X-Ray Photoelectron Spectroscopy of Metallo Porphyrins Having Bulky Substituents: Standard Values of Core Ionization Potentials

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X-ray photoelectron spectra of four porphyrins which hardly aggregate were measured. The C1s and N1s peak positions of these porphyrins showed almost identical values, so that these values can be used as a standard.

Recently, solid state chemistry and physics based on metal porphyrins are widely investigated as organic-inorganic hybrid advanced materials.[1] X-ray photoelectron spectroscopy (XPS) is one of the most powerful technique to investigate the electronic structure of these materials in solid state,[2] especially for functionalized thin layered films including self-assembled monolayers,[3] Langmuir-Blodget films,[4] and biological proteins such as *cytochrome c*.[5] However, porphyrins tend to aggregate in solid state.[6] This aggregation induces the perturbation to the electronic structure of an individual molecule. Therefore, the reported XPS spectra so far might be influenced by the intermolecular interaction. In this respect, XPS study on non-aggregate porphyrins is highly required to know the standard values of various core ionization potentials (IPs). In this communication, we wish to report XPS core IPs of bulky porphyrins, **1a-d**,[7] which hardly aggregate in solid state.

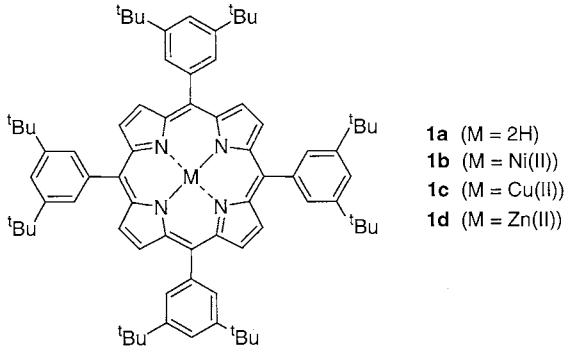

Figure 1.

Compounds **1a-d** were prepared according to the reported method[7] and the detailed conditions of the XPS measurements were reported elsewhere.[8] The observed XPS core IPs for thin films (*ca.* 50 nm thickness) prepared by sublimation *in situ* were summarized in Table 1. The observed IPs for C1s and N1s of **1b-d** are not different so much with each other. This is in marked contrast to the reported results where C1s and N1s values differ by 0.5 and 0.8 eV, respectively.[9,10]

The following three evidences clearly show that there exists negligible π-π interaction in **1a-d** under the XPS measurement conditions. First, absorption spectra of **1a-d** of both solid state and solution are nearly identical in respect to the peak position and the full width at half maximum (FWHM) as shown in Figure 2. This is a remarkable finding, since the peak position and FWHM of solid state and solution absorption spectra of usual porphyins differ from each other. Second, single crystal diffraction studies for **1a**, **1b**, and **1d** showed that the mean interplane distances are 6.91, 7.03, and 7.02 Å for **1a**, **1b**, and **1d**, respectively.[11] The packing structure of **1b** is shown, as a typical example, in Figure 3. Due to the introduction of eight *tert*-butyl groups, interplane distances are quite large and π-π interactions are negligible.[12] Third, magnetic susceptibility of the paramagnetic species **1d** completely obeys the Curie law in the range of 1.8-300 K indicating that the intermolecular magnetic exchange interaction is negligible. However, the central paramagnetic metals interact in a ferromagnetical or antiferromagnetical manner in the case of non-bulky porphyrins.[13]

Table 1. XPS core IPs (eV) for **1a-d** [a]

	C1s	N1s	Metal $2p_{1/2}$	Metal $2p_{3/2}$
1a	285.3	398.2, 400.1		
	(1.9)	(1.7) (1.7)		
1b	285.2	399.0	872.5	855.2
	(1.8)	(1.5)	(1.8)	(1.7)
1c	285.3	399.0	954.5	934.7
	(1.8)	(1.6)	(2.2)	(1.8)
1d	285.3	398.9	1043.8	1021.0
	(1.9)	(1.7)	(2.0)	(2.0)

[a] The spectrometers were calibrated so that the Au $4f_{7/2}$ peak of the clean sputtered metals appeared at 84.00 eV. IPs are reproducible to a precision of ≤±0.1 eV. Values in parentheses are the full width at half maximum.

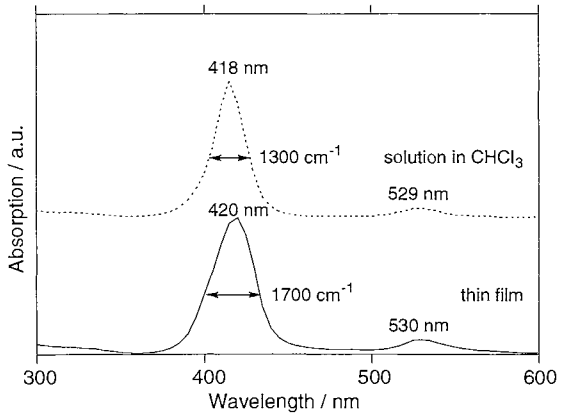

Figure 2. Absorption spectra of **1b** in $CHCl_3$ (dotted line) and for evaporated thin film (solid line).

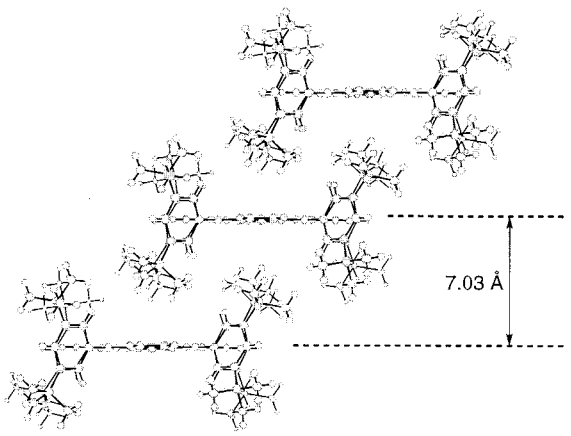

Figure 3. Packing structure of **1b**. Mean interplane distance is 7.03 Å.

It is well known that IPs of N1s behave as a sensitive probe for the effect of the electron densities of porphyrins, *e.g.*, a large shifts, 2.0 eV, induced by substituents were reported.[14] Especially, net electron population of metals and ligands are considered to behave as a function of electronegativity of the incorporated metals.[15] However, the differences of our reproducible values among **1b-d** are quite small and in the range of 0.1 eV. This concludes that the electronegativity of the incorporated metals has only small influence on IPs of N1s. The shift induced by the metals reported in the literature (0.8V)[9] may be attributable to the intermolecular π-π interaction, *i.e.*, highly polarized porphyrin macrocycle induced by electropositive metals, such as zinc, interact strongly with the adjacent porphyrin to cancel the charge in a slipped stacked manner in solid state.[16] The degree of this aggregation in the solid state will be expected to obey the electronegativity of the metals.[16] Therefore, we conclude that the present IP values can be used as standard values for XPS study on various porphyrins.

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10 The FWHM of C1s are larger than usual single component organic molecules, because the peaks arising from twenty carbon atoms of porphyrin nucleus are overlapped by those of fifty five carbon atoms of the substituents.
11 Crystal Data. **1a**: [**1a**]$_1$[*n*-heptane]$_2$: $C_{90}H_{126}N_4$, triclinic, $P\bar{1}$(#2), 0.55 X 0.18 X 0.18 mm^3, -49.7 °C, Mo-Kα, a = 14.271(3), b = 15.538(3), c = 9.417(2) Å, α = 95.62(2), β = 104.93(1), γ = 90.37(2)°, V = 2006.8(7) Å^3, Z = 1, R = 0.063, R_w = 0.062, GOF = 1.09 for 5302 independent reflections (I>3.00σ(I)), Reflection/Parameter Ratio = 11.28. **1b**: [**1b**]$_1$[*n*-heptane]$_2$: $C_{90}H_{124}N_4Ni_1$, triclinic, $P\bar{1}$(#2), 0.80 X 0.30 X 0.30 mm^3, -49.7 °C, Mo-Kα, a = 14.333(3), b = 15.461(4), c = 9.417(2) Å, α = 96.59(2), β = 105.48(2), γ = 89.94(2)°, V = 1996.9(8) Å^3, Z = 1, R = 0.051, R_w = 0.069, GOF = 1.78 for 8042 independent reflections (I>3.00σ(I)), Reflection/Parameter Ratio = 18.66. **1d**: [**1d**]$_1$[*n*-heptane]$_2$: $C_{90}H_{124}N_4Zn_1$, triclinic, $P\bar{1}$(#2), 0.95 X 0.13 X 0.05 mm^3, -45.7 °C, Mo-Kα, a = 14.474(3), b = 15.574(3), c = 9.471(2) Å, α = 96.40(2), β = 103.69(2), γ = 91.44(2)°, V = 2058.4(7) Å^3, Z = 1, R = 0.077, R_w = 0.077, GOF = 1.50 for 3556 independent reflections (I>3.00σ(I)), Reflection/Parameter Ratio = 8.25.
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