Highly Conducting Iodinated Fluoroaluminium and Fluorogallium Phthalocyanine Polymers

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Summary Partial oxidation of the quasi-one dimensional fluoroaluminium and fluorogallium phthalocyanines with iodine yields species with appreciable electrical conductivities (0 01—1 ohm^{-1} cm^{-1}), thermogravimetric, Raman spectroscopic, and mass spectrometric techniques have provided useful information about their composition and nature

THERE is currently intense activity[2] aimed at the development of highly conducting organic and inorganic polymeric materials Reports of greatly increased conductivity of oxosilicon and oxogermanium phthalocyanine polymers (PcSiO)$_x$ and (PcGeO)$_x$[3] when iodinated[2a] prompted us to examine the isoelectronic fluoroaluminium and fluorogallium phthalocyanine polymers (PcAlF)$_x$ and (PcGaF)$_x$[4] Key interests were the conductivities of iodinated species and the evaluation of effects of ring separation and iodine/metal ratio on conductivity

(PcAlF)$_x$ and (PcGaF)$_x$ were prepared by a template reaction between the respective metal trichlorides and phthalonitrile The phthalocyanines thus formed were treated with base, aqueous hydrofluoric acid, and pyridine, and then heated under vacuum at *ca* 300 °C[4]† Vacuum sublimation of these fluorides (Al *ca* 500 °C, Ga *ca* 460 °C) gives mats of fine crystals These needle-like crystals exhibit a strong dichroism (blue for light polarized perpendicular to the needle axis, colourless for light polarized parallel to the axis) and *X*-ray reflections in the 0 35—0 40 nm range which are strong and orientation dependent Some crystals of the aluminium compound yield micrographs showing layer lattice lines parallel to the needle axis and spaced by *ca* 1 4 nm These data, together with the low solubility, low volatility, and low reactivity of the two fluorides, and the known propensity of aluminium and gallium for achieving octahedral co-ordination when possible, provide evidence that the fluorides are linear polymer analogues of (PcSiO)$_x$, (PcGeO)$_x$ and (PcSnO)$_x$[3]

Iodinations of (PcMF)$_x$ were carried out at room temperature One approach involved exposure of solid (PcMF)$_x$ to iodine vapour, using grease-free vacuum line techniques until constant weight was attained (7—21 days) A second approach involved stirring a slurry of (PcMF)$_x$ in a solution of iodine in heptane until maximum iodination was achieved (*ca* 24 h) In both cases 'maximum uptake' samples were generally divided into two portions One portion was taken for immediate analysis and characterization while the second portion was pumped on *in vacuo* to constant weight at room temperature to remove readily volatile iodine before being examined The iodinated (PcAlF)$_x$ samples appear as fine purple-black powders whereas the iodinated gallium derivatives range from magenta to purple-black The undoped materials are blue-violet powders

Compositions of the iodinated materials are presented in the Table along with room temperature conductivity data Since the iodine content was sensitive to preparative conditions, it was essential to have a rapid and reliable analytical method for obtaining I/M ratios Thermogravimetric analysis (TGA) proved to be a useful technique for this purpose, and in addition yielded valuable information on relative thermal stabilities A characteristic thermogram was observed for 'maximum uptake' compositions Weight loss processes centred at *ca* 80 and 180 °C were observed The onset of a major plateau at *ca* 230 °C signalled complete loss of iodine ‡ Above 230 °C the thermograms follow those for the undoped

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† Satisfactory elemental analyses were obtained

‡ Mass spectral analysis reveals only loss of iodine below 300 °C We thank Dr William Allen for running the spectra

materials which show weight loss beginning at >450 °C. A low temperature (*ca* 80 °C) loss of iodine is also observed for iodinated $(PcSiO)_x$, but the plateau corresponding to complete loss of iodine is reached at 340 °C. To demonstrate the analytical utility of TGA we note that for one iodinated PcAlF sample (Table, last entry) a 44% weight loss was recorded up to the plateau at *ca* 230 °C, in agreement with an independent iodine weight uptake experiment which showed 43·1% iodine content. These percentages translate to an I/M ratio of 3·4 as noted in the Table.

TABLE. Compositions and conductivities[a] for iodinated $(PcAlF)_x$ and $(PcGaF)_x$

I/Al	σ/ohm^{-1} cm^{-1}	I/Ga	σ/ohm^{-1} cm^{-1}
0	$1{\cdot}5 \times 10^{-4}$[b]	0	$< 10^{-6}$[b]
0·21[c,f]	$1{\cdot}8 \times 10^{-2}$	0·17[d,f]	$1{\cdot}9 \times 10^{-4}$
0·29[d,f]	$1{\cdot}5 \times 10^{-2}$	0·62[c,f]	$1{\cdot}7 \times 10^{-2}$
0·38[c,f]	$2{\cdot}0 \times 10^{-2}$	0·77[d,e]	$4{\cdot}4 \times 10^{-2}$
0·87[d,f,h]	0·70	0·97[d,f]	$7{\cdot}2 \times 10^{-2}$
1·0[d,e]	0·13	0·98[e,g]	$8{\cdot}6 \times 10^{-2}$
1·5[e,g]	0·19	2·3[f,g]	0·15
2·4[d,f]	0·63		
3·4[f,g]	0·59		

[a] Room temperature, linear four-probe technique, pressed pellets. [b] Conductivities obtained using the four-probe van der Pauw method were $6{\cdot}3 \times 10^{-4}$ and $6{\cdot}5 \times 10^{-9}$ ohm^{-1} cm^{-1} at 300 and 133 K, respectively, for $(PcAlF)_x$ and $8{\cdot}2 \times 10^{-10}$ ohm^{-1} cm^{-1} at 300 K for $(PcGaF)_x$. [c] Iodine uptake interrupted before maximum weight gain reached. [d] Pumped on *in vacuo* to constant weight. [e] Heptane slurry reaction. [f] Solid-vapour reaction *in vacuo*. [g] Maximum iodine uptake. [h] $(PcAlF)_x$ purified by sublimation was used.

As seen in the Table, striking increases in electrical conductivity[5] for both $(PcAlF)_x$ and $(PcGaF)_x$ result from their iodination. The largest increases, observed for highest iodine content, are 10^3 (Al) to 10^8 (Ga) greater than the parent $(PcMF)_x$ compounds.§ Also, for a comparable concentration of iodine, the conductivity of iodinated $(PcAlF)_x$ is greater than that of its gallium analogue.¶ These observations correlate with the closer inter-ring spacing for $(PcAlF)_x$.[4] This suggests that the conductive pathway involves significant π–π overlap between phthalocyanine rings.

Both Raman and iodine-129 Mossbauer spectroscopy have been used to advantage for identification of the form(s) of iodine present in iodine-doped substances.[6] Initial Raman spectra of iodinated $(PcMF)_x$ (spinning discs, 514·5 nm excitation) show strong scattering attributable to I_3^- (106—108 cm^{-1}) and I_5^- (164—168 cm^{-1}).[6] The expected overtones and combinations are also present. There was no evidence of I_2 scattering (ν *ca* 180—210 cm^{-1}).[7]**

The Raman data in combination with the TGA results suggest that initial loss of iodine (temperature invariant) arises from dissociation of I_5^- (and perhaps higher polyiodides). Complete loss of iodine owing to tri-iodide decomposition and electron transfer back to the phthalocyanine polymer chain occurs at a higher temperature [$(PcMF)_x$ *ca* 230 °C, $(PcSiO)_x$ *ca* 340 °C]. Supporting this view, the mass spectral profiles of I_2^+ intensity *vs* temperature for $(PcAlF)_x$ and $(PcGaF)_x$ show two peaks between 30 and 300 °C, consistent with the two-stage TGA weight loss. Significantly, the I_2^+ intensity *vs* temperature profile of iodinated polyacetylene, $(CH)_x$, also exhibits a low and a high temperature peak.[8]

This work makes it clear that oxidized fluorometal phthalocyanine polymers constitute a new class of conducting polymers. In addition, the usefulness of TGA for obtaining I/M ratios and relative thermal stabilities of iodine-doped conducting material has been demonstrated.

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§ The high conductivity (6×10^{-4} ohm^{-1} cm^{-1}) of $(PcAlF)_x$ is probably due to impurities; the conductivity drops to 6×10^{-9} ohm^{-1} cm^{-1} at 133 K.

¶ Variable temperature-conductivity data for iodinated samples are in the process of being collected.

** I_2 would be detectable in the presence of I_3^- and/or I_5^- (see ref. 6).

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