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Synthesis of *meso*-Polyphosphorylporphyrins and Example of Self-Assembling

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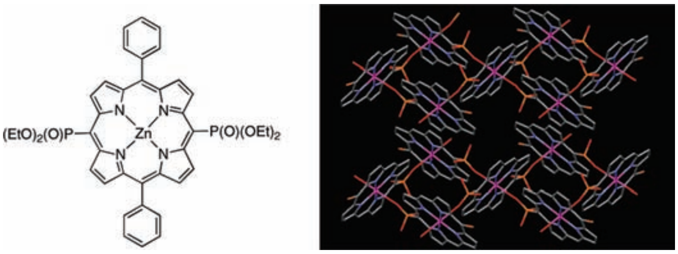
ABSTRACT



Pd-catalyzed coupling reactions have been used to prepare *meso*-phosphorylporphyrins. A 2D metal−organic network formed via P═O···Zn axial supramolecular coordination of 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyrin is the first example of a 2D framework based on phosphorylporphyrin derivatives.

The design of coordination networks formed upon a mutual interconnection between organic ligands and a metal center is a rapidly developing field.[1−7] The strategy of formation of these molecular architectures takes place under self-assembly conditions and exploits ionic interactions, hydrogen bonding, coordination bonds, and dispersion forces. For example, the self-organization of porphyrins is of particular interest.[8−10] This robust ligand can be metalated by a very large number of metallic elements and may be functionalized with various coordinating groups at the periphery of the macrocycle. Porphyrin-based architectures have been used to fabricate photonic materials, for fundamental studies of biological systems or the generation of molecular solids displaying chemical and catalytic properties.[11] Owing to these features, pyridyl, imidazolyl, carboxylate, amino, hydroxyl, nitro, cyano, aryl, sylfonyl, and alkyl porphyrins have been used as precursors in the synthesis of noncovalent architectures.[12−23] The key role of metallophosphonates in the fabrication of molecular assemblies is also well-known,[24−27] but surprisingly very few studies have been dedicated to the design of porphyrin derivatives containing phosphonate groups at the periphery of the macrocyclic ligand. The interest of these synthons has been demonstrated a long time ago by the studies on grafting phosphonated porphyrins at

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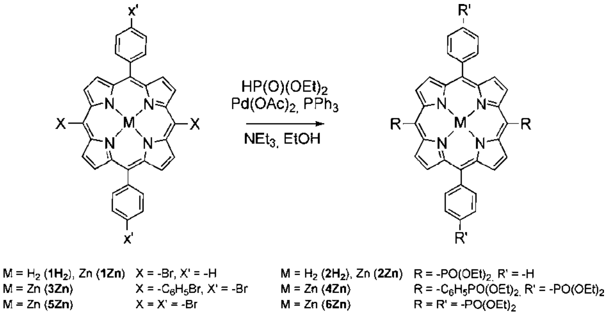
the surface of zirconium oxide or incorporating these derivatives in isomorphous matrices.[28−31] Very recently, it was proven that an appropriate choice of a porphyrin backbone makes possible the assembly of phosphonate porphyrins in extended 1D chains.[32,33] Due to the nonplanar character of the phosphonate group, it is clear that the fabrication of phosphonate porphyrin-based 2D and 3D architectures is a priori more difficult than the elaboration of such materials using carboxylic or pyridyl porphyrins as a precursor. In this work, we describe the first example of a *meso*-phosphorylporphyrin-based polymer exhibiting a 2D structure and the self-organization of such a porphyrin ligand in solution.

One of the major challenges that still lies ahead to fabricate materials containing phosphonato-substituted porphyrins is the finding of an efficient synthetic method for these precursors. Only a multistep synthesis developed by Lindsey's group,[34] or a Pd-catalyzed phosphorylation according to Hirao's conditions,[35,36] gives porphyrins possessing (4-dialkoxyphosphorylaryl) groups at the periphery of the macrocycle. Two monosubstituted *meso*-phosphoryl porphyrin derivatives have been recently obtained via a Cu-catalyzed phosphorylation reaction.[37] The widely applicable transition-metal-catalyzed cross-coupling methodology is a powerful tool in porphyrin series synthesis. For example, the formation of carbon−carbon bonds is obtained by Suzuki or Sonogashira reactions, and more recently hetero-cross-coupling reactions (C−N, C−O, C−S, C−B, C−P) have been successfully realized.[38−40] However, compared to regular classical methods used for common aryl halide derivatives, particular experimental conditions should be found to allow the catalytic transformations due to the electronic structure of the porphyrins or their solubility. We have probed a catalytic methodology to prepare polyphosphoryl-substituted porphyrins which are suitable precursors to elaborate 2D- or 3D-ordered architectures (Scheme 1).

Scheme 1. Pd-Catalyzed Coupling of *meso*-Bromoporphyrins with Diethylphosphite



The results are summarized in Table 1.[41] When classical Hirao's conditions are applied for the diphosphorylation of 5,15-dibromo-10,20-diphenylporphyrin **1Zn**, the target product **2Zn** was obtained as traces. Our attempts to optimize the synthesis have shown that the nature of the solvent is a key parameter on the reaction pathway. A high yield of the product **2Zn** (51%) was obtained in the presence of 10 mol % of catalytic precursor $Pd(OAc)_2/3PPh_3$ when ethanol was used as a solvent. The phosphorylation of **1Zn** was more efficient and gave a higher yield of the target product compared to the reaction involving the free base **1H$_2$**. Indeed, only traces of product **2H$_2$** were observed under catalytic conditions (10 mol % $Pd(OAc)_2/3PPh_3$). **2H$_2$** has been obtained only in the presence of a stoichiometric amount of palladium precursors and a large excess (24 equiv) of diethylphosphite using **1H$_2$** as starting

Table 1. Synthesis of *meso*-Polyphosphorylporphyrins

bromide derivative	$Pd(OAc)_2/3PPh_3$ equiv	$HOP(OEt)_2$ equiv	product	yield %
1H$_2$	0.1	2.4	**2H$_2$**	<5
1H$_2$	1.0	24	**2H$_2$**	32
1Zn	0.1	2.4	**2Zn**	51
3Zn	0.1	14	**4Zn**	68
5Zn	0.3	14	**6Zn**	50

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compound. The formation of a catalytically nonefficient Pd−porphyrin complex cannot be excluded, but such a complex has never been observed by MALDI-TOF analysis of the reaction mixtures. It is remarkable to note that the polyphosphorylation of the *meso*-tetra(4-bromoaryl)-substituted porphyrin **3Zn** can be carried out under the same conditions. Four consecutive catalytic cycles were carried out in a one-pot reaction in the presence of 10 mol % of the catalyst precursor (2.5 mol % for each bromide). The yield of the porphyrin phosphonate **4Zn** was much higher (68%) than the yield in the phosphorylation of the corresponding free base of **3Zn** in a toluene/THF mixture (28%).[35] Thus, the palladium-catalyzed polyphosphorylation of the studied porphyrin bromides in ethanol have produced a wide variety of novel polyphosphoryl porphyrins. In particular, the Pd-catalyzed polyphosphorylation methodology allows the phosphorylation of the compound **5Zn** where two bromide atoms are directly linked to the macrocyclic ring and two bromides are located at the *para* position of the *meso*-phenyl substituents. The target tetrasubstituted porphyrin **6Zn** was isolated in 50% yield. Polyphosphoryl-substituted compounds **2Zn**, **4Zn**, and **6Zn** prepared according to this route are suitable precursors for the elaboration of well-ordered porphyrin assemblies due to their symmetry and the presence of appropriate ligands at the periphery of the macrocycle.

Compound **2Zn** gives violet monocrystals by slow evaporation from a chloroform or chloroform−ethanol mixture. It is interesting to note that upon slow diffusion of a solution of Zn(OAc)$_2$ in MeOH into a solution of **2H$_2$** in CHCl$_3$ the same violet monocrystals have been obtained. The three isomorphous crystals (monoclinic, $Z = 2$, space group $P2_1/a$) are formed of **2Zn** units without any solvent molecules. The porphyrin core of **2Zn** is almost planar. The zinc atom located exactly in the center of the ring exhibits a six-coordinate square bipyramidal stereochemistry as shown in Figure 1.[41,42] The two apical coordination sites are occupied by O$_1$ oxygen atoms belonging to the diethoxyphosphoryl substituents of two adjacent complexes, and the Zn−O bond is slightly tilted from the vertical to the four nitrogen plane with angles $N_2-Zn-O_{1\#3} = 92.07(9)°$ and $N_1-Zn-O_{1\#3} = 82.84(10)°$. The average equatorial Zn−N distance is 2.061(3) Å. The axial Zn−O$_1$ bond distance is equal to 2.465(2) Å. This coordination configuration propagates along two axes to produce a 2D coordination polymer, as illustrated in Figure 2. The 2D sheets are composed by slightly deformed square mesh formed by four zinc porphyrins. This arrangement contributes to create cavities which are in fact not accessible due to the bulky ethyl groups of phosphonates located onto the *meso*-position of the porphyrin macrocycle and pointing into the cavity.

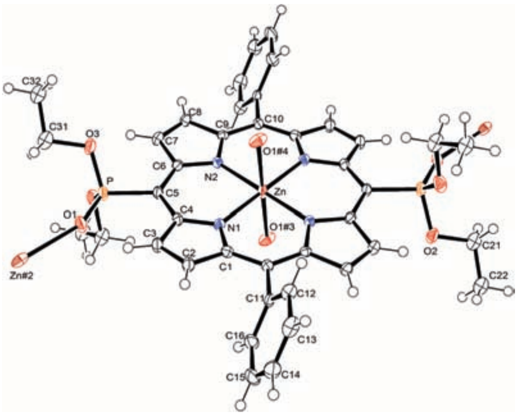

Figure 1. ORTEP view of the molecular structure of **2Zn**. 50% probability ellipsoids. Disordered parts of ethyl groups are omitted for clarity.[42]

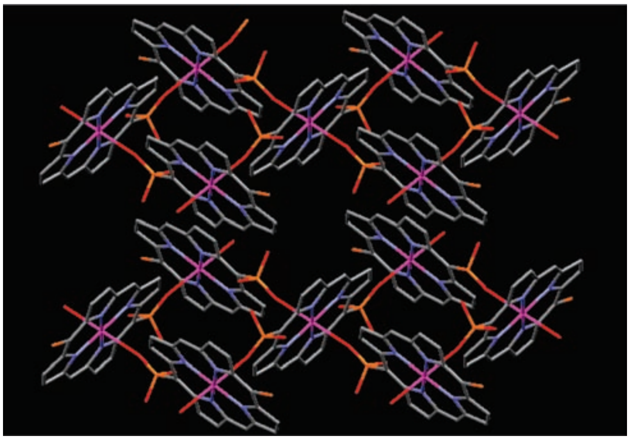

Figure 2. 2D network structure of **2Zn** in monocrystal. The *meso*-aryl substituents, hydrogen atoms, and ethyl groups are omitted for clarity.

The degree of ordering of complex **2Zn** in the solid state can be efficiently estimated using infrared spectroscopy.[41] The P═O stretching vibrations (1250−1300 cm^{-1}) in aryl phosphonates are sensitive to the environment variation, and a bathochromic shift of 30−80 cm^{-1} occurs when this bond is involved in a hydrogen-bond formation or coordinated to the metal ion.[43] Only one ν(P═O) band at 1233 cm^{-1} was observed in the IR spectrum of the monocrystal of complex **2Zn** (Figure 3, red curve). Indeed, a molecular self-assembling via P═O···Zn interactions in the monocrystal leads to the appearance in the spectrum of a band corresponding to the vibrations of the coordinated phosphoryl group. On the contrary, two strong P═O stretching bands at 1259 and 1235 cm^{-1} are observed in the spectrum of polycrystalline compound **2Zn** (Figure 3, blue curve). The relative intensity of these bands depends on the method of sample preparation (pure, KBr pellet or thin film prepared by the evaporation of a chloroform/ethanol solution on the surface of a KBr plate). The second band at 1259 cm^{-1} can be assigned to the vibrations of an uncoordinated phosphoryl group.

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(42) Crystal data for **2Zn**: C$_{40}$H$_{38}$N$_4$O$_6$P$_2$Zn, Mr = 798.05, monoclinic, space group $P2_1/a$, $a = 12.1377(5)$ Å, $b = 11.4995(4)$ Å, $c = 12.4813(4)$ Å, $\beta = 91.668(2)°$, $V = 1741.37(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.522$ Mg/m^3, $T = 115(2)$ K, Mo Kα radiation ($\lambda = 0.71073$ Å), $\mu = 0.854$ mm^{-1}, 6730 measured reflections, 3970 [R(int) = 0.0424] independent reflections, $R_1 = 0.0593$ ($I > 2\sigma(I)$), wR$_2$ = 0.1208 (all data), GOF = 1.134 ($I > 2\sigma(I)$). Structure information is given in the Supporting Information. CCDC-730343 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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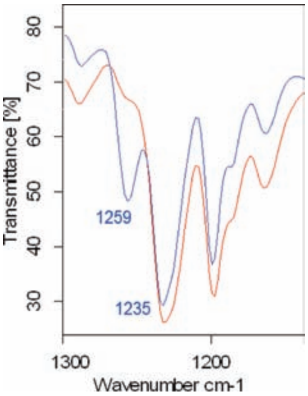

Figure 3. Infrared data of **2Zn** and P═O stretching bands for the monocrystalline (red curve) and the powder forms (blue curve).

The influence of the molecular aggregation in solution on the crystal growth is a topic of special interest for crystal engineering.[20,21,44,45] For this purpose, we have studied the aggregation of **2Zn** in solution by using different spectroscopic techniques. Chloroform was chosen as an appropriate solvent due to the low solubility of **2Zn** in dichloromethane, toluene, and other nonpolar solvents.

The ^{1}H NMR spectrum of **2Zn** in $CDCl_3$ ($10^{-3}-10^{-2}$ M) at room temperature exhibits very broad signals.[41] It is interesting to note that a narrowing and a downfield shift of the signals in more diluted solutions suggest that the aggregation is responsible for signals broadening. The aggregates already exist in a 8.7×10^{-5} M solution where distinct signals of all proton resonances expected for the molecule **2Zn** are observed, but some signals are still broad.[41] The low intensity of signals in more diluted solutions does not allow us to determine the precise limit of the concentration where the compound **2Zn** exists only as a monomer. A more strong coordinating solvent (MeOH-d_4, 25% v/v) was added to confirm the aggregation phenomenon.[41] Under these conditions, distinct and sharp signals for all the protons were observed. Moreover, the ^{1}H NMR titration of the compound **2Zn** was carried out in $CDCl_3$ by methanol-d_4 and trifluoroethanol, a less coordinating alcohol.[41] Sharp signals of all protons were observed after addition of 20 μL of methanol-d_4, while 120 μL of trifluoroethanol is needed to observe a well-resolved spectrum. Similar changing was observed in the ^{31}P NMR spectrum where narrowing of a broad signal ($\delta = 23.5$ ppm) was observed after the addition of 20 μL of methanol-d_4 or 120 μL of trifluoroethanol. These data allow us to conclude that the molecular aggregates are formed in the chloroform solution through the coordination of the diethoxyphosphoryl group to the zinc atom as observed by X-ray study in the solid state. The chemical shifts of pyrrolic protons as well as the protons of the diethoxyphosphoryl group are less pronounced than for Zn-porphyrins having intramolecularly connected diethoxyphosphoryl groups or for Zn-porphyrin dimers where the P═O···Zn coordination bond occurs.[37,46] The P═O···Zn bond in **2Zn** assembly is weaker compared to the intermolecular bonds of Zn-phosphoryl porphyrin dimers.[37,46]

UV−vis absorption spectroscopy can be used to estimate more precisely the range of concentration where the self-assembling of compound **2Zn** takes place. We have shown that no evolution of the UV−vis spectrum of **2Zn** in chloroform occurs in the range 10^{-7} to 2×10^{-5} M. A further increase of the concentration leads to a bathochromic shift (2−3 nm) of all the bands (Figure 4). Such spectral changes indicate the formation of extended supramolecular aggregates with brickwall structure.[47] Considering deviation from the Beer−Lambert law of Soret-band ($\lambda = 420$ nm), the self-organization of compound **2Zn** via P═O···Zn bonds occurs when the concentration of the compound in chloroform is higher than 2×10^{-5} M.

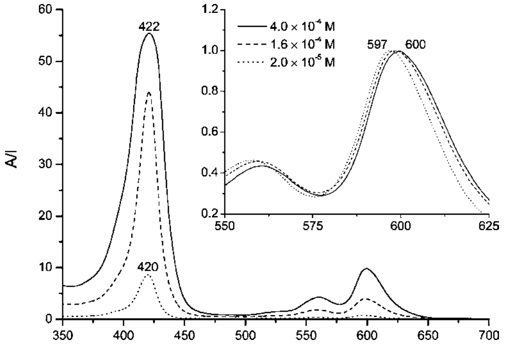

Figure 4. UV−vis absorption spectra of **2Zn** in chloroform at various concentrations and the normalized spectra in the range 500−650 nm (inset).

To prove the coordination of phosphoryl groups to the Zn center in the chloroform solutions, we have also monitored the spectral changing induced by diethylphosphite addition to 2×10^{-5} M solution of compound **2Zn** where only a monomer form exists.[41] The bathochromic shifts of the bands (3 nm) induced by diethylphosphite coordination to Zn were similar to those observed for the aggregation phenomenon.

In summary, we have successfully applied a transition-metal-catalyzed cross-coupling methodology for the synthesis of a series of novel *meso*-polyphosphorylporphyrins which are suitable building blocks to give new 2D and 3D coordination networks. A stable phosphonate porphyrin based 2D metal−organic framework was fabricated via a supramolecular self-assembling involving P═O···Zn axial bond formation. These aggregates are also observed in chloroform solution. The properties of this new and novel phosphonato porphyrin-based network are studied to develop photonic materials and to mimic biological derivatives.

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Supporting Information Available: Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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