STACKED OR BRIDGE STACKED POLYMERIC STRUCTURES OF METALLOPORPHYRINS AND PHTALOCYANINES INVESTIGATED BY DIFFERENCE EXAFS SPECTROSCOPY

M. Loos, P. Friant, I. Ascone, J. Goulon, J. Barbe, A. Coutsolelos, R. Guilard

To cite this version:

HAL Id: jpa-00226020
https://hal.archives-ouvertes.fr/jpa-00226020
Submitted on 1 Jan 1986

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
STACKED OR BRIDGE STACKED POLYMERIC STRUCTURES OF METALLOPORPHYRINS AND PHTHALOCYANINES INVESTIGATED BY DIFFERENCE EXAFS SPECTROSCOPY


*Laboratoire de Chimie Théorique, Université de Nancy-I, U.A. 510 CNRS, B.P. 239, F-54506 Vandoeuvre-Les-Nancy Cedex, France
**LURE, L.P. CNRS, MEN, CEA, Université de Paris-Sud, Batiment 209D, F-91405 Orsay Cedex, France
***Laboratoire de Synthèse et Electrolytise Organométalliques, U.A. 33 CNRS, Faculté des Sciences Gabriel, 6, Boulevard Gabriel, F-21100 Dijon, France

Résumé:
Une extension de la technique d’analyse différentielle des spectres EXAFS a permis d’obtenir l’extinction au premier ordre des signaux intenses des macrocycles porphyriniques et donc d’observer les signaux faibles intermoléculaires qui témoignent de structures polymériques empilées, empilées mais décalées ou pontées. Cette méthode a été utilisée pour préciser la structure de phthalocyanines de nickel dopées ou non et celle d’un composé polymérique [TpTF:Ge-CrO₄].

Abstract:
An “extended” differential analysis of EXAFS spectra makes it possible to achieve a first order cancellation of the intense porphyrinic pattern and therefore to extract weaker intermolecular signals which give evidence for stacked, slipped-stacked or bridge-stacked polymeric structures. Recent applications of the method include structural characterizations of β-Pc:Hi, Pc:Hi/I and of a polymeric compound [TpTF:Ge-CrO₄].

I INTRODUCTION.
Intensive efforts are directed toward the synthesis of highly conducting molecular materials with metallomacrocyclic complexes as fundamental units. Such “molecular metals” were prepared recently by partial oxidation of nickel or fluorogallium phthalocyanines (Pc) or related porphyrins [1,2]. A prerequisite for obtaining a high electric conductivity is the formation of a stacked or bridge-stacked polymeric structure. It is the purpose of this paper to show that EXAFS can be used in order to check if newly synthesized materials are featuring the required polymeric structure or not.

Most often conventional analyses of EXAFS fail to give reliable answers to this question because the strong signatures of the porphyrin macrocycle dominate the spectra and are masking the much weaker intermolecular signals or even worse — interfere with them. Recently we have developed a “perturbed” difference FT analysis [3] yielding a nearly perfect cancellation of the porphyrin pattern even in the presence of a small contraction of the macrocyclic cavity or when the metal is shifted out of the porphyrin plane as occurring for most pentacoordinated species.

This “extended” differential analysis was first used in order to ascertain the bridge-stacked polymeric structure of a fluorogallium porphyrin. As this study has already been reported in details elsewhere [3] we shall focus the present report on more recent applications of the method.
II STACKING AND SLIPPED-STACKING OF NICKEL PHTALOCYANINES

The EXAFS spectra of a series of oxidised/unoxidised nickel porphyrins and phthalocyanines have been recorded at L.U.R.E. on the EXAFS-II station. The corrected FT spectra \( \text{Im}[\mathcal{X}(R)] \) of both Pc:Ni and the partially oxidised system Pc:Ni/I are reproduced in Figure 1 and exhibit rather small differences in the range of intermolecular distances. According to its X-ray powder diffraction pattern, the unoxidised Pc:Ni was identified to the \( \beta \)-phase for which also short intermolecular distances \( \text{Ni} \ldots \text{N}_{m+1} \) are expected between 3.2 \( - \) 3.5 \( \text{A} \). The FT spectrum of \( \beta \)-Pc:Ni is also compared in Figure 2 to the FT spectrum of octamethyl tetrabenzoporphyrinato nickel(II), \( Z = \text{OMTP} : \text{Ni} \), for which no short intermolecular distances should interfere in this range of distances.

As illustrated by Figure 3, the two complexes exhibit enough structural similarities to make possible a first order cancellation of all signatures of the macrocycles when two successive perturbations of the FT spectrum of \( Z \) are made: (i) a uniform contraction of the macrocycle cavity, (ii) an additional shift toward larger distances of the signal of the meso carbons within some appropriate gaussian window. The result of such a perturbation is illustrated by Figure 4 which also reproduces as a reference the unperturbed spectrum of Pc:Ni/I.

Figure 1: Corrected FT spectra \( \text{Im}[\mathcal{X}(R)] \) of \( \beta \)-Pc:Ni and Pc:Ni/I. The arrow indicates the range of first intermolecular distances.

Figure 2: Corrected FT spectra \( \text{Im}[\mathcal{X}(R)] \) of \( \beta \)-Pc:Ni and OMTPB:Ni.

Figure 3: Structural differences between Pc:Ni/I and OMTPB:Ni according to crystal structure data [1,4].

Figure 4: FT spectrum of (OMTPB:Ni)\(^*\) after two successive structural perturbations. The unperturbed FT spectrum of Pc:Ni/I is also reproduced for comparison.
It becomes then possible to extract by differential FT analysis \([3]\) the contribution of the weak intermolecular signals in Pc:Ni/I (Figure 5) and \(\beta\)-Pc:Ni (Figure 6). For Pc:Ni/I, the observed Ni-Ni distance \(3.2 \pm 0.1 \text{ Å}\) agrees quite well with the known crystal structure data \([3, 2, 1]^{11}\). In the case of \(\beta\)-Pc:Ni, the signal provisionally assigned to the axial azamethine nitrogens is peaking at ca. \(3.20 \pm 0.05 \text{ Å}\): such a distance is of the order of magnitude of the distance found by X-ray crystallography for other phthalocyanines \((M = Mn, Fe, Co, Cu, Zn, ...)\) \([5]\) but shorter than the distance \((3.3 \pm 0.1 \text{ Å})\) reported in 1937 for \(\beta\)-Pc:Ni \([6]\). It is our present interpretation that these early data were not yet accurate enough to be used as reference.

![Figure 5: "Extended" difference FT spectrum of (Pc:Ni/I) - (OMTBP:Ni)](image)

![Figure 6: "Extended" difference FT spectrum of (\(\beta\)-Pc:Ni) - (OMTBP:Ni)](image)

**III POLYMERIC STRUCTURE OF 3 = \([\text{TpTP:Ge-CrO}_4]\)\(_n\)**

Due to an extremely poor solubility of 3 in non reactive solvent, no single crystal suitable for X-ray crystallography has yet been grown \([7]\). However a combination of the structural informations extracted from the EXAFS spectra recorded at both germanium and chromium K-edges led us to propose the polymeric structure shown in Figure 7. Bidentate ligation of the bridging chromate fragment is supported unambiguously by the corrected FT spectrum reproduced in Figure 8 and which refers to the distribution of the nearest neighbours around the Cr\(^{*}\) centers: two non equivalent sets of Cr\(^{*}\)...0 distances at \(1.59 \pm 0.01\) and \(2.07 \pm 0.01\) Å are clearly observed whereas an additional signature at \(3.3 \pm 0.1\) Å can be provisionally assigned to the Cr\(^{*}\)...Ge distance.

![Figure 7: Proposed polymeric structure of 3 = \([\text{TpTP:Ge-CrO}_4]\)\(_n\)](image)

![Figure 8: Corrected FT spectra of the K-edge data relative to 3](image)
Using two additional reference compounds, i.e. $4 = [\text{TpTP:GeBr}_2]$ and $5 = [\text{TpTP:GeF}_2]$, it became also possible to extract further informations from the difference FT spectra $\gamma_i[3 - 4]$ and $\gamma_i[3 - 5]$ reproduced in figures 9/10: the Ge$^{+}...O$ signal was found to peak at $1.89 \pm 0.02 \text{ Å}$ in $\chi_i[3 - 4]$, whereas a quite clean Ge$^{+}...\text{Cr}$ signal did show up in $\chi_i[3 - 5]$ again at $R = 3.35 \pm 0.05 \text{ Å}$. On the other hand, the hexacoordination of germanium in the polymeric structure of 3 is clearly supported by the fact that it is not all displaced out of the porphyrin mean plane.

![Figure 9: Difference FT spectra $[\text{TpTP:Ge-Cr}_4]_n - [\text{TpTP:GeBr}_2]$](image1)

![Figure 10: Difference FT spectra $[\text{TpTP:Ge-Cr}_4]_n - [\text{TpTP:GeF}_2]$](image2)

**Abbreviations used:**

Pc = Phtalocyaninato
OCTBEP = 1,4,5,8,9,12,13,16 octamethyltetrabenzporphyrinato
TpTP = 5,10,15,20 tetraparatolylporphyrinato

**REFERENCES**

    J. Am. Chem. Soc. 102, 6702 (1980)


    J. Am. Chem. Soc. 102, 3435 (1980)

    Inorg. Chem. 18, 1865 (1979)

    J. Chem. Soc. 219 (1937)

    Thèse de 3e cycle, Université de DIJON (1985)