Crystal structure determination of (H$_2$pc)$_3$ PF$_{6-x}$Cl$_x$ by synchrotron powder diffractometry

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A new partially oxidized metal-free phthalocyanine (H$_2$pc) salt was electrochemically synthesized from neutral H$_2$pc in 1-chloronaphthalene solution with (n-Bu)$_4$N PF$_6$ as the electrolyte. The electric conductivity along the growth axis of a needle-like crystal was about 9 S cm^{-1} at room temperature. The results of chemical analysis have implied that the composition is nominally H$_2$pc (PF$_{5.28}$Cl$_{0.72}$)$_{0.28}$. It has been suggested that the fluorine atoms in the PF$_6$ ions were partly substituted by chlorine atoms during the electrochemical process.

Powder X-ray diffraction data have been collected with a high-resolution powder diffractometer MDS [1] on beamline BL4B2 at the Phothon Factory. The incident beam wavelength was 1.2072(4) Å. A Lindemann glass capillary of 1.0 mm φ in diameter filled with 9 mg of the grinded powder sample was used as the specimen for the powder diffraction measurement. The collected diffraction data range was 1 to 150º in 2θ at a step size of 0.004º using a counting time of 8 s per point.
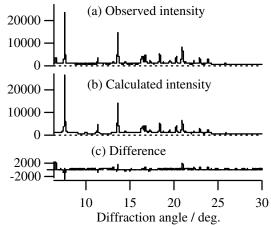
All the detectable diffraction peaks were indexed by assuming a rhombohedral (R3) unit cell with the refined lattice parameters of a = 21.3427(4) Å and α = 119.42784(2)º. The cell volume of 1909.5(1) Å^3 indicates the existence of three H$_2$pc molecules in the unit cell. The periodicity of 4.8687(2) Å along the [111] direction coincides with the observed periodicity along the growth axis in the oscillation photograph taken for a bundle of thin needle-like crystals in our laboratory.

The chemical composition of (H$_2$pc)$_3$ PF$_{6-x}$ Cl$_x$ was assumed to satisfy the requirement of the symmetry. The powder diffraction pattern was simulated for further simplified composition, (H$_2$pc)$_3$ PF$_6$ (x = 0). The position and orientation of the H$_2$pc and PF$_6$ molecules were optimized by a least-squares method to fit the observed diffraction intensity data, treating H$_2$pc and PF$_6$ molecules as rigid bodies. The common isotropic atomic displacement parameter of 0.01 Å^2 was assumed for all the atoms.

Figure 1 shows the experimental powder diffraction data, calculated curve for the optimized structure of (H$_2$pc)$_3$ PF$_6$, and the difference plot. The reliability factor for the profile fitting was 11.89 %.

The projection of the refined crystal structure along the [111] direction is shown in Fig. 2. H$_2$pc molecules are uniformly stacked along the [111] direction. The optimized angle between the [111] and the normal direction of the H$_2$pc molecular plane was 46.88(1)º, which gives the interplanar distance between the neighboring H$_2$pc molecules to be 3.33 Å. The orientation of each H$_2$pc molecule relative to the stacking axis is very similar to that of the X-polymorph of neutral

H$_2$pc [2].

Fig. 1 (a) Synchrotron powder diffraction pattern of (H$_2$pc)$_3$ PF$_{6-x}$ Cl$_x$, (b) calculated curve for the optimized (H$_2$pc)$_3$ PF$_6$, and (c) the difference.
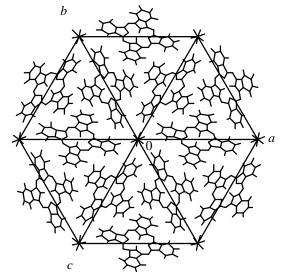

Fig. 2 Projection of the optimized crystal structure of (H$_2$pc)$_3$ PF$_6$.

References

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