Bisporphyrins with Bischlorin Features Obtained by Direct Anodic Coupling of Porphyrins

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Abstract: The proximity of two or more porphyrin or chlorin-like structures has been shown to be crucial in numerous biological processes, such as electron transfers. The one-pot electrochemical synthesis of a dimeric tetraphenylporphyrin with one 1,2-(diphenylphosphonium)benzene as a spacer and of its porphyrin-monomer precursor are reported. These new compounds have been characterized by ^1H and ^{31}P NMR, ESR, and UV-visible spectroscopy and microanalysis. Electrochemical data are reported, and the redox behavior is analyzed for the monomers and the dimers. Important interactions between the two chromophores and a phosphonium–phosphonium interaction have been observed. UV-visible and ^1H NMR data along with electrochemical behavior suggest that the positive charge carried by the two phosphonium units is in part delocalized onto the π system of the porphyrins, this gives an unexpected bis-porphyrin with bischlorin spectroscopic features.

Keywords: chlorins · electrochemistry · electrosynthesis · phosphonium · porphyrinoids

Introduction

Sunlight-energy conversion in nature, such as effected by photosynthetic bacteria in the primary processes of photosynthesis,[1–3] is a process of both paramount importance and great complexity. It originates with the capture of solar energy by hundreds of chlorophyll arrays in membrane-bound pigment protein complexes known as light-harvesting (antenna) complexes (LHC).[1] This initial step is followed by the funneling of that energy into a reaction center (RC)[2–3] through efficient energy migration and transfer. A subsequent set of electron-transfer events within the RC then produces a long-lived charge separation.[4] This charge separation is actually a storage of chemical energy for further use in various biochemical reactions.

In such RCs, the primary electron source is dimeric bacteriochlorophylls (Bchl), the so-called "special pair".[2a]

Chlorins are an important group of dihydroporphyrins that are actually the parent structure for many of the chlorophylls[5] and other biologically important pigments.[6] Chlorins give rise to prominent absorptions in the long-wavelength region of the visible spectrum,[7] typically near 650 nm, which make these pigments potential candidates as photosensitizers for photodynamic therapy.[8] Although a desire to understand the intricacies of natural photosynthesis prompted many chemists to synthesize and study a large variety of artificial models based on highly conjugated porphyrins,[9] dimeric or trimeric porphyrins,[10] or porphyrin arrays,[11] not much work has been carried out on the synthesis of chlorin analogues,[12] bischlorins or chlorin–porphyrin heterodimers.[13] Effective methods for the preparation of a bischlorin with a covalent link, with the aim of mimicking physiological electron-transfer systems,[14] would be a significant step toward the synthesis of more relevant model systems.

Phosphorus-containing ligands are powerful nucleophiles and are known to be prone to nucleophilic attack on the π cation radicals of metalloporphyrins.[15–19] We reported recently on the synthesis of a dimeric porphyrin, which included a diphosphonium spacer, in a direct one-pot electrochemical reaction.[20] This synthesis of porphyrin dimers by controlled potential electrolysis readily provides convenient access to a large variety of porphyrin dimers with good yields.[21] However all the dimers synthesized so far exhibited significant interactions between the different π systems only when a short spacer was used.

To favor the interactions between the two porphyrins in such dimers, we used a spacer that behaves as an aromatic system to link the two chromophoric subunits. The starting point in this synthesis was the electrochemical oxidation of the zinc *meso*-tetraphenylporphyrin, ZnTPP, in the presence of

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1,2-bis(diphenylphosphino)benzene. The present paper reports on the electrochemical synthesis, in a direct one-pot reaction, of a new interactive bisporphyrin with bischlorin spectroscopic features that has a diphosphonium bridge as spacer (Scheme 1).

UV-visible spectra of the porphyrin dimers were characteristic of a chlorin structure (Figures 1 and 2). Moreover, both the ^1H NMR spectrum (for the free-base **2**-H_2-H_2) and the redox behavior of the porphyrin dimers have been analyzed. They clearly demonstrated an analogy with those of known bischlorin dimers and they also indicated a delocalization of the positive charge carried by the two phosphonium units on to the π-system of the porphyrins. To probe the degree of intercommunication between the chlorin analogues, we incorporated into each chlorin macrocycle of the dimer metal ions of varying electronegativity (M–M = Zn–Zn or Cu–Cu) and we measured the redox potentials then characterizing these dimers. We have characterized the electrogenerated reduced and oxidized species by their absorption spectra.

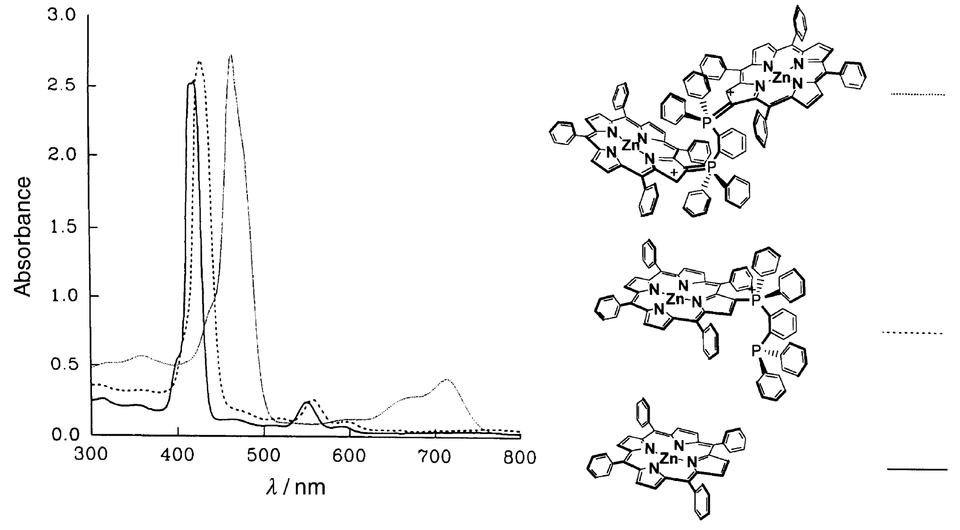
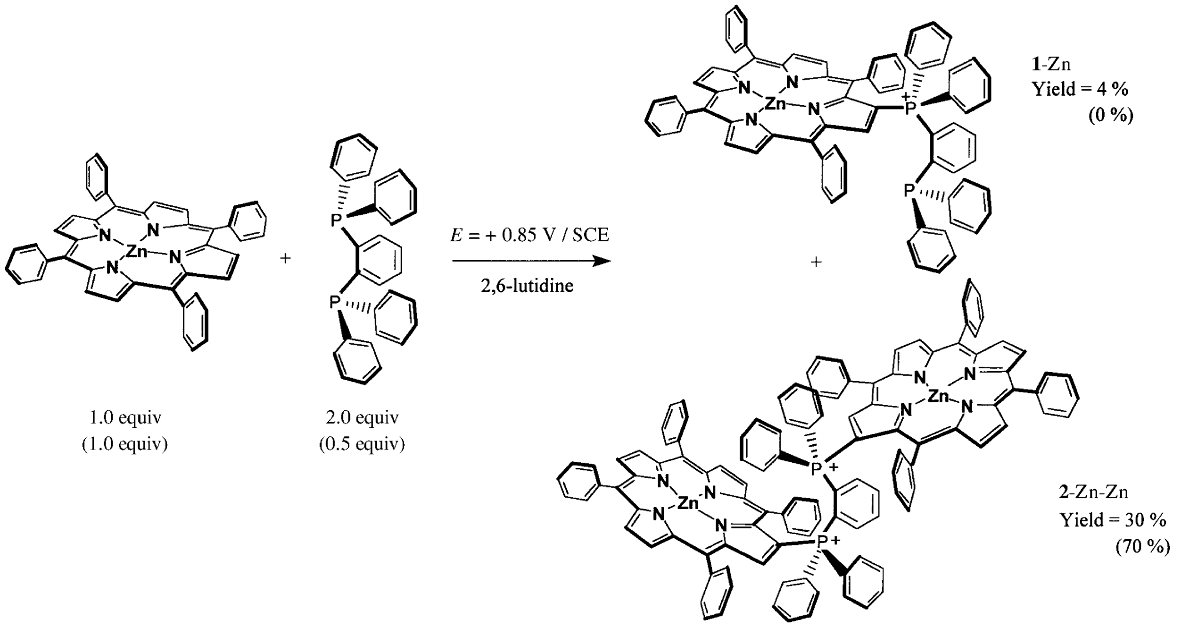


Figure 1. UV-visible absorption spectra of the bisporphyrin **2**-Zn-Zn, of its monomeric subunit **1**-Zn, and of ZnTPP in CH_2Cl_2.

An interesting feature was observed in the reduction of these dimers. During the stepwise reduction of the dimer, an unusual alternated sequence in the sites of the electron transfer was observed, the reduction occurring on the porphyrins and then on the spacer. The porphyrin chromophores were reduced before the diphosphonium spacer. This unusual behavior suggests a significant delocalization of the phosphonium positive charge onto the π system of the porphyrins.

Results

Eletrosynthesis: Exhaustive electrochemical oxidation was performed under conditions previously reported.[18–21] Metalloporphyrin ZnTPP (1 equiv) in solution was oxidized in the presence of 1,2-bis(diphenylphosphino)benzene (½ equiv) and of 2,6-lutidine (2,6-Lut) at a potential corresponding to the generation of porphyrin radical cations (first oxidation). The 2,6-Lut was used to trap protons that were liberated in the



Scheme 1. A mixture of the monomer and the dimer **1**-Zn/**2**-Zn-Zn was obtained by oxidation of ZnTPP at +0.85 V vs. SCE in the presence of 1,2-di(phenylphosphino)benzene.

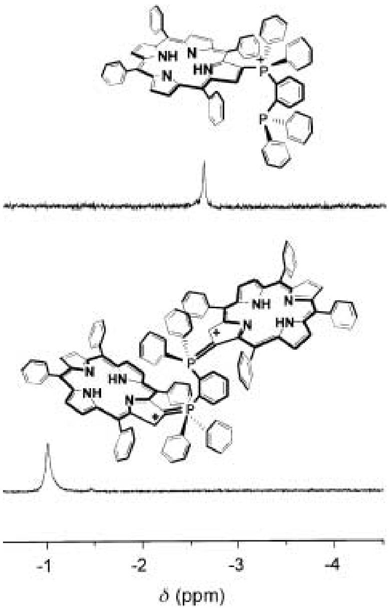


Figure 2. N–H proton signals in the ^1H NMR spectra of **1**-H_2 (top) and of **2**-H_2-H_2 (bottom) (300 MHz, $(CD_3)_2CO$, 25 °C).

course of the porphyrin oxidation. After the working potential had been maintained at +0.85 V vs. SCE for six hours, the initial violet solution turned green, and the electrolysis current decreased to the initial background current value. The electrolysis was stopped at this point. The amount of consumed coulombs calculated from the recorded current–time curve ($I = f(t)$) indicated that 2 faradays were consumed per mole of ZnTPP in the reaction. This electrolysis produced the target dimer **2**-Zn-Zn in a rather good yield (70%). Nevertheless, by using 2 molar equivalents of 1,2-bis(diphenylphosphino)benzene with 1 molar equiv of ZnTPP, the electrolysis at +0.85 V vs. SCE gave a mixture of two products. The minor product was identified and characterized as the mono-β-substituted porphyrin **1**-Zn (yield 4%), and the major product as the dimer **2**-Zn-Zn (yield 30%). The reaction is presented in Scheme 1.

Thus, an increase in the concentration of the diphosphane caused a drastic decrease in the yield of the β substitution leading to the zinc monomer and dimer, even when using a large excess of 2,6-Lut. The yield of this electrosynthesis of **1**-Zn and/or **2**-Zn-Zn went down to zero when using more than ten equivalents of diphosphane. In this case, the major products of the reaction were the diphosphane oxide and the violin.[17] The overall yield of these two compounds was important (40%) when high concentrations of diphosphane and 2,6-Lut were used. In these conditions the quantity of consumed Coulombs calculated from recorded current–time $I = f(t)$ indicated that $(1+4n)$ faradays were consumed per mole of ZnTPP in the reaction ($n \geq 10$ being the number of equivalents of diphosphane).

UV/Vis absorption spectra: Spectra of some of the porphyrins studied here are presented in Figure 1. The Soret and other absorption maxima and extinction coefficients of the **1**-M (M = H_2, Cu, and Zn) and **2**-M-M series (M = H_2-H_2, H_3^+-H_3^+, Cu-Cu, and Zn-Zn) are given in Table 1. Complete UV/Vis data are reported in the Experimental Section for the electrosynthesized monomeric and dimeric porphyrins.

Monomers: All the porphyrins synthesized exhibited a red shift in the Soret (B) and visible (Q) bands when compared with the corresponding unsubstituted porphyrins (Figure 1). This bathochromic shift resulted from the electron-withdrawing effect[22–23] of the phosphonium cation linked to the β position on the porphyrin ring. The shifts of the Soret bands were similar to those already reported for other β-substituted porphyrins.[18–21]

The β-substituted free-base porphyrin showed an intense Q-band at 654 nm (Table 1) typical of the presence of a nucleophilic β substituent on the porphyrin ring.[18–21]

Table 1. Soret absorption maxima and extinction coefficient of the monomers **1**-M (M = H_2, Cu and Zn) and the dimers **2**-M-M (M = H_2, H_3^+, Cu and Zn).

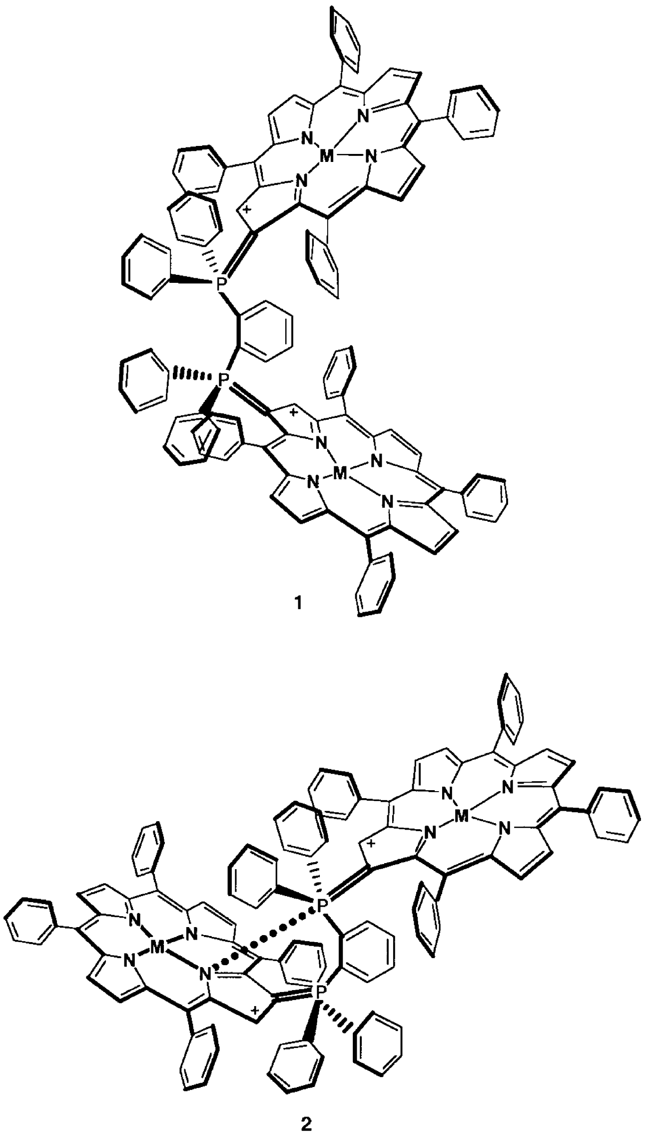
Compound	λ_{max} [nm] (ε [mol L^{-1} cm^{-1}])					
1-H_2	426 (242500)	521 (19600)	560 (1300)	600 (13700)	654 (16700)	
1-Cu	423 (289700)	546 (9300)	582 (9300)			
1-Zn	430 (237900)	557 (6500)	597 (1900)			
2-H_2-H_2	463 (237900)	532 (6100)	569 (11300)	619 (10100)	679 (9300)	737 (30900)
2-H_3^+-H_3^+	475 (153900) 507 (108000)	708 (34100)	771 (75800)			
2-Cu-Cu	448 (285600)	544 (11600)	584 (14900)	635 (27600)	647 (27300)	
2-Zn-Zn	467 (272700) 480 (203000)	613 (3100)	664 (6200)	717 (9500)		

Dimers: UV-visible absorption spectra (Figure 1) of all dimers exhibited red shifts that were very significant if compared with the spectra of the corresponding monomers. The Soret band of the dimer **2**-Zn-Zn also exhibited a significant broadening associated with a shoulder corresponding to some extent, to a splitting of the Soret band (see Table 1 and Figure 1). The corresponding extinction coefficients were approximately half those expected. This result suggests excitonic interactions[24] between the two chromophores in the dimer. In dimeric or trimeric porphyrins[25] similar spectral effects have been previously reported and analyzed[26] as being dependent on the interporphyrin dihedral angles, on the orientation of the transition dipole moments in the monomer subunits,[27] and, of course, on the distance between the chromophores.

On the other hand, the Soret band and the visible (Q) bands were red-shifted by about 65 nm and more than 100 nm, respectively, from the corresponding unsubstituted porphyrins. Such drastic bathochromic shifts could not result from the sole electron-attraction effects exerted by the positive charge carried by the phosphonium cations. Previous results reported on such dimers, with bis(diphenylphosphonium)acetylene as spacer, revealed a red shift of only 10 nm for the Soret and Q bands if compared to the monomer.[20]

This important red shift observed for the UV-visible absorption bands of **2**-Zn-Zn was also noticed in the dimers **2**-H_2-H_2 and **2**-Cu-Cu. Such shifts and the intensity of both the Soret and the Q bands are actually characteristic of a chlorin structure.[12–13] In addition, it was observed that the red band of the dimers was increasingly blue-shifted when electronegativity of the central metal increased. This result suggests some delocalization of the positive charges on the porphyrin units (see Scheme 2), which is of course affected by the electronegativity of the central metal. Smith et al.[28] have reported such delocalization in an octaethylporphyrin substituted with a triphenylphosphonium at a *meso* position.

Addition of trace amounts of hydrochloric acid to a solution of the free-base dimer **2**-H_2-H_2 induced significant changes in the UV-visible spectrum of **2**-H_2-H_2, including clear splitting of the Soret band at 475 nm and 510 nm. The UV-visible spectrum of the protonated form of **2**-H_2-H_2 exhibited many similarities to those previously reported elsewhere for a chlorin-analogue monocation.[12f] As a consequence, such delocalization of the positive charge onto the π system of the chlorin analogues will unfavorably affect the protonation of the nitrogen atom on the reduced ring. Thus, the splitting of the Soret band could be the result to the formation of the related monocation. Such splitting may actually result from the disappearance of the degenerated Soret transitions $B_{\parallel}$ and $B_{\perp}$ ($m_{\parallel}$ and $m_{\perp}$ being the corresponding transition dipoles). This was not observed for the monomer **1**-H_4^{2+}.



Scheme 2. Possible conformations for the dimer **2**-M-M (M = H_2, Cu, and Zn).

^{1}H and ^{31}P NMR spectra

Monomers: In the monomeric porphyrin **1**-M (M = H_2, Zn), the pyrrolic protons all appeared downfield from those on the phenyl ring of the porphyrin and of the substituent; this indicated that the aromaticity of the porphyrin ring was not interrupted.[17] ^{1}H NMR spectroscopic studies of the monomer **1**-M showed that the signal corresponding to the proton in the β-position adjacent to the phosphonium cation appeared as a singlet at 8.47 ppm in the free base **1**-H_2 and 8.34 ppm in **1**-Zn. The other six β-protons of the porphyrin appeared as six doublets. These signals characterize the mono-β-substitution on the porphyrin. The signals of the β-H proton adjacent to the phosphonium was not the most downfield shifted; five of the six other β-H proton signals appeared at lower fields. That might be explained by assuming that the β proton is located in the shielding cone of the phenyl bearing the substituent. The signal for the phenyl protons of TPP and its substituent appeared as a complex multiplet in the range 8.26 – 6.63 ppm.

As usually observed in TPP series, the core N–H protons gave a singlet at high field (– 2.64 ppm).

In the symmetrical 1,2-bis(diphenylphosphino)benzene ligand taken as reference, the two phosphorus atoms resonated as one singlet at high field (– 14.15 ppm) in the ^{31}P spectrum. As expected, in the monomer **1**-M, the phosphonium and the neutral phosphorus atom are clearly discriminated by signals at 21.90 and – 30.17 ppm for **1**-Zn (36.76 and – 17.03 ppm for **1**-H_2) respectively. The signal of the neutral phosphorus atom for the monomer **1**-Zn resonated at higher field than the corresponding signal of 1,2-bis(diphenylphosphino)benzene (– 14.15 ppm) and hence characterized the location of the neutral phosphorus atom located inside the shielding cone of the porphyrin bearing the diphosphane. The corresponding upshift was not important in the case of the free base **1**-H_2 (– 17.03 ppm), and therefore suggests that the phosphane is now just near the shielding cone of the porphyrin in the free base monomer.

Dimers: In the synthesized dimers, the 14 β-H signals of the diphosphane appeared downfield from those corresponding to the phenyl rings of TPP and to the phenyl rings of the substituent in the mono-β-substituted porphyrin. The two β-H protons adjacent to each phosphonium merged in a large singlet, whose integral was for 2 protons, at 9.28 ppm in **2**-Zn-Zn and 9.03 ppm in **2**-H_2-H_2. Surprisingly the core N–H proton signals appeared in **2**-H_2-H_2 as a singlet of four protons at only -1.00 ppm, whereas they resonated at higher field (-2.64 ppm) for the monomeric porphyrin.

In our preliminary work with bis(diphenylphosphonium)-acetylene as spacer,[20] the free base dimer showed two singlets for the core N–H protons at -2.48 (2H) and -2.51 ppm (2H). In the corresponding precursor monomer, the N–H resonated as one singlet at -2.57 ppm.[20] Thus, in the dimer **2**-H_2-H_2 studied here, the shift was much lower than in the dimer studied with another spacer in our previous work and it was also lower than in the precursor monomer **1**-H_2 (-2.64 ppm). These results may be explained, as were the observed UV-visible spectral changes, by partial delocalization of the positive charge of the phosphonium substituent over the two porphyrin subunits due to an electrostatic repulsion of the two positive charges as shown in Scheme 2. With such a delocalization of the positive charge, the bischlorin-like structure was obtained. The upfield shift of the core N–H protons ($\delta = -1.00$ ppm) is consistent with a bischlorin structure carrying positive charges. In such a case, the N–H protons are mostly localized on the nitrogen atoms adjacent to the reduced rings,[30–31] because of the less symmetric chlorin subunits; this must be related to the single broad N–H resonance with a shift at higher magnetic field than usually observed for porphyrins (δ in the range -1.00 to -1.50 ppm for the neutral chlorins).[32]

In the ^{31}P NMR spectrum of dimers, as expected, the diphosphonium dication spacer gives signals at lower fields. Three well-separated signals are observed for **2**-Zn-Zn at 34.90, 24.76, and 4.00 ppm; this indicates distinct conformations of the dimer in solution.[21] The signal at 34.90 ppm could be attributed to conformer 2 (Scheme 2), which is the most symmetrical conformer. In this case, the two phosphorus atoms are nearly equivalent and resonate as one singlet at high field ($\delta = 34.90$ ppm).

The two other broadened signals observed at 24.76 and 4.00 ppm may correspond to conformer 1 (Scheme 2), in which the two phosphorus atoms are not equivalent. A reasonable explanation may rely here on the assumption that one of the two phosphorus atoms is significantly shielded in the chlorine analogue. In this case this phosphorus atom resonates at higher field (4.00 ppm) than the other (24.76 ppm). Similar results were obtained with **2**-H_2-H_2.

Electrochemistry: The electrochemical behavior of free-base porphyrins and metalloporphyrins involving nonelectroactive metals is well documented.[33–34] On the potential range of +2 V to -2 V versus SCE, oxidations and reductions of the π ring proceed by four reversible one-electron steps generating, respectively, π-radical cations and dications upon oxidation and π-radical anions and dianions upon reduction. The redox behavior of porphyrin monomers and dimers β-substituted with bipyridinium, viologen, or bis(diphenylphosphonium)-acetylene bridges has been already reported.[19–20] Redox studies of these compounds have shown that, in addition to the typical oxidations and reductions of the porphyrins, reductions of the substituent were observed before the reductions of the porphyrin. As expected, also in the presence of such electron-withdrawing substituents, the oxidation of the substituted porphyrins was more difficult than the oxidation of the corresponding unsubstituted porphyrins.

All redox potentials E, evaluated from cyclic voltammetry as $(E_p^a + E_p^c)/2$, will be given here in V versus the standard saturated calomel electrode (SCE). The number of exchanged electrons for each studied redox system was determined by exhaustive coulometry or by comparison between the limiting currents of the different waves characterizing a given system. The assignment of the site undergoing the electron transfers resulted from spectroelectrochemistry or from comparison of the recorded voltammograms with those of well known parents. All electrochemical data are gathered in Table 2 and a typical cyclic voltammogram is presented in Figure 3.

Table 2. Electrochemical data for the studied porphyrins and bisporphyrins. All potentials in V vs. SCE obtained from stationary (RDE) voltammetry in $CH_3CN/1,2\text{-}C_2H_4Cl_2$ (1:4), TEA • PF_6 (0.1M), Pt working electrode.

Porphyrins	Ring oxidation		$P(Ph)_2^+$ reduction		Ring reduction		
	$E_{1/2}^{III}$	$E_{1/2}^{II}$	$E_{1/2}^{I}$	$E_{1/2}^{II}$	$E_{1/2}^{I}$	$E_{1/2}^{I}$	$E_{1/2}^{II}$
H_2TPP		1.34	1.10			-1.10	-1.48
CuTPP		1.33	1.06			-1.22	-1.68
ZnTPP		1.16	0.80			-1.37	-1.75
violin[a]		1.52^{irr}	1.08^{irr}			-0.82	-1.30^{irr}
1-H_2			1.18^{irr}	-1.02		-1.29	-1.65
1-Cu	1.58	1.34	1.12	-1.14		-1.48	-1.80
1-Zn	1.42	1.25^{irr}	0.91	-1.28		-1.58	-1.84
2-H_2-H_2			$1.28^{2e.irr}$	-0.78	-1.17	-0.57^{2e}	-0.95^{2e}
2-Cu-Cu		–	1.30, 1.13	-0.88	-1.30	-0.60^{2e}	-1.06^{2e}
2-Zn-Zn		1.45^{2e}	1.13^{2e}	-0.97	-1.53	-0.58, -0.71	-1.23^{2e}

[a] By product obtained when working with diphosphane and 2,6-lutidine in large excess.

Monomers: With the substituted monomers, the known oxidations and reductions of the porphyrin were observed, plus an additional one-electron transfer, which took place before the first reduction of the porphyrin ring and corresponded to the reversible one-electron reduction of the $P(Ph)_2^+$ substituent.[20–21]

The measured reversible one-electron reduction potentials of the phosphonium substituents (-1.02 V for **1**-H_2, -1.14 V for **1**-Cu, and -1.28 V for **1**-Zn vs. aqueous SCE) matched the usual reduction potentials of these cationic species. Hence, the observation that the reduction of the phosphonium became more difficult when the net ring charge[34b] increased on the porphyrins provides a good indication that the chromophores do interact with their substituents, as expected. These increasingly negative potential values in the series **1**-H_2 > **1**-Cu > **1**-Zn match the sequence proposed by Fuhrhop and Kadish[34b] for the electronegativity (χ_M^P, Pauling values) of the central metal of the porphyrins.

There were significant changes in the measured potentials for the reduction of the substituted porphyrins compared with

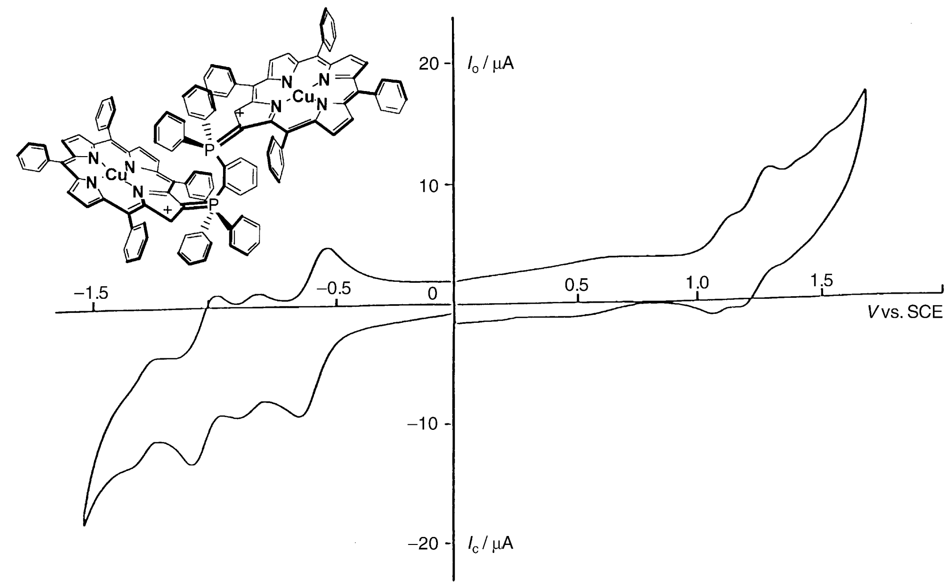


Figure 3. Cyclic voltammograms of **2**-Cu-Cu in CH_3CN + 1,2-$C_2H_4Cl_2$ (1:4) + TEA·PF_6 (0.1M), scan rate: $v = 100$ mV s^{-1}; Pt working electrode.

the corresponding unsubstituted porphyrins. As documented in Table 2, after the reduction of the phosphonium, the first and second reductions of the porphyrin cycle became more difficult when the substituent was neutral. This result indicates an electron-donating character of the reduced substituent (phosphane). The monomers **1**-M (M = H_2, Cu, and Zn) exhibited two reversible one-electron reduction steps after the one-electron reduction of the phosphonium substituent. The differences of potentials

$$\delta E_{1/2} = E^{II}_{1/2} - E^{I}_{1/2}$$

between the second and the first porphyrin reduction range from 0.26 to 0.32 V. The values are close to those typically observed for ring reductions of substituted metalloporphyrins.[34b]

The oxidation potentials of the substituted porphyrins were more positive than those corresponding to the unsubstituted chromophores (Table 2). These shifts may be ascribed to the well-known electron-withdrawing effect[35] of the positively charged spacer. Conspicuously, the monomer **1**-H_2 exhibited an irreversible two-electron oxidation at +1.28 V versus SCE. This feature, already observed in various substituted free-base porphyrins, may be explained by the instability and the high chemical reactivity of the radical cation resulting from the first electron transfer. The electrochemical oxidation at 1.28 V versus SCE generated the corresponding protonated porphyrin (**1**-H_4^{2+}) with an exchange of two electrons.[36b] The metalloporphyrins revealed a very different oxidative pattern. After the two first reversible oxidations (at 1.12 and 1.34 V vs. aqueous SCE for **1**-Cu, see Table 2), corresponding to the formation of the porphyrin π cation radical and dication, an additional one-electron transfer was observed that corresponded to the formation of an isoporphyrin.[37]

Dimers: The dimers exhibited three distinct electroactive sites, namely the spacer and the two chlorin analogues. The oxidation potentials of the chlorin analogues were more positive in the dimers than those of the corresponding monomer precursors. The observed shifts (+220 mV from **1**-Zn-Zn to **2**-Zn-Zn) may be ascribed to the electron-withdrawing effect of the positively charged spacer on each chlorin subunit. The **2**-Cu-Cu or **2**-H_2-H_2 dimers qualitatively behave as the above **2**-Zn-Zn compound. On reduction, four distinct reversible reduction peaks were recorded. Their respective heights were in the ratio 2:1:2:1. Coulometric measurements carried out at the first reduction step of the dimers indicated that two electrons were exchanged per molecule of dimer during the reaction. This result implies that the four reduction steps observed correspond to as sequence 2-1-2-1 electron(s) successively exchanged. This indicates an alternated sequence in the sites of the electron transfer, which involved, respectively, the chromophore and the spacer. This sequence was clearly discriminated in particularly by the fact that the two reductions expected for the spacer were each monoelectronic, whereas the two reductions of the two porphyrin rings were each bielectronic reversible reactions as already reported for the reductions of analogous metallodimers.[19–31]

For instance, in **2**-Cu-Cu, the reversible one-electron reductions of the diphosphonium bridge occurred at the second and the fourth steps, (−0.88 and −1.30 V vs. SCE, respectively). The first and the third two-electron steps observed at −0.60 and −1.06 V versus SCE generated respectively π radical anions and dianions on each of the two porphyrins (Figure 3).

The interesting feature in the dimers is the easy reduction of the two porphyrin rings, which occurs at very low potentials before the reduction of the diphosphonium spacer, at variance with previous results with others spacers.[19–21] This specific behavior may be ascribed to the partial delocalization onto the porphyrin rings of the two positive charges carried by the spacer, in agreement with the proposed structure of a chlorin-like compound supported by the UV-visible and NMR results.

Remarkably, the reduction potentials of the π-ring chlorin analogue in the dimers were 500 (**2**-H_2-H_2) to 800 mV (**2**-Zn-Zn) more positive than those measured in the corresponding monomeric porphyrin precursor (Table 2). These large shifts are clearly the result of i) the powerful electron-withdrawing capability of the two positives charges carried by the spacer and ii) some delocalization of these positive charges over the π system in the porphyrins.

Interestingly also, in **2**-Zn-Zn, the first reduction of the two porphyrin subunits (with chlorin spectroscopic features) occurred by two well-separated one-electron reversible transfers, before the first reversible one-electron reduction step of the spacer. This redox splitting ($\Delta E = 130$ mV, Table 2) is indicative of $\pi - \pi$ interactions between the two chromophores in the dimer **2**-Zn-Zn. Analogous effects have already been discussed in cofacial dimeric porphyrins.[36a]

Moreover, a redox splitting was also observed in the dimer **2**-Cu-Cu derivative, but this split redox process occurred in the first oxidation step of the dimer, with $\Delta E = 170$ mV. Such different splitting (on oxidation or on reduction) has already been reported[36a] but is not yet well understood. Spectroelectrochemical observations were carried out, and the corresponding results will be discussed further.

Discussion

Perusal of the redox-potential values reported (Table 2) leads to interesting observations. It has been widely demonstrated that ring-oxidation and ring-reduction potentials for a monomer free-base porphyrin and the corresponding metal derivatives are governed by the electronegativity of the central cation χ_M^P through inductive effects:[34b,g] the more electronegative the cation, the more difficult the first oxidation, while the reduction of the porphyrin becomes easier. These results suggest that an increase in χ_M^P should cause a shift of the N-σ electrons toward the metal, which would substantially lower the potential of the N-π and C-π (inductive effect).[34g] This rule is verified with the studied monomers **1**-M (M = H_2, Zn or Cu).

In the dimers, however, the observed pattern is quite different. Unexpectedly, the electronegativity of the central ion has only a small effect on the first ring-oxidation and -reduction potentials in the dimers, as evidenced by the quasiparallelism of the plotted $E_{1/2}$ values to the axis of the electronegativities χ_M^P (Table 2). This feature would suggest that the structural "bischlorin effect" induces such an important electronic repulsion in the dimer that the electronegativity of the central ion is almost without effect. As a matter of fact, the hypothesis that these original characteristics of the dimers originate from intrinsic interactions specific to these molecules is supported by another analysis of the measured redox potentials. In the given monoporphyrin **1**-M, when the electronegativity of the central ion is changed, a correlation is found between the first oxidation potential E_{ox_1} and first reduction potential E_{red_1} of the porphyrin, reflecting the inductive effect of the cation: the more difficult the ring is to oxidize, the easier it is to reduce, and vice versa (Figure 4).[34b] In the dimer studied here, when the central ion is changed, such correlation—which would exist with two independent rings—is not found.

Therefore the dimers cannot be considered as involving two redox-independent rings, but rather as a single entity from (or to) which electrons are abstracted (or added); and consequently this implies an electronic delocalization between the two chromophores.

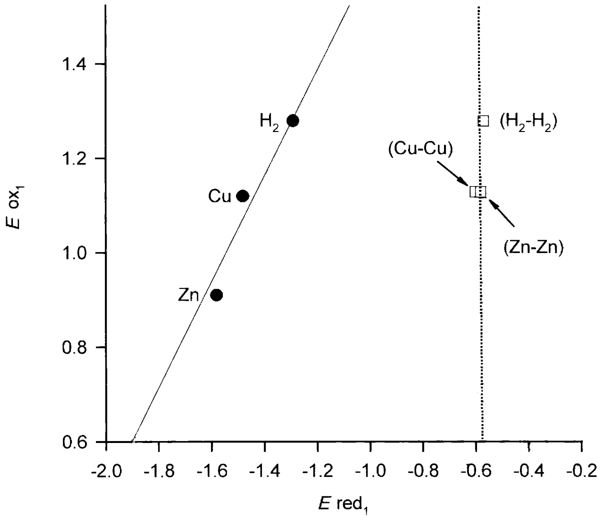


Figure 4. Variation of the first oxidation potential E_{ox_1} with the first reduction potential E_{red_1} for the monomer **1**-M and the dimer **2**-M-M (M = H_2, Cu and Zn).

It should be added that the reduction potentials of the phosphonium substituent are also governed by the electronegativity of the central ion in the porphyrins, both for the monomer and the dimer. Its reduction became more difficult when the net charge[34b] increased on the bound porphyrin or chlorin analogue.

Spectroelectrochemistry: In order to assign the observed electrochemical signals to the sites of the redox reactions, either the porphyrins or the diphosphonium spacer, spectroelectrochemical studies were carried out with a Pt mini-grid as working electrode, in CH_3CN/1,2-$C_2H_4Cl_2$ (1:4) + TEA$\cdot PF_6$ (0.1 M). The first oxidation of **2**-Zn-Zn induced a decrease in the intensity of the Soret band (Figure 5A), as usually observed in the generation of porphyrin cation radicals.[34–35, 38–39] The second oxidation step of **2**-Zn-Zn, monitored at a controlled constant potential of +1.45 V versus SCE, exhibited the typical spectrum of a bisporphyrin dication,[34–35, 38–39] with a flattening of the Soret band (Figure 5B). After this second oxidation had been carried out, the initial spectra of **2**-$Zn^{\bullet +}$-$Zn^{\bullet +}$ and **2**-Zn-Zn were each fully recovered after reverse electrolysis at +1.25 and 0 V versus SCE, respectively. This result, which exemplifies the reversible interconversion of the three redox forms, is in good agreement with the reversibility observed on the cyclic voltammetry curves in studying the oxidation of the dimer **2**-Zn-Zn.

The reduction reaction for **2**-Zn-Zn at −0.75 V versus SCE, the first reduction step (transfer of $2e^-$) of the chlorin analogue subunits, did not exhibit the decrease in the intensity of the Soret band usually associated with the generation of the anion radical $TPP^{\bullet -}$ (Figure 6).[40] Instead, a blue shift of (about) 20 nm for the Soret and Q bands was observed without the expected weakened Soret band. Such observation indicated that the first reduction (−0.75 V) carried out on the two chromophore subunits did not produce the expected species: $P^{\bullet -}$-diphosphonium^{2+}-$P^{\bullet -}$. The blue shifts of the Soret and of the Q bands would rather suggest a reduction of the

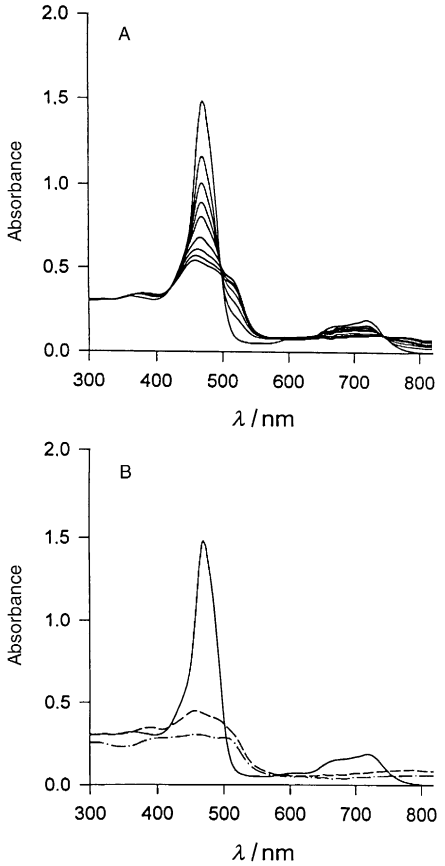


Figure 5. A) UV-visible absorption spectra recorded during the oxidation of **2**-Zn-Zn in $CH_3CN/1,2\text{-}C_2H_4Cl_2$ (1:4), TEA $\cdot$ PF_6 (0.1 M) at 1.13 V vs. SCE. B) UV-visible absorption spectra of **2**-Zn-Zn. (——) unoxidized form, (----) two-electron-oxidized species (first wave, 1.13 V), (– · – · –) four-electron-oxidized species (second wave, 1.45 V).

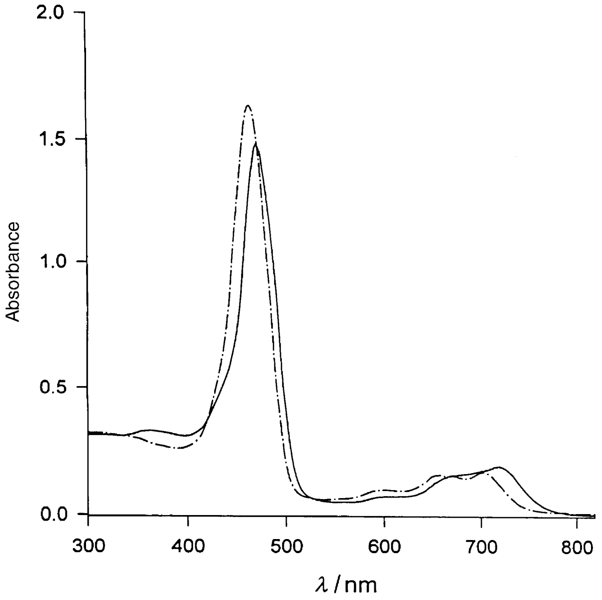


Figure 6. UV-visible absorption spectra recorded during the reduction of **2**-Zn-Zn in $CH_3CN/1,2\text{-}C_2H_4Cl_2$ (1:4), TEA $\cdot$ PF_6 (0.1 M) at -0.75 V vs. SCE. (——) Unoxidized form, (– · – · –) two-electron reduced species (second wave, -0.75 V).

diphosphonium spacer to its neutral form. If we assume that the π rings of **2**-Zn-Zn are first reduced upon applying -0.71 V versus SCE to the working electrode—which is consistent with the general redox pattern of the dimer—such behavior could be explained by a fast rearomatization of the chromophoric subunits to the final stable species P-diphosphane-P, according the following sequence:

$$\text{P-diphosphonium-P} \xrightarrow{+2e^-} \text{P}^{\bullet-}\text{-diphosphonium-P}^{\bullet-} \xrightarrow{\text{fast}} \text{P-diphosphane-P}$$

If, according the consistent indications from the above reported results, the electron distribution interacts in a given dimer from one macrocycle to the second one through the spacer, such a sequence is not surprising. Under such conditions, a species simultaneously containing two negative charges ($P^{\bullet-}$) and two positive charges (bisphosphonium) will have a very poor stability and might spontaneously become neutral. We have observed that this new neutral dimer reverted quantitatively to the initial charged dimer by reversing the polarization applied to the working electrode. Similar spectral evolutions were observed for **2**-Cu-Cu and **2**-H_2-H_2.

ESR: As reported above, UV/Vis spectroscopic, electrochemical, and spectroelectrochemical studies indicated that interactions do not occur between the two porphyrin π systems via the diphosphonium spacer.

Hence, the possible existence of intramolecular interactions in these dimers should be considered. We have therefore synthesized chlorin-like dimers containing two divalent copper ions, namely **2**-Cu-Cu. In such molecules, the paramagnetic copper(II) may be used as a sensor to detect metal–metal interactions in cofacial and noncofacial dimer conformations.[36a] To this aim, the magnetic susceptibility ($\chi^{-1} = f(\mathrm{T})$) of the dimeric **2**-Cu-Cu solid was studied. The values of χ were obtained by double integration of the ESR signal characteristic of Cu^{II} in the dimer. In the dimer **2**-Cu-Cu, the low value obtained for g (2.0605_{58} at 295 K) indicated an important spin–orbit coupling. Hence, each unpaired electron was localized on one copper in **2**-Cu-Cu. The plot $\chi(\mathrm{T})$ showed that, in the dimer **2**-Cu-Cu, the susceptibility obeyed a Curie–Weiss relationship ($\chi = C/(T - T_c)$) in which $T_c = -16$ K (T_c = coupling temperature). Actually, the exchange-interaction energy was estimated as -1.3 meV ($J = k_B T_c$ for an assumed one dimensional cubic stacking).

These ESR results obtained on solid dimers therefore indicated the absence of intramolecular copper–copper interactions and the occurrence of an intermolecular copper–copper antiferromagnetic coupling in dimer **2**-Cu-Cu. ESR experiments carried out with solutions at different concentrations (10^{-3}–10^{-4} M) of these dimers did not reveal any antiferromagnetic coupling. These results indicated that the antiferromagnetic coupling observed in the solid state was intermolecular.

Thus, the absence of intramolecular interactions between the Cu^{II} atoms suggests that the tetrapyrrole macrocycles are not cofacial in the dimer, so that the two copper atoms are too far apart to allow significant copper–copper interactions.

Conclusion

A new type of dimeric porphyrin exhibiting chlorin-like characteristics has been synthesized by electrochemistry. The generated species have been unambiguously identified. This method was based on nucleophilic substitution carried out on two electrooxidized porphyrins.

UV-visible spectra of **2**-M-M (M = H_2-H_2, H_3^+-H_3^+, Zn-Zn, Cu-Cu) revealed excitonic interactions between the two chromophores. The dimers also exhibited significant red shifts in their UV-visible absorption spectra. These shifts were strongly enhanced if compared with the corresponding monomers, and the spectral characteristics were typical of a chlorin-like structure. In the ^{1}H NMR spectra of **2**-H_2-H_2, the inner N–H appeared only at -1.00 ppm; this indicated a delocalization of the positive charge of the diphosphonium spacer over the two porphyrin subunits and also demonstrated that the dimer conformation is not cofacial. Such delocalization of the positive charge results chlorin-like structures.

ESR analysis of the dimer **2**-Cu^{II}-Cu^{II} indicated a weak intermolecular antiferromagnetic interaction between the copper atoms. This is consistent with the above proposed noncofacial conformation of the dimers.

Interestingly, the redox characteristics of all the studied dimers revealed that the oxidation and reduction potentials of the chlorin subunits are not located on both sides of the electroactive range characterizing the diphosphonium spacer; this is at variance with previous results obtained with other spacers.

An unexpected feature in the reduction of the dimers was the alternated sequence in the sites of the electron transfers respective to the chlorin-like analogues or porphyrins and to the spacer. In contrast to the previous results,[19–21] in the present dimers electrons are added first to the chromophore subunits. The first and the third two-electron reductions generated π-radical anions and dianions. The reduction of the diphosphonium spacer corresponded to the second and the fourth reduction steps, both being reversible one-electron reductions. All these results are in good and consistent agreement with a delocalization of the positive charges of the diphosphonium spacer over the π system of the porphyrins.

The synthetic method reported here allows, with the appropriate choice of spacer, specific electrochemical synthesis of interactive chlorin analogue dimers with good yields and through a one-pot reaction. It opens a new avenue for the preparation of new bis-porphyrin derivatives with bischlorin spectroscopic features, subject to appropriate selection of the porphyrin subunits and of the spacers. The availability of such new molecules is of major interest for better understanding of the interactions and the charge transfers between the subunits in the molecule, and ultimately for effectively mimicking photosynthetic pathways, or for creating new molecular materials.

Experimental Section

Materials: All solvents and chemicals were reagent grade, purchased commercially, and used without further purification except as noted below. CH_2Cl_2, for use in exhaustive electrolysis or UV-visible spectroscopy, was heated at reflux with and distilled from CaH_2. The supporting electrolyte tetraethylammonium hexafluorophosphate (TEA·PF_6) was used without purification. 1,2-Bis(diphenylphosphino)benzene was purchased from Strem Chemical Inc. Thin layer chromatography (TLC) was performed on commercially prepared silica gel plates purchased from Roth Sochiel.

Apparatus: All electrochemical measurements were carried out under argon at 25 °C on a dropping mercury electrode or on a platinum disk electrode. Voltammetric data were obtained with a standard three-electrode system by using a Bruker E130M potentiostat and a high-impedance millivoltameter (Minisis 6000, Tacussel). Current–potential curves were obtained from an Ifelec If3802 X-Y recorder. The working electrode was a platinum disk (E.D.I. type, Solea-Tacussel) of 3.14 mm^2 surface area. 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 a potentiostat (PRT 20-2X), and a voltage pilot unit (Servovite).

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) of 60 cm length. In the large cell, the working electrode was a cylindrical platinum grid (Ø = 5 cm, H = 7 cm). For the controlled-potential electrolysis, a fritted glass disk to prevent diffusion of the electrogenerated species separated the anodic and cathodic compartments.

Spectroelectrochemical studies were carried out in the solvent mixture CH_3CN/1,2-$C_2H_4Cl_2$ (1:4), on OTTLE (optically transparent thin layer electrode). The working electrode was a Pt grid (1000 mesh). The spectra were recorded on a Hewlett–Packard 8452 A diode array spectrophotometer. The thin-layer spectroelectrochemical cell has been previously described.[41]

UV-visible spectra were recorded on a Shimazu UV-260 spectrophotometer.

^{1}H and ^{31}P NMR spectra were obtained in $(CD_3)_2CO$ on a Bruker AC300 spectrometer (300 MHz and 120 MHz respectively).

Elementary analyses were performed by the microanalysis services of IUT Ilkirch (Strasbourg).

ESR spectra were recorded at X-band frequencies on a Bruker ESP300 spectrometer equipped with a variable temperature accessory.

Synthesis: Compounds H_2TPP, ZnTPP, and CuTPP were prepared and purified by known procedures.[42–43]

Electrochemical synthesis of 1-Zn and/or 2-Zn-Zn: Prior to electrolysis, the mixtures were stirred and degassed by bubbling argon through the solution for 10 minutes. Then the desired working potential was applied. During anodic oxidation, the electrolyzed solution was continuously stirred and maintained under argon. After electrolysis, solvents were removed by rotary evaporation. The residue was dissolved in a minimum of CH_2Cl_2, then the mixture was poured into water and the organic layer was washed twice.

ZnTPP (200 mg, 2.95×10^{-4} mol), 2,6-Lut (50 μL, 4.30×10^{-4} mol) and 2 equiv of 1,2-bis(diphenylphosphino)benzene (263 mg, 5.89×10^{-4} mol) were dissolved in a mixture (300 mL) of 1,2-$C_2H_4Cl_2$/CH_3CN (4:1) and TEA·PF_6 (0.1 M).

The electrolysis was carried out for 6 h at +0.85 V vs. SCE. After treatment, the organic extract was concentrated to 5 mL and chromatographed on silica gel. The first fraction, eluted with CH_2Cl_2/hexane (80:20), was unreacted ZnTPP. The second fraction (violet), eluted with CH_2Cl_2/hexane (90:10), was the monomer **1**-Zn (15 mg, 0.118×10^{-4} mol, yield: 4% after recrystallized from CH_2Cl_2/*n*-hexane). The desired product **2**-Zn-Zn (dimer) was eluted with CH_2Cl_2/CH_3OH (99:1). After evaporation of the solvent, **2**-Zn-Zn was recrystallized from CH_2Cl_2/*n*-hexane to give a green powder (92.5 mg, 0.441×10^{-4} mol, 30%).

By the same procedure, anodic oxidation of 1 equiv of ZnTPP (100 mg, 1.475×10^{-4} mol), 2,6-Lut (50 μL), and 0.5 equiv of the diphosphane (33 mg, 0.739×10^{-4} mol), gave, after treatment and purification, exclusively the desired dimer **2**-Zn-Zn with a yield of 70% (216 mg, 1.033×10^{-4} mol).

1-Zn: m.p. >300 °C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 8.93$ (d, $J_{cis} = 4.65$ Hz, 1H; β-H), 8.9 (d, $J_{cis} = 4.65$ Hz, 1H; β-H), 8.86 (d, $J_{cis} = 4.65$ Hz, 1H; β-H), 8.83 (d, $J_{cis} = 4.65$ Hz, 1H; β-H), 8.67 (d, $J_{cis} = 4.67$ Hz, 1H; β-H), 8.47 (s, 1H; β-H adjacent to $P^+(Ph)_2$), 8.25 (d, $J_{cis} = 4.67$ Hz, 1H; β-H), 8.23–8.00 (m, 6H; *o*-H of $P^+(Ph)_2$ and of Ph adjacent to $P^+(Ph)_2$), 7.96–6.64 (m, 34H; Ph); ^{31}P NMR (120 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 21.90$ (d, $^{3}J_{P\text{-}P} = 27.37$ Hz, $P^+(Ph)_2$), −30.17 (d, $^{3}J_{P\text{-}P} = 27.37$ Hz, $P^+(Ph)_2$), −145.44 (hpt, $^{1}J_{P\text{-}F} = 700.4$ Hz, PF_6^-); UV/vis (CH_2Cl_2), λ_{max} (ε) = 430 (266700), 557 (6500), 597 nm (1900 $M^{-1}cm^{-1}$); elemental analysis calcd (%) for $C_{74}H_{51}N_4P_3F_6Zn$: C 70.06, H 4.05, N 4.42, P 7.33, Zn 5.15; found: C 70.22, H 4.15, N 4.32, P 7.21, Zn 5.20.

2-Zn-Zn: m.p. >300 °C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$), 25 °C): $\delta = 9.28$ (s large, 2H; β-H adjacent to $P^+(Ph)_2$), 8.74 (d, $J_{cis} = 4.77$ Hz, 2H; β-H), 8.69 (d, $J_{cis} = 4.77$ Hz, 2H; β-H), 8.68 (d, $J_{cis} = 4.77$ Hz, 2H; β-H), 8.62 (d, $J_{cis} = 4.80$ Hz, 4H; β-H), 8.49 (d, $J_{cis} = 7.71$ Hz, 4H; *o*-H of $P^+(Ph)_2$), 8.44 (d, $J_{cis} = 7.71$ Hz, 4H; *o*-H of $P^+(Ph)_2$), 8.35–6.85 (m, 56H; Ph); ^{31}P NMR (120 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 36.74$ (s, $P^+(Ph)_2$), 26.44 (s low intensity, $P^+(Ph)_2$), 4.00 (s low intensity, $P^+(Ph)_2$), −145.44 (hpt, $^{1}J_{P\text{-}F} = 700.4$ Hz, PF_6^-); UV/Vis (CH_2Cl_2), λ_{max} (ε) = 467 (272700), 480 shoulder (203000), 613 (3100), 664 (6200), 717 nm (9500 $M^{-1}cm^{-1}$); elemental analysis calcd (%) for $C_{118}H_{78}N_8P_4F_{12}Zn_2$: C 67.79, H 3.76, N 5.36, P 5.93, Zn 6.25; found: C 67.92, H 3.83, N 5.47, P 6.18, Zn 6.40.

1-H$_2$ and 2-H$_2$-H$_2$: A mixture of HCl (25%) and acetone (1:4, 100 mL) was added to a solution of **1**-Zn or **2**-Zn-Zn in acetone, and the mixture was stirred for 30 min at room temperature. After addition of water (200 mL), the organic phase was washed with 20 equiv of water (*v*/*v*, 4×), and neutralized by the addition of 2,6-lutidine. The solution was washed again, dried over $CaSO_4$, and evaporated. After separation by chromatography on alumina, recrystallization from CH_2Cl_2/*n*-hexane gave a brown powder of **2**-H_2-H_2 in almost quantitative yield.

1-H$_2$: m.p. >300 °C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 8.97$ (d, $J_{cis} = 4.77$ Hz, 1H; β-H), 8.96 (d, $J_{cis} = 4.77$ Hz, 1H; β-H), 8.89 (d, $J_{cis} = 4.77$ Hz, 1H; β-H), 8.79 (d, $J_{cis} = 4.77$ Hz, 1H; β-H), 8.73 (d, $J_{cis} = 5.16$ Hz, 1H; β-H), 8.34 (s, 1H; β-H adjacent to $P^+(Ph)_2$), 8.33 (d, $J_{cis} = 5.16$ Hz, 1H; β-H), 8.26–8.18 (m, 6H; *o*-H of $P^+(Ph)_2$ and of Ph adjacent to $P^+(Ph)_2$), 7.95–6.63 (m, 38H; Ph), −2.64 (s, 2H; N-H interns); ^{31}P NMR (120 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 36.76$ (s, $P^+(Ph)_2$), −17.03 (s, $P(Ph)_2$); UV-vis (CH_2Cl_2), λ_{max} (ε) = 426 (242500), 521 (19600), 560 (1300), 600 (13700), 654 nm (16700 $M^{-1}cm^{-1}$); elemental analysis calcd (%) for $C_{74}H_{53}N_4P_2Cl$: C 81.12, H 4.89, N 5.11, Cl 3.24; found: C 81.02, H 4.97, N 5.05, Cl 3.20.

2-H$_2$-H$_2$: m.p. >300 °C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 9.55$ (d, $J_{cis} = 5.16$ Hz, 2H; β-H), 9.10–8.96 (s large, 2H; β-H adjacent to $P^+(Ph)_2$), 8.93 (d, $J_{cis} = 5.16$ Hz, 2H; β-H), 8.88 (d, $J_{cis} = 5.16$ Hz, 2H; β-H), 8.81 (d, $J_{cis} = 5.16$ Hz, 2H; β-H), 8.76–8.64 (m, 4H; *o*-H of Ph adjacent to $P^+(Ph)_2$), 8.62 (d, $J_{cis} = 5.16$ Hz, 2H; β-H), 8.55 (d, $J_{cis} = 5.16$ Hz, 2H; β-H), 8.57 (d, $J_{cis} = 6.90$ Hz, 4H; *o*-H of $P^+(Ph)_2$), 8.46 (d, $J_{cis} = 6.90$ Hz, 4H; *o*-H of $P^+(Ph)_2$), 8.33–6.41 (m, 52H; Ph), −1.00 (s, 4H; N-H interns); ^{31}P NMR (120 MHz, $(CD_3)_2CO$, 25 °C): $\delta = 34.87$ (s large, $P^+(Ph)_2$), 28.13 (s large, $P^+(Ph)_2$), 24.91 (s, $P^+(Ph)_2$), 4.28 (s, $P^+(Ph)_2$), −145.44 (hept, $^{1}J_{P\text{-}F} = 700.4$ Hz, PF_6^-); UV-vis (CH_2Cl_2), λ_{max} (ε) = 463 (237900), 532 (6100), 569 (11300), 619 (10100), 679 (9300), 737 nm (30900 $M^{-1}cm^{-1}$); elemental analysis calcd (%) for $C_{118}H_{82}N_8P_2Cl_2$: C 81.22, H 4.73, N 6.42, Cl 4.06; found: C 81.37, H 4.87, N 6.39, Cl 4.23.

1-Cu and 2-Cu-Cu: **1**-H_2 or **2**-H_2-H_2 was dissolved in CH_2Cl_2/CH_3OH (1:1) 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 $TEA \cdot PF_6$ (100 equiv). After evaporation of the solvent, the residue was dissolved in a minimum amount of CH_2Cl_2, washed with H_2O (4×), and dried over $CaSO_4$ during 6 h. The solution was concentrated on a rotary evaporator (≈5 mL) and separated by chromatography on the silica-gel column (eluent CH_2Cl_2) to afford **1**-Cu (black violet powder) or **2**-Cu-Cu (green powder) in an over 90% yield.

1-Cu: m.p. >300 °C; UV/Vis (CH_2Cl_2), λ_{max} (ε) = 423 (289700), 546 (9300), 582 nm (9300 $M^{-1}cm^{-1}$); elemental analysis calcd (%) for $C_{74}H_{51}N_4P_3F_6Cu$: C 70.17, H 4.06, N 4.42; found: C 70.32, H 4.22, N 4.31.

2-Cu-Cu: m.p. >300 °C; UV/Vis (CH_2Cl_2), λ_{max} (ε) = 421 (110100), 448 (285600), 544 (11600), 584 (14900), 635 (27600), 647 nm (27300 $M^{-1}cm^{-1}$); elemental analysis calcd (%) for $C_{118}H_{78}N_8P_4F_{12}Cu_2$: C 67.91, H 3.77, N, 5.37; found: C 68.05, H 3.92, N 5.29; EPR spectra of powder (300 K): $g_{\parallel} = 2.182_{22}$, $A_{\parallel} = 199 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.019_{17}$, $A_{\perp} = 111 \times 10^{-4}$ cm^{-1} (superhyperfine coupling 16×10^{-4} cm^{-1}).

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