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Radiation Damage of Halogenated Phthalocyanine Complexes Correlated to Molecular Occupancy

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Stability of vanadyl- phthalocyanine (VOPc), copper- phthalocyanine (CuPc), and their peripherally halogenated derivatives is investigated from thermal analysis and electron radiation damage analysis including electron energy-loss spectroscopy (EELS).

From thermal analysis by TG-DTA and DSC, it is found that there is a linear correlation between phase-change temperature (T_t) and 'effective molecular occupancy (O_e),' defined as $100(V_{vdw}/V_{unit})$, from the ratio of the van der Waals volume (V_{vdw}) to the unit volume (V_{unit}) as shown in FIG. 1a. The 'effective molecular occupancy' is estimated either from crystal structures or the density for the compounds with different polymorph, and the obtained values are listed in Table 1. An exothermic reaction occurs at higher temperature irrelevant to the difference between VOPc and CuPc, with increasing the 'effective molecular occupancy', in which molecules are more closely packed. From radiation damage analysis, an exponential correlation between the characteristic dose ($D_{1/e}$) at which initial intensity decreases to 1/e and 'effective molecular occupancy' is observed among CuPc derivatives, whereas the difference between VOPc and CuPc derivatives is clearly observed (FIG.1b). The highest sensitivity of fluorinated vanadyl- phthalocyanine ($VOPcF_{14.5}$) and fluorinated copper- phthalocyanine ($CuPcF_{16}$) can be explained by the enhanced intermolecular empty space due to the fluorination, as found in the case of TCNQ and F_4TCNQ [1]. Thermal stability may be simply affected by intermolecular force that relates to the 'effective molecular occupancy', but the sensitivity to the radiation damage appears more complex, probably due to additional contributions; e.g. from dissociated ions or radicals, produced during electron irradiation.

In order to clarify the difference between $VOPcF_{14.5}$ and $CuPcF_{16}$, detailed analysis by EELS is applied to investigate changes in mass as well as in chemical bonding within $VOPcF_{14.5}$ and $CuPcF_{16}$. From mass analysis, the amount of content elements is almost constant within the dose up to 0.5 Ccm^{-2} in both $VOPcF_{14.5}$ and $CuPcF_{16}$, except oxygen in $VOPcF_{14.5}$ (Fig.2). The released oxygen might contribute to the secondary radiation damage; the diffusion of oxygen in $VOPcF_{14.5}$ must contribute to higher sensitivity to the radiation damage. It is also found that the π^* peaks of nitrogen and carbon K-edges of $VOPcF_{14.5}$ and $CuPcF_{16}$ decrease beyond the characteristic dose. Different sensitivity of content elements to radiation is found as the π^* peak intensity of nitrogen K-edge decreases at low dose followed by the decrease in the π^* peak of carbon K-edge in both $VOPcF_{14.5}$ and $CuPcF_{16}$. From theoretical interpretation of carbon and nitrogen K-edges in $CuPcF_{16}$, it becomes clear that π resonant system at nitrogen is initially damaged, followed by the destruction of π system of carbon as observed in the study of poly GeO-Pc [2].

References

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[2] H. Kurata et al., Ultramicroscopy, 41 (1992) 33.
[3] J. R. Fryer, Ultramicroscopy, **14** (1984) 227.

TABLE 1. Correlation between effective molecular occupancy (O_e) and temperature (T_t) as well as characteristic dose ($D_{1/e}$) determined at a specific lattice space d.

substances	O_e (%)	T_t (K)	$D_{1/e}$ (Ccm^{-2})	d (nm)
VOPc	77.3 - 79.9	667.3	0.3	0.55
$VOPcF_{14.5}$	76.1 - 79.8	652.6	0.1	0.74
CuPc	77.9 - 80.8	650.3	0.6	0.51
$CuPcF_{16}$	72.0 - 74.4	614.1	0.2	0.32
$CuPcCl_{16}$	82.5 - 82.7	712.9	12.8	0.44
$CuPcCl_8Br_8$	88.7 - 90.2	746.0	17.9	0.44
$CuPcBr_{16}$ [3]	90.6	746.0	30.7-38.7	-

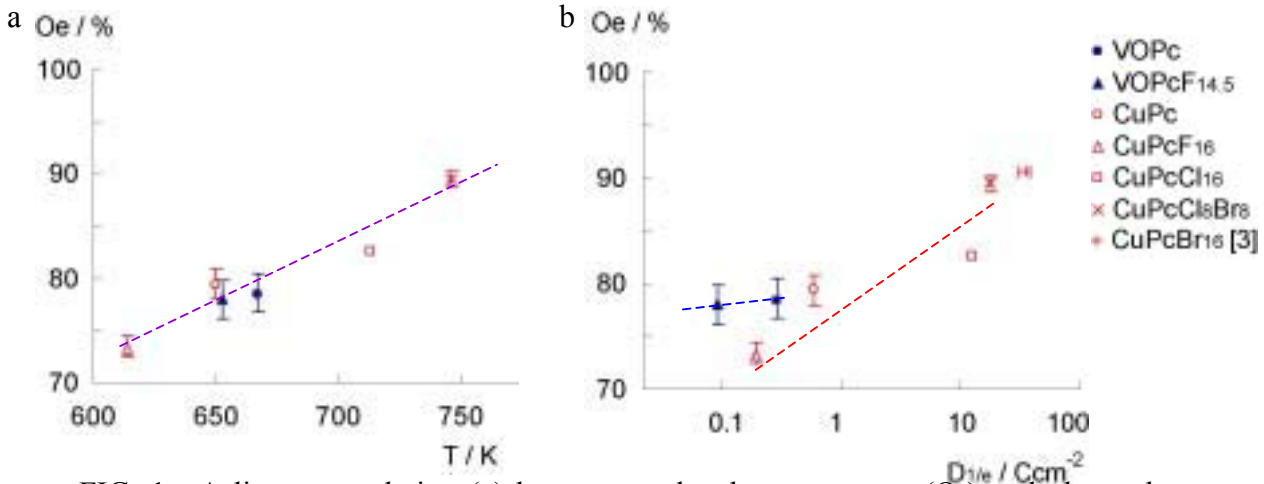

FIG. 1. A linear correlation (a) between molecular occupancy (O_e) and phase-change temperature (T_t) and an exponential correlation (b) between molecular occupancy (O_e) and the characteristic dose ($D_{1/e}$).

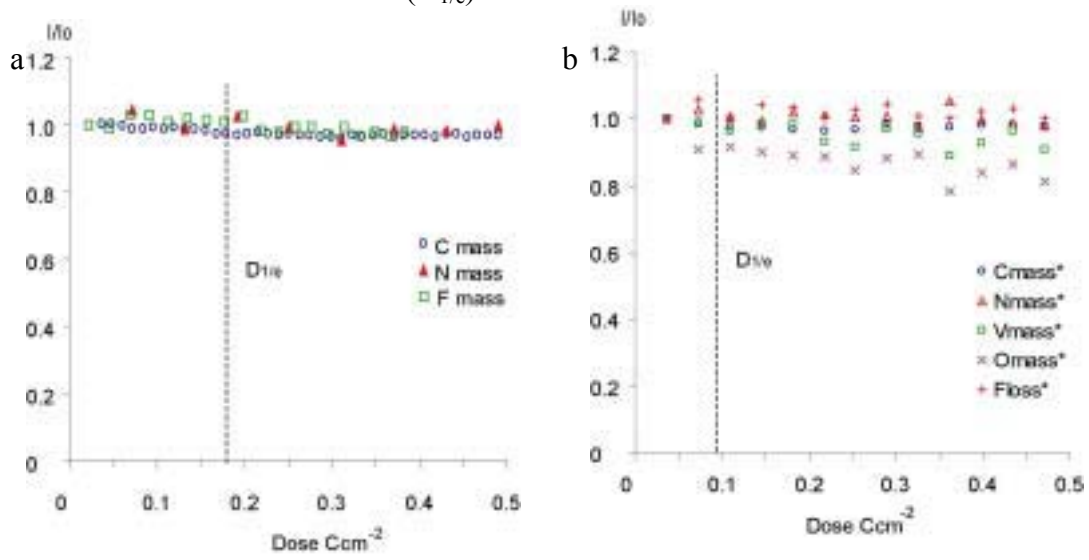

FIG. 2. Mass change of content elements in (a) $CuPcF_{16}$ and (b) $VOPcF_{14.5}$.

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