.13 [t, J_o = 7.71 Hz, 2 H, *p*-H of Ph adj. to $-P(Ph)_2^+$], 7.00 [t, J_o = 7.71 Hz, 4 H, *p*-H of $-P(Ph)_2-^+$], 3.71 (d, ^1J = 12.12 Hz, 1 H, $-CH_2$), 3.65 (d, ^1J = 12.12 Hz, 1 H, $-CH_2-$). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 20.02 [d, $^2J_{P-P}$ = 15.01 Hz, $-P(Ph)_2^+$], 18.64 [d, $^2J_{P-P}$ = 15.01 Hz, $-P(Ph)_2-^+$], −145.44 (sept, $^1J_{P-F}$ = 700.80 Hz, PF_6^-). − $C_{113}H_{76}F_{12}N_8P_4Zn_2$ (2028.54): calcd. C 66.91, H 3.77, N 5.52, P 6.11; found C 66.80, H 3.87, N 5.61, P 6.08. − M.p. > 300 °C.

1-H_2-H_2: Hydrochloric acid (25%, 100 mL) was added to a solution of **1-Zn-Zn** in acetone, and the mixture was stirred for 30 min at room temperature. After the addition of water (200 mL), the organic layer was separated, washed with water and neutralized with saturated sodium acetate solution. The solution was again washed with water, dried with $CaSO_4$ and concentrated. Recrystallization of the residue with CH_2Cl_2/*n*-hexane gave **1-H_2-H_2** in almost quantitative yield. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 432 (461600), 530 (22600), 560 (8200), 604 (8300), 670 nm (16000). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 9.08 [s, 1 H, β-H adj. to $-P(Ph)_2-^+$], 9.04 [s, 1 H, β-H adj. to $-P(Ph)_2-^+$), 9.04 (d, J_{cis} = 4.41 Hz, 2 H, β-H), 9.02 (d, J_{cis} = 4.41 Hz, 2 H, β-H), 8.82 (d, J_{cis} = 4.41 Hz, 2 H, β-H), 8.76 (d, J_{cis} = 4.41 Hz, 2 H, β-H), 8.71 (d, J_{cis} = 4.41 Hz, 2 H, β-H), 8.40 (d, J_{cis} = 4.41 Hz, 2 H, β-H), 8.24 [d, J_o = 7.35 Hz, 4 H, *o*-H of $-P(Ph)_2-^+$], 8.18 [d, J_o = 7.35 Hz, 4 H, *o*-H of $-P(Ph)_2-^+$], 8.11 [d, J_o = 7.35 Hz, 4 H, *o*-H of Ph adj. to $-P(Ph)_2-^+$], 7.85−7.39 (m, 42 H, H of Ph), 7.21 [t, J_o = 6.99 Hz, 2 H, *p*-H of Ph adj. to $-P(Ph)_2-^+$], 7.05 (t, J_o = 6.99 Hz, 4 H, *p*-H of Ph), 3.72 (d, ^1J = 12.12 Hz, 1 H, $-CH_2-$), 3.67 (d, ^1J = 12.12 Hz, 1 H, $-CH_2-$), −2.47 (s, 4 H, N−H). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 19.83 [d, $^1J_{P-C}$ = 14.18 Hz, $-P(Ph)_2^+$], 18.08 [d, $^2J_{P-P}$ = 14.18 Hz, $-P(Ph)_2$]. − $C_{113}H_{80}Cl_2N_8P_2$ (1682.80): calcd. C 80.65, H 4.79, N 6.66, P 3.68; found C 80.81, H 4.83, N 6.52, P 3.60. − M.p. > 300 °C.

1-Cu-Cu: 1-H_2-H_2 was dissolved in a CH_2Cl_2/CH_3OH (1:1) mixture with an excess of $Cu^{II}(CH_3COO)_2 \cdot H_2O$ (10 equiv.). The mixture was heated at reflux for 3 h, and after cooling, was treated with tetraethylammonium hexafluorophosphate (100 equiv.). After evaporation of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2, washed with water (4 times) and dried with $CaSO_4$ for 6 h. The solution was concentrated to 5 mL in a rotary evaporator and then purified on a silica gel column (CH_2Cl_2) to afford black−violet crystals of **1-Cu-Cu** in more than 90% yield. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 440 (246500), 576 (13600), 625 (16500), 643 nm (15000). − $C_{113}H_{76}Cu_2F_{12}N_8P_4$ (2024.89): calcd. C 66.97, H 3.78, N 5.53, P 6.11; found C 66.81, H 3.82, N 5.48, P 6.01. − M.p. > 300 °C.

2-Zn-Zn: The same procedure as described for **1-Zn-Zn** was applied using ZnTPP (200 mg, 29.5 mmol, 1 equiv.), 2,6-Lut (50μL, 43 mmol) and $(Ph)_2P-CH_2-CH_2-P(Ph)_2$ (57 mg, 14.8 mmol, 0.5 equiv.). The product **2-Zn-Zn** (196 mg; 9.6 mmol) was obtained in 65% yield. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 436 (420800), 568 (18500), 614 nm (22100). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$), 25 °C]: δ = 9.04 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.91 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.82 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.79 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.76 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.68 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.66 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.16 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.12 [d, J_o = 6.60 Hz, 4 H, *o*-H of $-P^+(Ph)_2-$], 8.04 [d, J_o = 7.70 Hz, 4 H, *o*-H of $-P^+(Ph)_2-$], 8.00 [d, J_o = 6.60 Hz, 4 H, *o*-H of Ph adj. to $-P^+(Ph)_2$], 7.83−7.35 (m, 48 H, H of Ph), 2.40−2.17 (m, 4 H, $-CH_2-$). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 31.55 [d, $^3J_{P-P}$ = 53.00 Hz, $-P^+(Ph)_2-$], 24.11 [d, $^3J_{P-P}$ = 53.0 Hz, $-P^+(Ph)_2-$], −145.35 (sept, $^1J_{P-F}$ = 700.70 Hz, PF_6^-). − $C_{114}H_{78}F_{12}N_8P_4Zn_2$ (2042.57): calcd. C 67.03, H 3.84, N 5.49; found C 67.17, H 3.80, N 5.53.

2-H_2-H_2: The same procedure as described for **1-H_2-H_2** was used to obtain quantitatively **2-H_2-H_2**. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 432 (450000), 532 (22400), 560 (8000), 604 (7800), 668 nm (16000). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$), 25 °C]: δ = 9.02 (d, J_{cis} = 5.1 Hz, 2 H, β-H), 8.96 (d, J_{cis} = 5.1 Hz, 2 H, β-H), 8.79 (d, J_{cis} = 5.1 Hz, 2 H, β-H), 8.76 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.73 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.72 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.67 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.41 (d, J_{cis} = 5.1 Hz, 2 H, β-H), 8.20 [dt, J_o = 6.6 Hz, J_m = 1.5 Hz, 4 H, *o*-H to $-P^+(Ph)_2-$], 8.16 [dt, J_o= 6.6 Hz, J_m = 1.5 Hz, 4 H, *o*-H of $-P(Ph)_2-^+$], 8.08 [d, J_o= 6.6 Hz, J_m = 1.5 Hz, 4 H, *o*-H of Ph adj. to $-P^+(Ph)_2$], 7.87−7.45 (m, 44 H, H of Ph), 7.26 [t, J_o = 7.7 Hz, 4 H, *p*-H of $-P^+(Ph)_2-$], 2.35−2.15 (m, 4 H, $-CH_2-$), −2.53 (s, 4 H, N−H internal). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 29.70

[s, $-P^+(Ph)_2-$], 26.81 [s, $-P^+(Ph)_2$]. – $C_{114}H_{82}Cl_2N_8P_2$ (1758.78): calcd. C 80.70, H 4.87, N 6.60; found C 80.72, H 4.92, N 6.55.

3-Zn-Zn: This was prepared by the same method as **1-Zn-Zn** using ZnTPP (200 mg, 29.5 mmol, 1 equiv.), 2,6-Lut (50 μL, 43.0 mmol) and $(Ph)_2P-CH_2-CH_2-CH_2-P(Ph)_2$ (61 mg, 14.8 mmol, 0.5 equiv.). After 5 h of electrolysis at 0.85 V vs. S.C.E., **3-Zn-Zn** (213 mg, 10.4 mmol) was obtained in 70% yield. – UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 438 (308400), 572 (12900), 620 nm (15900). – ^1H NMR [300 MHz, $(CD_3)_2CO$), 25 °C]: δ = 8.91 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.88 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.81 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.80 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.79 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.77 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.64 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.18 (d, J_{cis} = 4.8 Hz, 2 H, *β*-H), 8.18–8.10 [m, 8 H, *o*-H to $-P^+(Ph)_2-$], 8.01 [dt, J_o= 6.2 Hz, J_m = 1.5 Hz, 4 H, *o*-H of Ph adj. to $-P^+(Ph)_2$], 7.86–7.30 (m, 48 H, H of Ph), 2.64 (dt, ^1J = 10.65 Hz, ^3J = 7.35 Hz, 2 H, $-CH_2-$), 2.46 (dt, ^1J = 10.65 Hz, ^3J = 7.35 Hz, 2 H, $-CH_2-$), 1.94 (m, 2 H, $-CH_2-$ internal). – ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 28.19 (s, $-P^+(Ph)_2-$], 18.68 (s, $-P^+(Ph)_2$], −145.47 (sept, $^1J_{P-F}$ = 700.8 Hz). – $C_{115}H_{80}N_8P_4F_{12}Zn_2$ (2056.60): calcd. C 67.16, H 3.92, N 5.45; found C 67.27, H 4.01, N 5.40.

3-H_2-H_2: 3-H_2-H_2 was obtained quantitatively by the same method described for **1-H_2-H_2**. – UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 432 (427600), 530 (22300), 568 (5700), 612 (6800), 670 nm (17800). – ^1H NMR [300 MHz, $(CD_3)_2CO$), 25 °C]: δ = 9.05 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 9.00 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.96 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.93 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.84 (d, J_{cis} = 5.1 Hz, 2 H, β-H), 8.74 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.69 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.44 (d, J_{cis} = 5.1 Hz, 2 H, β-H), 8.22 [dt, J_o = 5.9 Hz, J_m = 1.8 Hz, 4 H, *o*-H of $-P^+(Ph)_2-$], 8.18 [dt, J_o = 5.9 Hz, J_m = 1.8 Hz, 4 H, *o*-H of $-P^+(Ph)_2-$], 8.12 [d, J_o = 6.6 Hz, J_m = 1.8 Hz, 4 H, *o*-H of Ph adj. to $-P^+(Ph)_2$], 7.86–7.58 (m, 44 H, H of Ph), 7.46 [t, J_o = 5.9 Hz, 4 H, *p*-H of Ph adj. to $-P^+(Ph)_2-$], 7.41 [tt, J_o = 5.9 Hz, J_m = 1.8 Hz, 4 H, *p*-H of $-P^+(Ph)_2-$], 7.32 (tt, J_o = 7.0 Hz, J_m = 2.8 Hz, 8 H, *p*-H of Ph), 2.78 (dt, ^3J = 10.68 Hz, ^1J = 7.40 Hz, 2 H, $-CH_2-$), 2.66 (dt, ^3J = 10.68 Hz, ^1J = 7.40 Hz, 2 H, $-CH_2-$), 2.13 (m, 2 H, $-CH_2-$), −2.53 (s, 4 H, N–H internal). – ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 27.66 [s, $-P^+(Ph)_2-$], 18.08 [s, $-P^+(Ph)_2$]. – $C_{115}H_{84}Cl_2N_8P_2$ (1710.86): calcd. C 80.73, H 4.95, N 6.55; found C 80.74, H 4.93, N 6.48.

4-Zn-Zn: 4-Zn-Zn was prepared by the same method as **1-Zn-Zn** using ZnTPP (200 mg, 29.5 mmol, 1 equiv.), 2,6-Lut (50 μL, 43.0 mmol) and $(Ph)_2P-CH_2-CH_2-CH_2-CH_2-P(Ph)_2$ (63 mg, 14.8 mmol, 0.5 equiv.). After recrystallization, **4-Zn-Zn** was obtained (284 mg; 13.8 mmol, 93%). – UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 444 (293700), 536 (5300), 580 (11200), 638 nm (15800). – ^1H NMR [300 MHz, $(CD_3)_2CO$), 25 °C]: δ = 8.94 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.91 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.80 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.74 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.70 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.67 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.53 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.10–8.02 [m, 10 H, *o*-H of $-P^+(Ph)_2-$ + 2 β-H], 7.97 [d, J_o = 6.00 Hz, 4 H, *o*-H of Ph adj. to $-P(Ph)_2-^+$], 7.84–6.80 (m, 48 H, H of Ph), 2.35–2.25 (m, 2 H, $-CH_2-$), 2.00–1.75 (m, 2 H, $-CH_2-$) 1.30–1.15 (m, 2 H, $-CH_2-$), 0.92–0.80 (m, 2 H, $-CH_2-$). – ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 29.67 [s, $-P^+(Ph)_2-$], 18.52 [s, $-P^+(Ph)_2-$], −145.35 (sept, $^1J_{P-F}$ = 700.7 Hz, PF_6^-). – $C_{116}H_{82}F_{12}N_8P_4Zn_2$ (2070.63): calcd. C 67.29, H 3.99, N 5.41; found C 67.42, H 4.04, N 5.38.

4-H_2-H_2: 4-H_2-H_2 was obtained quantitatively as described for **1-H_2-H_2**. – UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 432 (418500), 530 (23300), 566 (7000), 612 (7500), 668 nm (16800). – ^1H NMR [300 MHz, $(CD_3)_2CO$), 25 °C]: δ = 9.09 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 9.06 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 9.01 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.98 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.87 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.79 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.74 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.42 (d, J_{cis} = 5.16 Hz, 2 H, β-H), 8.28–8.17 [m, 12 H, *o*-H to $-P^+(Ph)_2-$ and *o*-H Ph adj. to $-P^+(Ph)_2-$], 7.90–7.07 (m, 48 H, H of Ph), 2.49–2.38 (m, 2 H, $-CH_2-$), 1.90–1.81 (m, 2 H, $-CH_2-$) 1.37–1.21 (m, 2 H, $-CH_2-$), 0.92–0.75 (m, 2 H, $-CH_2-$), −2.46 (s, 4 H, N–H internal). – ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 30.02 [s, $-P^+(Ph)_2-$], 21.02 (s, $-P^+(Ph)_2$]. – $C_{116}H_{86}Cl_2N_8P_2$ (1724.87): calcd. C 80.78, H 5.03, N 6.50; found C 80.91, H 5.09, N 6.46.

5-Zn-Zn: This compound was prepared by the same method as **1-Zn-Zn** using ZnTPP (200 mg, 29.5 mmol, 1 equiv.), 2,6-Lut (50 μL, 43.0 mmol) and $(Ph)_2P-CH_2-CH_2-As(Ph)_2$ (65 mg, 1.7 mmol, 0.5 equiv.). The product **5-Zn-Zn** was obtained (184 mg, 0.881 mmol, 60%). – UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 436 (426000), 568 (15500), 614 nm(18300). – ^1H NMR [300 MHz, $(CD_3)_2CO$), 25 °C]: δ = 9.10 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 9.07 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 8.89 (d, J_{cis} = 4.77 Hz, 1 H, β-H), 8.86 (d, J_{cis} = 4.77 Hz, 1 H, β-H), 8.85 (d, J_{cis} = 4.77 Hz, 1 H, β-H), 8.82 (d, J_{cis} = 4.77 Hz, 1 H, β-H), 8.81 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.79 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.68 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.25 (d, J_{cis} = 4.80 Hz, 1 H, β-H), 8.22 (d, J_{cis} = 4.77 Hz, 1 H, β-H), 8.18–8.03 [m, 12 H, *o*-H of $-P^+(Ph)_2-$ and *o*-H of Ph adj. to $-P^+(Ph)_2$], 7.90–6.50 (m, 48 H, H of Ph), 2.68 (m, 2 H, $-CH_2-$), 2.39 (m, 2 H, $-CH_2-$). – ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 23.23 [s, $-P^+(Ph)_2-$], −143.39 (sept, $^1J_{P-F}$ = 700.7 Hz, PF_6^-). – $C_{114}H_{78}AsF_{12}N_8P_3Zn_2$ (2086.52): calcd. C 65.62, H 3.77, N 5.37; found C 65.72, H 3.82, N 5.34.

5-H_2-H_2: Compound **5-H_2-H_2** was obtained quantitatively as described for **1-H_2-H_2**. – UV/Vis (CH_2Cl_2), λ_{max} (ε, $M^{-1}cm^{-1}$) = 432 (370000), 500 (21100), 566 (7400), 612 (6700), 670 nm (12800). – ^1H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 9.13 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 9.10 [s, 1 H, β-H adj. to $-P^+(Ph)_2-$], 9.08 (d, J_{cis} = 5.16 Hz, 2 H, β-H), 9.05 (d, J_{cis} = 5.16 Hz, 2 H, β-H), 8.97 (d, J_{cis} = 5.1 Hz, 2 H, β-H), 8.79 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.74 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.47 (d, J_{cis} = 5.16 Hz, 1 H, β-H), 8.46 (d, J_{cis} = 5.16 Hz, 1 H, β-H), 8.28–8.12 [m, 12 H, *o*-H of $-P^+(Ph)_2-$ and *o*-H of Ph adj. to $-P^+(Ph)_2$], 7.92–7.20 (m, 48 H, H of Ph), 2.75 (m, 2 H, $-CH_2-$), 2.42 (m, 2 H, $-CH_2$), −2.44 (s, 4 H, N–H internal). – ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 22.54 [s, $-P^+(Ph)_2-$]. – $C_{114}H_{82}AsCl_2N_8P_3$ (2030.72): calcd. C 75.95, H 4.59, N 6.22; found C 76.11, H 4.64, N 6.20.

6-Zn and 6-Zn-Zn: ZnTPP (20 mg, 29.5 mmol), 2,6-Lut (20 μL, 17.20 × 10^{-5} mol) and $(Ph)_2P-C\equiv C-P(Ph)_2$ (11.6 mg, 2.95 × 10^{-5} mol) were dissolved in a solution of T.E.A.PF_6 (0.1 M) in 1,2-$Cl_2C_2H_4$/CH_3CN (4:1). The stirred reaction mixture was electrolyzed for 3 h at 0.80 V vs. SCE. After workup, the unchanged ZnTPP was separated from the monomeric (**6-Zn**) and dimeric (**6-Zn-Zn**) porphyrins by column chromatography (silica gel), eluting with CH_2Cl_2/0.1% CH_3OH. Further elution did not allow for the effective separation of the two porphyrins (**6-Zn** and **6-Zn-Zn**). Pure monomer and dimer were obtained only after demetallation of the mixture and chromatography as described below. After coulometry, the solvents were evaporated. The residue was dissolved in a minimum amount of CH_2Cl_2/CH_3COCH_3 (1:1) and dilute HCl (25%, 100 mL) was added. This mixture was stirred for 30 min at room temperature. After the addition of water (200 mL), the organic layer was collected, washed again and neutralized with sodium acetate. The porphyrins **6-H_2** and **6-H_2-H_2** were then separ-

ated by column chromatography (CH_2Cl_2/0.1% CH_3OH) to give, after recrystallization from CH_2Cl_2/*n*-hexane, brown powders: **6-H$_2$** (6.8 mg, 22%) and **6-H$_2$-H$_2$** (16.7 mg, 66%).

6-H$_2$: H$_2$TPP-β-P$^+$(Ph)$_2$−C≡C−P(Ph)$_2$, Cl$^-$: UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 426 (269200), 522 (17400), 558 (8400), 598 (7800), 655 nm (8300). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 8.93 (s, 1 H, β-H), 8.77 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.76 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.73 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.56 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.42 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.25−8.18 [m, 5 H, 4 *o*-H of −P$^+$(Ph)$_2$ − and 1 β-H], 8.06 [dt, J_o = 6.6 Hz, J_m = 1.7 Hz, 2 H, *o*-H of Ph adj. to −P$^+$(Ph)$_2$−], 7.86−7.76 (m, 10 H, *o*-H of Ph), 7.72−7.42 (m, 16 H, H of Ph), 7.36 (t, J_o = 7.7 Hz, 3 H, *p*-H of Ph), 7.35 [t, J_o = 7.0 Hz, 2 H, *p*-H of P(Ph)$_2$], 7.23 [t, J_o = 7.7 Hz, 1 H, *p*-H of Ph adj. to P$^+$(Ph)$_2$], 7.16 [t, J_o = 7.7 Hz, 2 H, *p*-H of −P$^+$(Ph)$_2$−], −2.57 (s, 2 H, N−H). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 18.95 [s, −P$^+$(Ph)$_2$−], 3.51 [s, −P(Ph)$_2$−]. − $C_{70}H_{49}ClN_4P_2$ (1043.60): calcd. C 80.57, H 4.73, Cl 3.40, N 5.37, P 5.94; found C 80.70, H 4.78, Cl 3.40, N 5.41, P 6.02.

6-H$_2$-H$_2$: H$_2$TPP-β-P$^+$(Ph)$_2$−C≡C−P$^+$(Ph)$_2$-β-H$_2$TPP, 2 Cl$^-$: UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 430 (214200), 527 (16600), 564 (4900), 607 (7300), 666 nm (10900). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ =9.06 (d, J_{cis} = 5.5 Hz, 2 H, β-H), 9.02 (d, J_{cis} = 5.5 Hz, 2 H, β-H), 8.87 (d, J_{cis} = 5.5 Hz, 1 H, β -H), 8.85 (d, J_{cis} = 5.5 Hz, 1 H, β-H), 8.76 [s, 1 H, -H adj. to −P$^+$(Ph)$_2$−], 8.71 [s, 1 H, β-H adj. to −P$^+$(Ph)$_2$−], 8.67 (s, 1 H, β-H), 8.64 (s, 1 H, β-H), 8.46 (d, J_{cis} = 5.5 Hz, 1 H, β-H), 8.41 (d, J_{cis} = 5.5 Hz, 1 H, β-H), 8.26−8.19 [m, 10 H, 8 *o*-H of −P$^+$(Ph)$_2$− and 2 β-H], 8.14−8.05 [m, 4 H, *o*-H of Ph adj. to −P$^+$(Ph)$_2$−], 7.93−7.14 (m, 48 H, H of Ph), −2.48 (s, 2 H, N−H), −2.51 (s, 2 H, N−H). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 24.80 [s, −P$^+$(Ph)$_2$−], 16.51 [s, −P$^+$(Ph)$_2$−]. − $C_{114}H_{78}Cl_2N_8P_2$ (1692.80): calcd. C 80.89, H 4.64, Cl 4.19, N 6.62, P 3.66; found C 80.75, H 4.78, Cl 4.34, N 6.70, P 3.81.

6-Zn: Compound **6-H$_2$** was dissolved in a solution of $(CH_3COO)_2Zn^{II}$ (10 equiv.) in CH_2Cl_2/CH_3OH (1:1). The mixture was maintained at reflux for 3 h. After cooling at room temperature, the mixture was treated with an excess of tetraethylammonium hexafluorophosphate (100 equiv.). After evaporation of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2. The mixture was then poured into water, and the organic layer was washed (4 times) and dried with $CaSO_4$ for 6 h. The solution was then concentrated (to 5 mL) and purified by chromatography on a silica gel column (elution with CH_2Cl_2/CH_3OH, 99:1) to give a dark green powder of **6-Zn** in 90% yield. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 428 (209200), 560 (9400), 603 nm (5000). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 8.84 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.800 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.798 [s, 1 H, β-H adj. to −P$^+$(Ph)$_2$−], 8.77 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.768 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.63 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.17 (d, J_{cis} = 4.8 Hz, 1 H, β-H), 8.11 [dd, J_o = 8.8 Hz, J_m = 1.8 Hz, 4 H, *o*-H of −P$^+$(Ph)$_2$−], 8.01 [dd, J_o = 8.1 Hz, J_m = 1.5 Hz, 2 H, *o*-H of Ph adj. to −P$^+$(Ph)$_2$−], 7.94−7.55 (m, 26 H, *o*-H and *m*-H of Ph), 7.49 [t, J_o = 7.4 Hz, 2 H, *p*-H of P(Ph)$_2$], 7.41 (t, J_o = 7.4 Hz, 3 H, *p*-H of Ph), 7.31 [t, J_o = 7.4 Hz, 1 H, *p*-H of Ph adj. to −P$^+$(Ph)$_2$], 7.03 [t, J_o = 7.4 Hz, 2 H, *p*-H of −P$^+$(Ph)$_2$], − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 4.64 [s, −P$^+$(Ph)$_2$−], 3.51 [s, −P$^+$(Ph)$_2$−], −145.44 (sept, $^1J_{P-F}$ = 700.8 Hz, PF_6^-). − $C_{70}H_{47}F_6N_4P_3Zn$ (1216.47): calcd. C 69.12, H 3.89, N 4.61, P 7.64, Zn 5.37; found C 69.31, H 4.05, N 4.74, P 7.75, Zn 5.56.

6-Zn-Zn: The same procedure described for **6-Zn** was used to obtain **6-Zn-Zn** from **6-H$_2$-H$_2$** in 90% yield. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 438 (215600), 569 (10600), 623 nm (11800). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ= 8.87 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.82 (d, J_{cis} = 4.8 Hz, 4 H, β-H), 8.80 [s, 1 H, β-H adj. to −P$^+$(Ph)$_2$−], 8.79 [s, 1 H, β-H adj. to −P$^+$(Ph)$_2$−], 8.78 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.65 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.18 (d, J_{cis} = 4.8 Hz, 2 H, β-H), 8.16 [d, J_o = 7.7 Hz, 4 H, *o*-H of −P$^+$(Ph)$_2$ −], 8.12 [d, J_o = 7.7 Hz, 4 H, *o*-H of −P$^+$(Ph)$_2$−], 8.03 [d, J_o = 7.7 Hz, 4 H, *o*-H of Ph adj. to −P$^+$(Ph)$_2$−], 7.90−7.10 (m, 48 H, H of Ph), − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 14.03 [s, −P$^+$(Ph)$_2$−], 13.62 [s, −P$^+$(Ph)$_2$−], 145.44 (sept, $^1J_{P-F}$ = 700.8 Hz, PF_6^-). − $C_{114}H_{74}F_{12}N_8P_4Zn_2$ (2038.54): calcd. C 67.17, H 3.66, N 5.50, P 6.08, Zn 6.41; found C 67.32, H 3.74, N 5.42, P 6.22, Zn 6.52.

7-Zn-Zn: This was prepared by the same method as **1-Zn-Zn**, using ZnTPP (200 mg, 2.95×10^{-4} mol, 1 equiv.), 2,6-Lut (50 μL, 4.3×10^{-4} mol) and 1,1,1-tris(diphenylphosphanylmethyl)ethane (61 mg, 0.98×10^{-4} mol. 0.33 equiv.). Product **7-ZnZn** was recovered (184 mg, 0.88×10^{-4} mol, 75%). − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 446 (298000), 582 (12100), 640 nm (19900). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 9.71 [s, 1 H, β-H adj. to −P$^+$(Ph)$_2$−], 9.68 [s, 1 H, β-H adj. to −P$^+$(Ph)$_2$−], 8.90 [d, J_{cis} = 4.80 Hz, 4 H, β-H adj. to −P$^+$(Ph)$_2$−], 8.82 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.80 (d, J_{cis} = 4.80 Hz, 2 H, β-H), 8.76 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.51 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.24 [dt, 4 H, J_m = 1.83 Hz, J_o = 6.99 Hz, *o*-H of Ph adj. to −P$^+$(Ph)$_2$−], 8.20−8.13 [m, 12 H, *o*-H of −P$^+$(Ph)$_2$− and PO(Ph)$_2$], 7.99−6.67 (m, 54 H, H of Ph), 4.60 [d, ^3J = 13.30 Hz, 2 H, −CH$_2$−PO(Ph)$_2$], 2.69 [d, ^1J = 13.30 Hz, 1 H, −CH$_2$−P$^+$(Ph)$_2$−], 2.62 [d, ^1J = 13.30 Hz, 1 H, −CH$_2$−P$^+$(Ph)$_2$−], 1.92 [d, ^1J = 13.30 Hz, 1 H, −CH$_2$−P$^+$(Ph)$_2$−], 1.86 (d, ^1J = 13.30 Hz,1 H, −CH$_2$−), 0.80 (s, 3 H, −CH$_3$−). − ^{31}P NMR (120 MHz, $(CD_3)_2CO$, 25 °C): δ = 26.43 [s,PO(Ph)$_2$- and −P$^+$(Ph)$_2$−], 15.88 [s, −P$^+$(Ph)$_2$−], −143.35 (sept, $^1J_{P-F}$ = 700.7 Hz, PF_6^-). − $C_{129}H_{93}F_{12}N_8OP_5Zn_2$ (2284.83): calcd. C 67.81, H 4.10, N 4.90, P 6.78; found C 68.00, H 4.08, N 4.88, P 6.61.

7-H$_2$-H$_2$: This was prepared by the same method as **1-H$_2$-H$_2$** and was obtained in 93% yield. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 438 (308000), 534 (16600), 578 (5300), 620 (5200), 680 nm (14200). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 9.82 [s, 1 H, β-H adj. to −P$^+$(Ph)$_2$−], 9.79 [s, 1 H, β-H adj. to−P$^+$(Ph)$_2$−], 9.13 (d, J_{cis} = 5.16 Hz, 2 H, β-H), 9.10 (d, J_{cis} = 5.16 Hz, 2 H, β-H), 8.92 (d, J_{cis} = 5.13 Hz, 2 H, β-H), 8.79 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.72 (d, J_{cis} = 4.77 Hz, 2 H, β-H), 8.63 (d, J_{cis} = 5.13 Hz, 2 H, β-H), 8.34−8.20 [m, 16 H, *o*-H of Ph of −P$^+$(Ph)$_2$− and PO(Ph)$_2$− and *o*-H of Ph adj. to P$^+$(Ph)$_2$−], 8.05−6.79 (m, 48 H, H of Ph), 4.12 [d, ^3J = 13.30 Hz, 2 H,−CH$_2$−PO(Ph)$_2$], 2.61 [d, ^1J = 14.10 Hz, 1 H, −CH$_2$−P$^+$(Ph)$_2$−], 2.59 [d, ^1J = 14.10 Hz, 1 H, −CH$_2$−P$^+$(Ph)$_2$−], 1.85 [m, 2 H, −CH$_2$−P$^+$(Ph)$_2$−], 0.80 (s, 3 H, −CH$_3$−). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 25.87 [s, PO(Ph)$_2$− and −P$^+$(Ph)$_2$−], 15.63 [s, −P$^+$(Ph)$_2$−]. − $C_{129}H_{97}Cl_2N_8OP_3$ (1939.09): calcd. C 79.90, H 5.04, N 5.78, P 4.79; found C 80.20, H 5.10, N 5.80, P 4.31.

8-Zn-Zn-Zn: The method employed in the synthesis of **1-Zn-Zn**, using ZnTPP (200 mg, 2.95×10^{-4} mol, 1 equiv.), 2,6-Lut (50 μL, 4.3×10^{-4} mol) and TRIPHOS (61 mg, 0.976×10^{-4} mol, 0.33 equiv.), led to the formation of product **8-Zn-Zn-Zn** (184 mg, 0.88×10^{-4} mol, 70%). − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 441 (298000), 583 (12100), 628 nm (19900),. − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 9.70 [m, 3 H, β-H adj. to −P$^+$(Ph)$_2$−], 9.88

[d, J_{cis} = 4.77 Hz, 3 H, β-H adj. to $-P^+(Ph)_2-$], 8.82 [d, J_{cis} = 4.77 Hz, 3 H, β-H adj. to $-P^+(Ph)_2-$], 8.77 (d, J_{cis} = 4.77 Hz, 3 H, β-H), 8.63 (d, J_{cis} = 4.77 Hz, 3 H, β-H), 8.22−8.04 [m, 19 H, 16 *o*-H of Ph adj. to $-P^+(Ph)_2-$ + 3 β-H], 7.91−7.06 (m, 69 H, H of Ph), 3.10−2.90 [m, 4 H, $-CH_2-P^+(Ph)_2-$], 2.72−2.36 [m, 12 H, $-CH_2-P^+(Ph)_2-$]. − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 29.82 [d, $^3J_{P-P}$ = 45.2 Hz, $-P^+(Ph)_2-$], 27.25 [t, $^3J_{P-P}$ = 45.2 Hz, $-P^+(Ph)_2-$], −143.54 (sept, $^1J_{P-F}$ = 700.7 Hz, PF_6^-). − $C_{166}H_{114}F_{18}N_{12}P_6Zn_3$ (3000.78): calcd. C 66.44, H 3.83, N 5.60, Zn 6.54; found C 66.27, H 3.76, N 5.58, Zn 6.41.

8-H_2-H_2-H_2: This was prepared by the same method as **1-H_2-H_2** and was obtained from **8-Zn-Zn-Zn** in 93% yield. − UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 432 (325100), 530 (18000), 567 (7000), 611 (7900), 667 nm (14400). − ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 25 °C]: δ = 9.88 [s, 3/2 H, β-H adj. to $-P^+(Ph)_2-$], 9.82 [s, 3/2 H, β-H adj. to $-P^+(Ph)_2-$], 8.98 [d, J_{cis} = 4.77 Hz, 3 H, β-H adj. to $-P^+(Ph)_2-$], 8.96 [d, J_{cis} = 4.77 Hz, 3 H, β-H adj. to $-P^+(Ph)_2-$], 8.90 (d, J_{cis} = 4.77 Hz, 3/2 H, β-H), 8.87 (d, J_{cis} = 4.77 Hz, 3/2 H, β-H), 8.76 (d, J_{cis} = 4.77 Hz, 3 H, β-H), 8.74 (d, J_{cis} = 4.77 Hz, 3 H, β-H), 8.69 (d, J_{cis} = 4.77 Hz, 3 H, β-H), 8.26−8.03 [m, 19 H, 16 *o*-H of Ph adj. to $-P^+(Ph)_2-$ + 3 β-H], 7.89−6.63 (m, 69 H, H of Ph), 3.43−3.10. [m, 4 H, $-CH_2-P^+(Ph)_2-$], 2.80−2.39.[m, 12 H, $-CH_2-P^+(Ph)_2-$], −2.67 (s, 4 H, N−H of H_2TPP external), −2.45 (s, 2 H, N−H of H_2TPP internal). − ^{31}P NMR [120 MHz, $(CD_3)_2CO$, 25 °C]: δ = 29.54 [d, $^3J_{P-P}$ = 45.2 Hz, $-P^+(Ph)_2-$], 26.74 [t, $^3J_{P-P}$ = 45.2 Hz, $-P^+(Ph)_2-$], −143.54 (sept, $^1J_{P-F}$ = 700.7 Hz, PF_6^-). − $C_{166}H_{120}Cl_3N_{12}P_3$ (2482.17): calcd. C 80.33, H 4.87, N 6.67, P 3.74; found C 80.47, H 4.69, N 6.74, P 3.93.

Acknowledgments

We warmly thank the Centre National de la Recherche Scientifique for financial support.

[1] M. J. Crossley, P. L. Burn, *J. Chem. Soc., Chem. Commun.* **1991**, 1569−1571.
[2] M.R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435−461.
[3] M. Bixon, J. Fajer, G. Feher, J. H. Freed, D. Gamlich, A. J. Hoff, H. Levanon, K. Möbins, R. Nechushtai, J. R. Norris, A. Scherz, J. L. Sessler, D. Stehlik, *Isr. J. Chem.* **1992**, *32*, 449−467.
[4] S. Prathapan, T. E. Johnson, J. S. Lindsey, *J. Am. Chem. Soc.* **1993**, *115*, 7519−7520.
[5] V. S. Y. Lin, M. J. Therien, *Chem. Eur. J.* **1995**, 1, 645−651.
[6] K. M. Kadish, N. Guo, E. V. Cæmelbecke, A. Froiio, R. Paolesse, D. Monti, P. Tagliatesta, T. Boschi, L. Prodi, F. Bolletta, N. Zaccheroni, *Inorg. Chem.* **1998**, *37*, 2358−2365.
[7] J. L. Sessler, V. L. Capuano, A. Harriman, *J. Chem. Soc., Chem. Commun.* **1999**, 1771−1782.
[8] G. Hungerford, M. V. der Auweraer, J.-L. Chambron, V. Heitz, J.-P. Sauvage, J.-L. Pierre, D. Zurita, *Chem. Eur. J.* **1999**, *5*, 2089−2100.
[9] J. L. Sessler, M. R. Johnson, S. E. Creager, J. C. Fettinger, J. A. Ibers, *J. Am. Chem. Soc.* **1990**, *112*, 9310−9329.
[10] E. J. Atkinson, A. M. Oliver, M. V. Paddon Row, *Tetrahedron Lett.* **1993**, *34*, 6147−6150.
[11] D. P. Arnold, L. J. Nitschinsk, *Tetrahedron Lett.* **1993**, *34*, 693−696.
[12] J. S. Lindsey, S. Prathapan, T. E. Johnson, R. W. Wagner, *Tetrahedron* **1994**, *50*, 8941−8968.
[13] H. L. Anderson, *Inorg. Chem.* **1994**, *33*, 972−981.
[14] P. Krausz, Ch. Giannotti, *J. Chim. Phys.* **1983**, *80*, 299−303.
[15] H. Tamiaki, S. Suzuki, K. Maruyana, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2633−2697.
[16] S. Matile, N. Berova, K. Nakanishi, J. Fleischhauer, R. W. Woody, *J. Am. Chem. Soc.* **1996**, *118*, 5198−5206.
[17] N. Bampos, V. Marvaud, J. K. M. Sanders, *Chem. Eur. J.* **1998**, *4*, 335−342.
[18] G. Märkl, M. Reiss, P. Kreitmeier, H. Nörth, *Angew. Chem. Int. Ed. Engl.* **1995**, *20*, 2230−2234.
[19] R. H. Jin, S. Aoki, K. Shima, *Chem. Commun.* **1996**, 1939−1940.
[20] A. K. Burrell, D. L. Officer, D. C. W. Reid, K. Y. Wild, *Angew. Chem.* **1998**, *110*, 998−1002.
[21] T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, H. Osuka, *J. Chem. Soc., Chem. Commun.* **1998**, 337−338.
[22] T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono, A. Osuka, *Angew. Chem. Int. Ed.* **1999**, *38*, 176−179.
[23] L. Ruhlmann, A. Giraudeau, *Chem. Commun.* **1996**, 2007−2008.
[24] A. Giraudeau, L. Ruhlmann, L. El Kahef, M. Gross, *J. Am. Chem. Soc.* **1996**, *118*, 2969−2979.
[25] L. Ruhlmann, A. Shulz, A. Giraudeau, C. Messerschmidt, J. H. Fuhrhop, *J. Am. Chem. Soc.* **1999**, *121*, 6664−6667.
[26] D. G. Davis, in *The Porphyrins* (Ed.: D. Dolphin), Academic Press, New York, **1979**, vol. 5, p. 53−125.
[27] A. Giraudeau, L. El Kahef, *Can. J. Chem.* **1991**, *69*, 1161−1165.
[28] A. S. Hinman, B. J. Pavelich, S. Pons, A. E. Kondo, *J. Electroanal. Chem.* **1987**, *234*, 145−162.
[29] A. El-Kasmi, D. Lexa, P. Maillard, M. Momenteau, J. M. Savéant, *J. Am. Chem. Soc.* **1991**, *113*, 1586−1595.
[30] K. M. Kadish, R. K. Rhodes, *Inorg. Chem.* **1981**, *20*, 2961−2996.
[31] K. M. Barkigia, M. W. Renner, H. Xie, K. M. Smith, J. Fajer, *J. Am. Chem. Soc.* **1993**, *115*, 7894−7899.
[32] P. J. Angiolillo, V. S. Y. Lin, J. M. Vanderkoi, M. J. Therien, *J. Am. Chem. Soc.* **1995**, *117*, 12514−12527.
[33] A. Helms, D. Heiler, G. Mc Lendon, *J. Am. Chem. Soc.* **1992**, *114*, 6227−6238.
[34] J. L. Sessler, V. L. Capuano, *Tetrahedron Lett.* **1993**, *34*, 2287−2290.
[35] H. J. Shine, A. G. Padilla, S. M. Wu, *J. Org. Chem.* **1979**, *44*, 4069−4075.
[36] Because the splitting of the signal of the two external $-CH_2-$ was more pronounced in [D_5]pyridine (δ = 3.00−2.80) than in [D_6]acetone (δ = 2.78−2.66), [D_5]pyridine was chosen for the representation of this splitting.
[37] E. E. Bonfantini, D. L. Officer, *Tetrahedron Lett.* **1993**, *34*, 8531−8534.
[38] A. K. Burrell, D. L. Officer, D. C. W. Reid, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 900−904.
[39] J. J. Gosper, M. Ali, *J. Chem. Soc., Chem. Commun.* **1994**, 1707−1708.
[40] Y. Le Mest, M. L'Her, N. H. Hendricks, K. Kim, J. P. Collman, *Inorg. Chem.* **1992**, *31*, 835−847.
[41] J. H. Fuhrhop, K. M. Kadish, D. G. Davis, *J. Am. Chem. Soc.* **1973**, *95*, 5140−5147.
[42] A. Giraudeau, H. J. Callot, M. Gross, *Inorg. Chem.* **1979**, *18*, 201−206.
[43] E. V. Nikitin, A. S. Romakhin, V. A. Zagumennov, Y. A. Balokin, *Electrochim. Acta* **1997**, *42*, 2217−2224.
[44] A. Giraudeau, H. J. Callot, J. Jordan, I. Ezahr, M. Gross, *J. Am. Chem. Soc.* **1979**, *101*, 3857−3862.
[45] D. Dolphin, D. J. Halko, E. C. Johnson, K. Rousseau, in *Porphyrin Chemistry Advances* (Ed.: F. R. Longo), Ann Arbor Science, MI, **1979**, chapter 10, p. 123−125.
[46] G. Wittig, *Angew. Chem.* **1956**, *68*, 505−509.
[47] C. Bernard, J. P. Gisselbrecht, M. Gross, E. Vogel, M. Lausmann, *Inorg. Chem.* **1994**, *33*, 2393−2401.
[48] A. D. Adler, F. R. Longo, F. Kampas, K. Kim, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443−2445.
[49] G. H. Barnett, M. F. Hudson, K. M. Smith, *Tetrahedron Lett.* **1973**, *30*, 2887−2888.

Received June 17, 2000
[I00249]