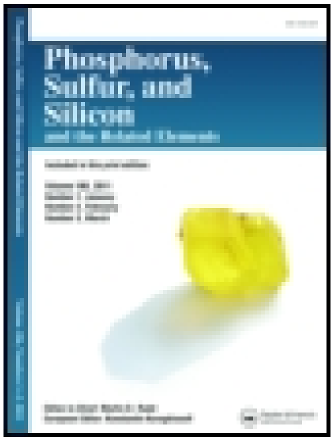
This article was downloaded by: [New York University]
On: 14 February 2015, At: 23:07
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Click for updates

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Supramolecular Architectures Based on Phosphonic Acid Diesters

Alla Lemeune[a], Alexander Yu. Mitrofanov[a], Yoann Rousselin[a], Christine Stern[a], Roger Guilard[a], Yulia Yu. Enakieva[b], Yulia G. Gorbunova[bc] & Sergey E. Nefedov[c]

[a] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR CNRS 6302, 9 avenue A. Savary, 21078 Dijon, France. E-mail:

[b] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Leninskiy p. 31-4, Moscow, 119071 Russia. E-mail:

[c] N.S. Kurnakov Institute of General and Inorganic Chemistry of RAS, Leninskiy p.31, Moscow, 119991 Russia. E-mail:

Accepted author version posted online: 31 Dec 2014.

To cite this article: Alla Lemeune, Alexander Yu. Mitrofanov, Yoann Rousselin, Christine Stern, Roger Guilard, Yulia Yu. Enakieva, Yulia G. Gorbunova & Sergey E. Nefedov (2014): Supramolecular Architectures Based on Phosphonic Acid Diesters, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2014.985823

To link to this article: http://dx.doi.org/10.1080/10426507.2014.985823

Disclaimer: This is a version of an unedited manuscript that has been accepted for publication. As a service to authors and researchers we are providing this version of the accepted manuscript (AM). Copyediting, typesetting, and review of the resulting proof will be undertaken on this manuscript before final publication of the Version of Record (VoR). During production and pre-press, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal relate to this version also.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

SUPRAMOLECULAR ARCHITECTURES
BASED ON PHOSPHONIC ACID DIESTERS

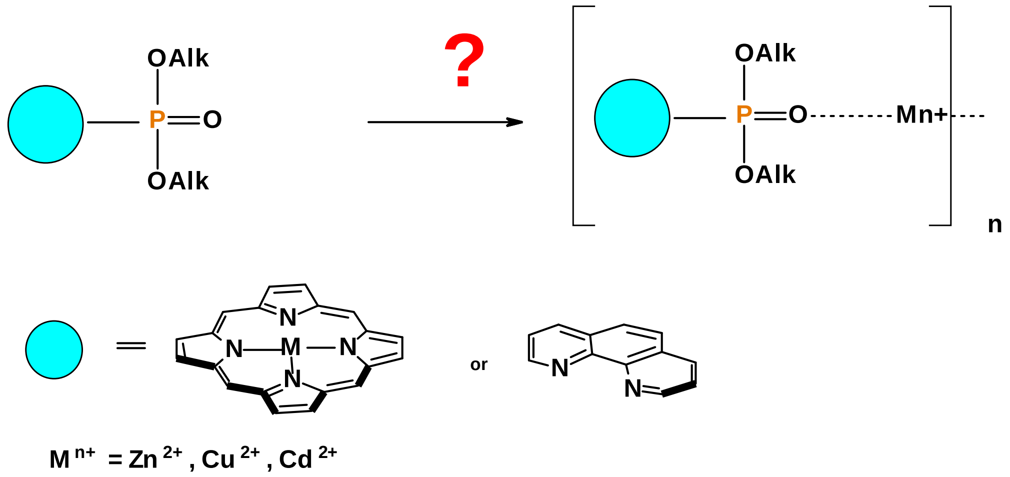
Alla Lemeune,[1]* Alexander Yu. Mitrofanov,[1] Yoann Rousselin,[1] Christine Stern,[1] Roger Guilard,[1] Yulia Yu. Enakieva,[2] Yulia G. Gorbunova[2,3] and Sergey E. Nefedov[3]

[1]*Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR CNRS 6302, 9 avenue A. Savary, 21078 Dijon, France. E-mails: Alla.Lemeune@u-bourgogne.fr; Roger.Guilard@u-bourgogne.fr*

[2]*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Leninskiy p. 31-4, Moscow, 119071 Russia. E-mail: yulia@igic.ras.ru*

[3]*N.S. Kurnakov Institute of General and Inorganic Chemistry of RAS, Leninskiy p.31, Moscow, 119991 Russia. E-mail: snef@igic.ras.ru*

Abstract *The interest of phosphonic acid dialkyl esters for generation of metal-organic materials is discussed using derivatives of porphyrin and 1,10-phenanthroline series as representative examples.*



Keywords Phosphonate diester, porphyrin, 1,10-phenanthroline, metal-organic material, coordination polymer, supramolecular assembly

INTRODUCTION

Hybrid organic-inorganic materials are drawing a lot of attention due to manifold attractive properties enabling their use in modern technologies. Ongoing researches are focused on the development of new scaffolds and design strategies for their assembly. Phosphonate derivatives have been recognized as convenient molecular precursors for functional materials starting from late 1970s. Indeed, these organic compounds are simple to prepare according to a variety of synthetic procedures. Moreover, phosphonic acids and their disilyl esters react with many metal derivatives under mild conditions providing robust metal−OP bonds which can be used for generation of coordination polymers including metal-organic frameworks (MOFs), for synthesis of organic-inorganic hybrid materials based on titania or zirconia as well as for fabrication of thin film materials.[1] To prepare these materials, phosphonic acids are currently used as key molecular precursors. Surprisingly the supramolecular assembly and grafting of phosphonate monoalkyl- and dialkyl esters are scarcely studied despite their availability and stability. This report briefly illustrates the interest of phosphonic acid dialkyl esters for generation of metal-organic materials (MOMs) using derivatives of porphyrin (**M-1a-c**, **M-2a-e** and **M-3a-e)** and 1,10-phenanthroline (**4a-d** and **5a-d**) series (Figure 1).

Porphyrinic N- or O-donors are widely used linkers for MOMs and important artificial models for natural supramolecular assemblies playing a key role in the photosynthesis process.[2] 1,10-Phenanthrolines are widely studied as excellent chelators in traditional coordination compounds but their use for preparation of coordination polymers are still limited by rare examples.[3] Comparative studies of these structurally different series are useful to demonstrate the general character of our synthetic approach providing new topologies and functionalities to MOMs.

RESULTS AND DISCUSSION

In this context, we have faced for the need of diethoxyphosphoryl substituted porphyrins and 1,10-phenanthrolines and developed experimental procedures of their synthesis according to Hirao reaction.[4] Free bases and zinc complexes of bromoporphyrins **M-6a-e**, **M-7a-e** react with diethyl phosphite in the presence of $Pd(OAc)_2/PPh_3$ catalytic system and triethylamine. Choice of the reaction solvent is crucial for the product yield. *meso*-(Diethoxyphosphoryl)porphyrins **M-2a-e**, **M-3a-e** were obtained in good yields only when the reactions were performed in ethanol at reflux (Scheme 1).[5]

In contrast, β-bromoporphyrin **M-8** does not react with diethyl phosphite under these conditions owing to its low solubility in this solvent. Fortunately, the reaction smoothly proceeds in toluene at reflux (Scheme 2).[6] For both porphyrin series, higher yields of the target products were obtained using a large excess of diethyl phosphite and base (up to 50 equivalents) and a high catalyst loading (up to 0.5 – 1 equivalent).

Being strong chelators, 1,10-phenanthroline halides competed with triphenylphosphine to coordinate the palladium centre, rending the catalytic reaction impractical. The target products were obtained in good yields in toluene or dioxane at reflux when PPh_3 was replaced by bidentate 1,1'-bis(diphenylphosphino)ferrocene (dppf) (Scheme 3).[7]

Investigation on the supramolecular organization of the newly synthesized phosphonic acid diesters was started using zinc porphyrinates **Zn-1a,b**, **Zn-2a-e** and **Zn-3a-e**, which are structurally programmed for self-assembly. Indeed, both *β*- and *meso*- derivatives generate supramolecular assemblies due to the connection of the molecules *via* weak M…O=P coordination bonds (Figure 2).[5,6] According to systematic studies of *meso*-porphyrinates **Zn-2a-e** and **Zn-3a-e**, it appears that the solid state supramolecular organization is determined by the number and position of phosphonate groups as well as the nature of the aryl substituents at the macrocycle periphery.

Varying only the substituent at the *para*-position of the benzene ring, tetrameric or infinite 1D structures were obtained for **Zn-2a-e**. According to NMR studies, these architectures also exist in toluene-*d8* and chlorinated solvents at low temperatures. Additional dimensionality of the polymers can be encoded *via* the introduction of the second phosphonate group at the tetrapyrrolic macrocycle.[5,8] For example, **M-3a** (M = Zn, Cu, Cd) and **Zn-3e** generate 2D networks in the solid state and in solution.

Thus, the complexes of diethoxyphosphoryl substituted porphyrin generate stable self-assemblies which are excellent models for natural porphyrinic systems and allow to get insight into the influence of structural parameters of molecular precursors on the self-assembly process.

Showing the possibility to generate supramolecular assemblies using M…O=P coordination bonds, our interest was also to develop a general approach to coordination polymers based on phosphonate diesters using external metal connectors. Binuclear paddle-wheel (PW) complexes $M_2(\mu\text{-}O_2CR)_4L_2$ are *a priori* appropriate assembling nodes.[9] Mixing $M_2(\mu\text{-}O_2C\text{-}t\text{-}Bu)_4(NCMe)_2$ and **M-3a (M=Cu, Ni, Pd),** homo- and heterometallic infinite architectures **M-11** were prepared and characterized by single crystal X-ray diffraction analysis (Scheme 4).

When phenanthroline **5a** was reacted with $Cu_2(\mu\text{-}OOCMe)_4(THF)_2$, a crystalline product $Cu_2(\mu\text{-}OOCMe)_4$(μ-O,O’-**5a**) (**12**) was obtained. This compound exhibits an unusual polymeric structure in the crystals. Indeed bimetallic PW fragments $Cu_2(\mu\text{-}OOCMe)_4$ are linked in axial positions to the disubstituted phenanthroline ligand **5a** coordinated to the metal atoms only by the two oxygen donor atoms of the phosphonate groups (Figure 3, left panel).

Evidently, to construct infinite architectures, various external metal nodes may replace PW linking moieties. Thus an interesting example was obtained reacting phenanthroline **4b** with $Cu(NO_3)_2{}^{\bullet}H_2O$ in a 1:1 ratio. 1D polymeric structure of the complex **13** results from the coordination of Cu(II) centers to the oxygen atoms of the phosphoryl groups of the neighbouring phenanthroline ligands (Figure 3, right panel).

CONCLUSIONS

Reported data show the propensity of the phosphonic acid diesters for the engineering of supramolecular coordination complexes and infinite frameworks by either direct interaction of molecular precursors or through their connection using external metal nodes.

Acknowledgements This work was carried out in the frame of the International Associated French–Russian laboratory LAMREM supported by the CNRS, the RAS and RFBR (grants 12-03-93110, 12-03-93114).

REFERENCES

1. (a) Shimizu, G. K. H.; Vaidhyanathan, R.; Taylor, J. M. *Chem. Soc. Rev.* **2009**, 38, 1430–1034; (b) Gagnon, K. J.; Perry, H. P.; Clearfield, A. Chem. Rev. **2012**, 112, 1034–1054 ; (c) Metal Phosphonate Chemistry, from Synthesis to Applications; Clearfield, A., Demadis, K. D., Eds.; RSC Publishing: Cambridge, U.K., 2012; 655 p; (d) Queffélec, C. E.; Petit, M.; Janvier, P.; Knight, D. A.; Bujoli, B. *Chem. Rev.* **2012**, 112, 3777−3807.
2. Beletskaya, I.; Tyurin, V. S.; Tsivadze, A. Y.; Guilard, R.; Stern, C. *Chem. Rev.* **2009**, 109, 1659-1713.
3. Bencini, A.; Lippolis, V. *Coord. Chem. Rev.* **2010**, 254, 2096–2180
4. (a) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *Synthesis* **1981**, 56; (b) Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982,** 55, 909; (c) Demmer, C. S.; Krogsgaard-Larsen, N.; Bunch, L. *Chem. Rev.* **2011**, 111, 7981-8006.
5. (a) Enakieva, Yu. Yu.; Bessmertnykh-Lemeune, A. G.; Gorbunova, Yu. G.; Stern, C.; Rousselin, Y.; Tsivadze, A. Yu.; Guilard, R. *Org. Lett.* **2009**, 11, 3842–3845; (b) Kadish, K. M.; Chen, P.; Enakieva, Yu. Yu.; Nefedov, S. E.; Gorbunova, Yu. G.; Tsivadze, A. Yu.; Bessmertnykh-Lemeune, A.; Stern, C.; Guilard, R. *J. Electroanal. Chem.* **2011**, 656, 61–71.
6. Vinogradova, E. V.; Enakieva, Yu. Yu.; Nefedov, S. E.; Birin, K. P.; Tsivadze, A. Yu.; Gorbunova, Yu. G.; Bessmertnykh-Lemeune, A.; Stern, C.; Guilard, R. *Chem. Eur. J.* **2012**, 18, 15092–15104.
7. Mitrofanov, A.; Bessmertnykh-Lemeune, A.; Stern, C.; Guilard, R.; Gulyukina, N.; Beletskaya, I. *Synthesis* **2012**, 44, 3805–3810.

8. Sinelshchikova, A. A.; Nefedov, S. E.; Enakieva, Yu. Yu.; Gorbunova, Yu. G.; Tsivadze, A. Yu.; Kadish, K. M.; Chen, P.; Bessmertnykh-Lemeune, A.; Stern, C.; Guilard, R. *Inorg. Chem.* **2013,** 52, 999–1008.
9. (a)Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, 34, 759–771; (b) Koberl, M.; Cokoja, M.; Bechlars, B.; Herdtweck, E.; Kuhn, F. E. *Dalton Trans.* **2011**, 40, 11490–11496.

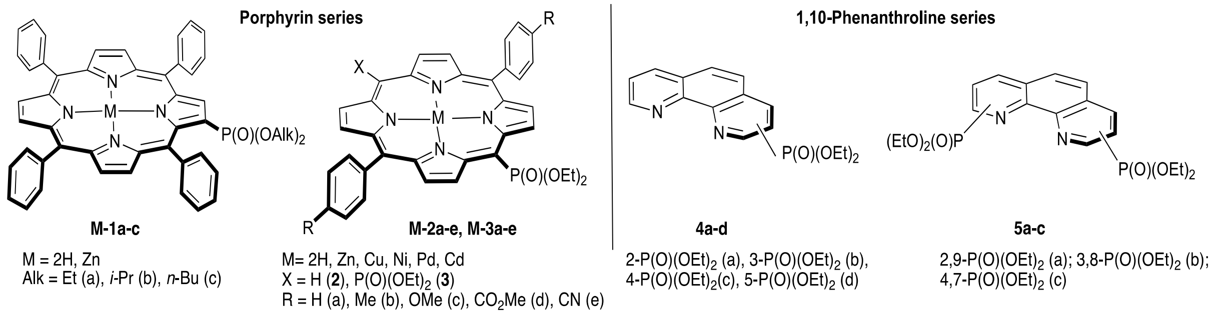


Figure 1 Structures of the studied diesters of phosphonic acids.

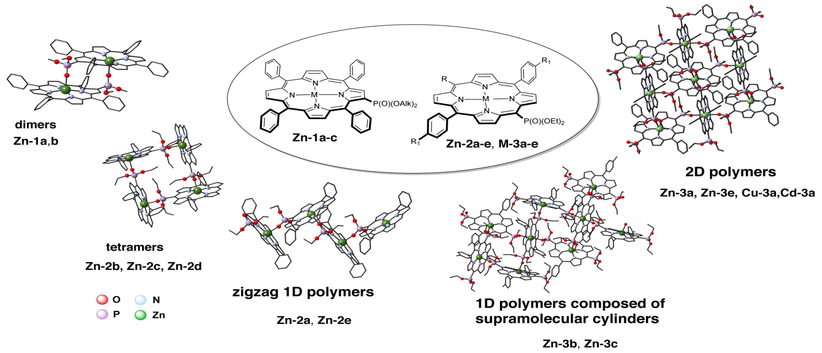


Figure 2 Schematic representation of supramolecular assemblies **Zn-1**, **Zn-2** and **M-3** determined by single crystal X-ray analysis.

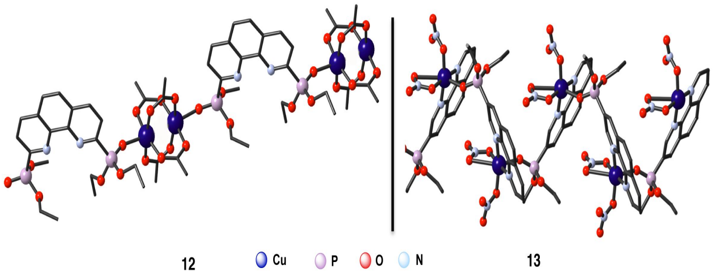
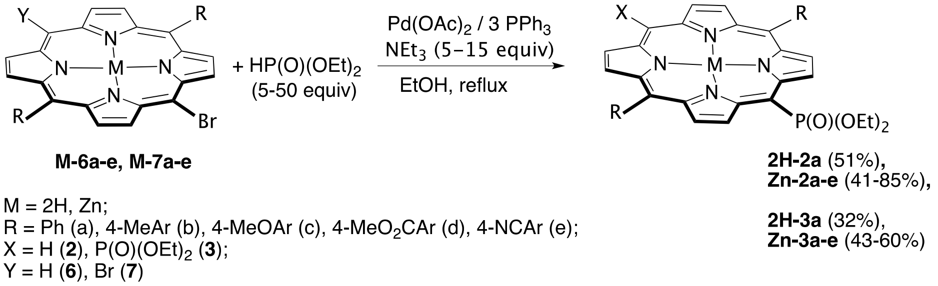
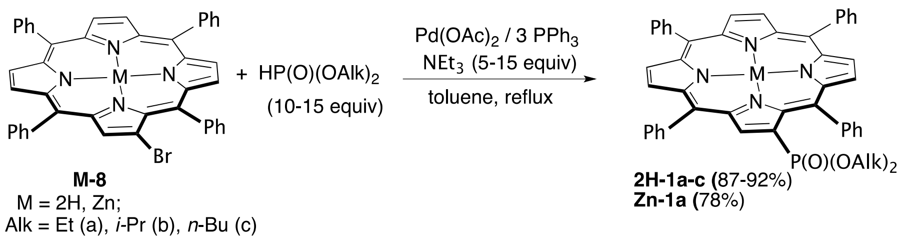


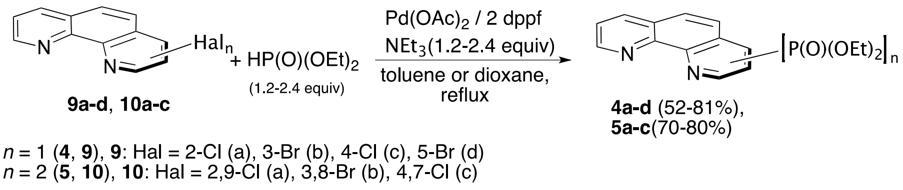
Figure 3 Structure of 1D polymers based on (diethoxyphosphoryl)phenanthrolines **5a** (left panel) and **4b (**right panel) determined by single crystal X-ray diffraction analysis.



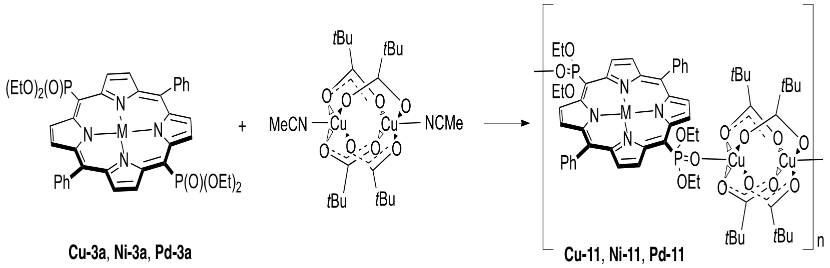
Scheme 1



Scheme 2



Scheme 3



Cu-3a, **Ni-3a**, **Pd-3a**

Cu-11, **Ni-11**, **Pd-11**

Scheme 4