

# Covalent Bonding of Phosphonates of Fullerene and Ru Complexes to $\gamma$ -Zirconium Phosphate as a Template for Building Chemical Devices in the Solid State

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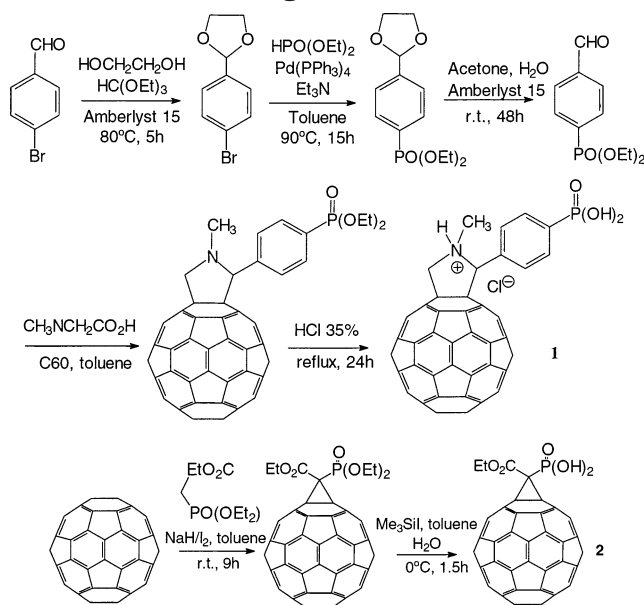
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Structure prediction and management of large supramolecular assemblies are certainly the most challenging goals faced by material chemists. The layered structure of zirconium phosphates ( $\text{ZrP}$ )<sup>1</sup> provides a template surface where organic structures of virtually any nature can be chemically deposited in an orderly, predicted manner.<sup>2</sup> The  $\gamma$ -phase of these salts [ $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ]<sup>3</sup> bears two kinds of phosphates, of which those bonded to Zr by means of two oxygen atoms may be easily replaced by organic phosphonates. These exchangeable phosphates are located in the surface of both faces of a layer forming a grid of ca.  $6.5 \times 5.5 \text{ \AA}$ . Their replacement may be total or partial, depending on the amount and steric volume of the phosphonate used in the toptactic exchange. Had it been performed in a low level, large void spaces are left to the access of solvent molecules or to the intercalation/exchange of additional species.

With these rather simple structural principles in mind, we initiated the study of phases to which electron donor and acceptor species were covalently attached to the inorganic layer, to achieve photoinduced electron transfer, as an approach to a new class of materials for artificial photosynthesis and light harvesting. Several hosting structures have been tried in the literature<sup>4</sup> to perform light-induced phenomena, including  $\text{ZrP}$ .<sup>5</sup> However, in almost all the cases, the active species are simply intercalated into the inorganic matrix. We hereby describe the building of covalent composite materials where, for the first time, phosphonates of

**Scheme 1. Reaction Paths Leading to Phosphonate-Containing Pyrrolidine- (1) and Bingel-C60 (2)**



fullerene and  $\text{Ru}^{\text{II}}(\text{bpy})_3$  are incorporated into the inorganic scaffold of  $\gamma\text{-ZrP}$ .<sup>6</sup>

The preparation of phosphonate-containing fullerenes has been accomplished following typical procedures for pyrrolidine-C60 formation and Bingel reaction<sup>7</sup> (Scheme 1).

Layered  $\gamma\text{-ZrP}$  has first to be exfoliated or preswelled to make accessible its interlayer region to bulky, hydrophobic phosphonates as those derived from fullerene. Preliminary experiments showed that among the usual methods to achieve exfoliation or preswelling (e.g., simple suspension of  $\gamma\text{-ZrP}$  in water/acetone at  $80^\circ\text{C}$  or intercalation of alkylamines, respectively) only the latter gave positive results (Table 1), albeit we observed no appreciable incorporation of fullerene for intercalated amines shorter than decylamine.

Elemental analysis indicates that decylamine-mediated incorporation of C60 (7–8%) is close to the calculated 12% maximum exchange level<sup>8</sup> and that 21–24% of the amine remains between the layers of  $\gamma\text{-ZrP}$ , even after thorough washing of the resulting solid with diluted HCl. We observed that more acid washing diminished amine content even further but gradually destroyed sample crystallinity.

The relatively high loading of fullerene indicates that C60 phosphonates are indeed in the inside of the inorganic matrix. It is easy to estimate that the incorporation of C60 solely in the surface of a typically sized particle (Coulter method,  $0.5\text{--}2 \mu\text{m}$ ) would not exceed

(1) Alberti G. *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Pergamon: New York, 1996; Vol. 7, Chapter 5. Clearfield, A.; Sharma, C. V. K.; Zhang, B. P. *Chem. Mater.* **2001**, *13*, 3099. Clearfield, A.; Wang, Z. K. *J. Chem. Soc., Dalton Trans.* **2002**, 2937.

(2) Brunet, E.; Huelva, M.; Rodríguez-Ubis, J. C. *Tetrahedron Lett.* **1994**, *35*, 8697. Brunet, E.; Huelva, M.; Vázquez, R.; Juanes, O.; Rodríguez-Ubis, J. C. *Chem. Eur. J.* **1996**, *12*, 1578. Alberti, G.; Brunet, E.; Dionigi, M.; Juanes, O.; Mata, M. J.; Rodríguez-Ubis, J. C.; Vivan, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3351.

(3) Salvado, M. A.; Pertierra, P.; García-Granda, S.; Barcina, L. M.; Llavona, R.; Rodríguez, J. Z. *Kristallogr.* **2001**, *216*, 326. Poojary, D. M.; Shepizer, B.; Clearfield, A. J. *Chem. Soc., Dalton Trans.* **1995**, 111.

(4) See for example, Kaschak, D. M.; Johnson, S. A.; Waraksa, C. C.; Pogue, J.; Mallouk, T. E. *Coord. Chem. Rev.* **1999**, *185–186*, 403.

(5) Krishna, R. M.; Kurshev, V.; Kevan, L. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2833.

(6) For an excellent review on fullerene-based organic–inorganic nanocomposites see: Innocenzi, P.; Brusatin, G. *Chem. Mater.* **2001**, *13*, 3126.

(7) Cheng, F. Y.; Yang, X. L.; Fan, C. H.; Zhu, H. S. *Tetrahedron* **2001**, *57*, 7331.

(8) Molecular modeling predicts a 12% maximum exchange if fullerenes from the face of one layer interdigitates (imbricates) with those from the opposing face of the consecutive layer. Loading of fullerene would reach 25% if imbrication does not occur.

**Table 1. Results for the Phosphate/Phosphonate Exchange of Decylamine-Intercalated  $\gamma$ -ZrP with C60 Derivatives 1 and 2 (see Scheme 1)**

material/exchange reaction	HCl washings <sup>a</sup>	elemental analysis			<i>d</i> <sub>001</sub> <sup>b</sup> (nm)	empirical formula <i>w,x,y,z</i> <sup>c,d</sup>
		%C, H, N obs.	%C, H, N calc.			
starting <b>C<sub>10</sub>H<sub>23</sub>N-γZrP</b>		25.4	5.5	2.9	2.58	0,0,95,100
		25.3	5.8	3.0		
exchange of <b>1</b>	until	27.7	3.7	1.8	2.34	0,8,50,150
	pH = 6	27.7	3.8	1.9		
	+10 addl.	22.1	2.4	1.2	2.40	0,8,21,130
		22.2	2.5	1.0		
double exchange ( <b>1</b> and <b>3</b> )		23.8	2.6	2.0	2.21	6,8,12,150
		23.9	2.4	1.8		
exchange of <b>2</b>	until	25.8	3.8	1.6	2.65	0,7,52,150
	pH = 6	25.9	3.9	1.6		
	+10 addl.	20.3	2.6	0.9	2.25	0,7,24,150
		20.3	2.7	0.8		
double exchange ( <b>2</b> and <b>3</b> )		22.1	2.8	1.7	2.13	5,7,17,120
		22.2	2.5	1.6		

<sup>a</sup> Acid washings (ca. 10 mL of 1 M HCl/g of solid) of exchanged  $\gamma$ -ZrP after isolation and centrifugation from reaction mixture. <sup>b</sup> Powder X-ray diffraction data. <sup>c</sup> For formulas: single-exchange  $\text{Zr}_{100}(\text{PO}_4)_{100}(\text{H}_2\text{PO}_4)_{100-x}(\text{C60-deriv.})_x(\text{decyl-NH}_2)_y(\text{H}_2\text{O})_z$ ; double-exchange  $\text{Zr}_{100}(\text{PO}_4)_{100}(\text{H}_2\text{PO}_4)_{100-x-2w}(\text{C60-deriv.})_x(\text{C}_{32}\text{H}_{30}\text{P}_2\text{O}_6\text{N}_6\text{Ru})_w(\text{decyl-NH}_2)_y(\text{H}_2\text{O})_z$ . <sup>d</sup> Water content ( $z$ ) was deduced from TGA. Ru content ( $w$ ) was measured by ICP-MS.

at the very most a phosphonate/phosphate exchange of 0.5%.<sup>9</sup> These facts strongly suggest that a previous interaction of the apolar C60 and the polar phosphonate ends of **1** and **2** with the amine long alkyl chains and the ammonium group, respectively, is a necessary step to C60 intercalation and subsequent phosphonate/phosphate exchange. The remaining of the decylamine appears to be essential for preserving the integrity of the fullerene-containing inorganic building in a similar way as a tensoactive agent isolates an apolar component from a highly polar environment. Yet despite the presence of the amine, the material still allows further incorporation of phosphonates derived from the  $\text{Ru}^{\text{II}}(\text{bpy})_3$  complex (see below).

Thermogravimetric curves of the decylamine-intercalated, **1**- and **2**-exchanged  $\gamma$ -ZrP showed weight losses in excellent agreement with the expected ones from the molecular formulas deduced from elemental analysis, considering that all of the organic components are lost in the interval 200–550 °C.

Powder X-ray diffraction showed relatively broad  $d_{001}$  peaks corresponding to interlayer distances of 2.40 and 2.25 nm for **1**- and **2**-exchanged  $\gamma$ -ZrP, respectively. Molecular modeling indicates that the observed distances implies interdigitation of fullerenes from consecutive layers.<sup>8</sup> The models also show that at a 7–8% of exchange, fullerenes should form, as an average, a grid of  $1.6 \times 1.8$  nm, 1.5 nm high, of which ca.  $3.5 \text{ nm}^3$  (80% of the total volume) remains accessible to other organic species. Intercalation of 20–25% of decylamine or incorporation of  $\text{Ru}^{\text{II}}(\text{bpy})_3$  complex was thus easily modeled by filling the void spaces (see Supporting Information).

MAS  $^{31}\text{P}$  solid-state NMR spectra of **1**- and **2**-exchanged  $\gamma$ -ZrP show the phosphate peaks of  $\gamma$ -ZrP at

–13 (exchangeable) and –26 (nonexchangeable) ppm and a broad signal centered at 11 (**1**-exchanged) and 7 (**2**-exchanged) ppm, which are assigned to the C60 phosphonates. Deconvolution-aided integration of the signals is in excellent agreement with the 7–8% incorporation level deduced from elemental analysis.

CP-MAS  $^{13}\text{C}$  solid-state NMR of **1**- and **2**-exchanged  $\gamma$ -ZrP showed two main groups of signals centered at 145 and 25 ppm, attributable in that order to fullerene and decylamine, the signals of the latter being heavily increased in intensity due to the CP technique. It should be noted that, in the case of **2**, the signals of the starting organic phosphonate at 60 and 15 ppm, assigned to the ethyl carbons of the ethoxycarbonyl group, are not visible in the  $\gamma$ -ZrP exchanged material. This suggests that ester cleavage (and perhaps decarboxylation) took place in the acidic phosphonate–phosphate exchange process.

The environment of fullerene is clearly manifested by UV–vis spectroscopy.<sup>10</sup> Absorption bands of **1** and **2** in a heterogeneous mixture with  $\gamma$ -ZrP in water dispersion (228, 290, and 359 nm) are strongly red-shifted, compared to the characteristic C60 bands in *n*-hexane<sup>11</sup> (210, 260, and 330 nm). The C60-containing  $\gamma$ -ZrP phases showed absorption bands in water dispersion at intermediate values (222, 275, and 340 nm), compatible with the less polar environment conferred by the surrounding decylamine molecules in the confinement within the polar layers of  $\gamma$ -ZrP.

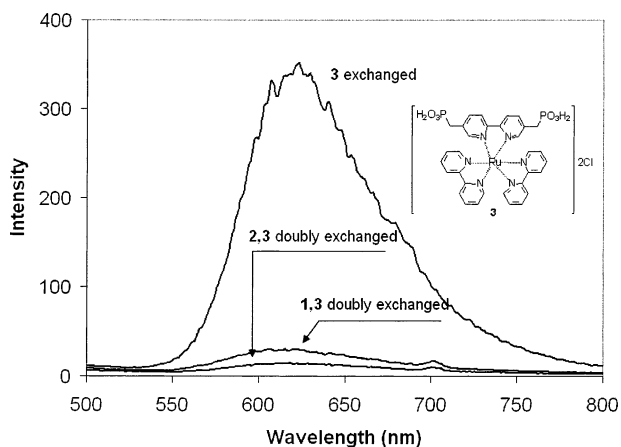
Finally, we have performed a second exchange reaction of the C60-containing  $\gamma$ -ZrP phases with a phosphonate derived from  $\text{Ru}^{\text{II}}(\text{bpy})_3$  complex (**3**),<sup>12</sup> by sus-

(10) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379.

(11) Bensasson, R. V.; Bienvenue, E.; Dellinger, M.; Leach, S.; Seta, P. *J. Phys. Chem.* **1994**, *98*, 3492.

(12) Gillaizeau-Gauthier, I.; Odobel, F.; Alebbi, M.; Argazzi, R.; Costa, E.; Bignozzi, C. A.; Qu, P.; Meyer, G. *J. Inorg. Chem.* **2001**, *40*, 6073.

(9) See for example: Alberti, G.; Dionigi, C.; Giontella, E.; Murcia-Mascarós, S.; Vivani, R. *J. Colloid Interface Sci.* **1997**, *188*, 27. Ferragina, C.; Massucci, M. A.; Patrono, P.; Ginestra, A.; Tomlinson, A. A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 851.



**Figure 1.** Emission spectra ( $\lambda_{\text{exc}} = 468$  nm) of the  $\gamma$ -ZrP phases exchanged with Ru complex **3** and doubly exchanged with fullerenes **1** or **2** and Ru complex **3**.

pending the **1**- or **2**-exchanged  $\gamma$ -ZrP phases in water/acetone at 80 °C containing **3**. Elemental analysis and ICP-MS analysis showed an incorporation of **3** of ca. 5–6% with no detected loss of exchanged C60 phosphonates (Table 1) and a diminution of decylamine content. The second exchange reaction with the bis-phosphonate **3** made the layers become closer, at a distance (Table

1) for which molecular simulations hint the formation of a pillared material.

Figure 1 shows the emission spectra in the solid state of the  $\gamma$ -ZrP phase 9% exchanged with **3**, as a reference material, and doubly exchanged with **1** or **2** and **3**. It can be seen that the Ru emission is heavily quenched in the material that contains fullerenes **1** and **2**, strongly suggesting photoinduced electron transfer between **3** (donor) and the fullerene (acceptor) within the walls of the inorganic framework. Work is in progress to measure the physical-chemical parameters of this composite system of promising optical properties.

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**Supporting Information Available:** Solid-state NMR spectra, thermogravimetric, X-ray powder data, and molecular models (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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