Highly Conducting Doped Metal–Phthalocyanines bound to a Polymer

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Doping of films formed by covalently binding metal–2,9,16,23-tetracarboxyphthalocyanines to poly(2-vinylpyridine–CO–styrene) yields highly conducting materials (σ_{RT} 10^{-4}—10^{1} ohm^{-1} cm^{-1}).

Highly conducting doped phthalocyanines have been reported, and for the one dimensional composition, Ni–$pcI_{1\cdot 0}$ (pc = phthalocyanine) metallic behaviour has been demonstrated.[1] Further investigations with stacked and bridge-stacked phthalocyanines {[(M–pc)$_n$, M = Si, Ge, and Sn][2] and [(M–pcF)$_n$, M = Al and Ga][3]} have shown that the presence of a central atom–oxygen and central atom–halogen bridge gives high conductivities on doping with iodine. Previously, we have prepared and studied the chemistry of some soluble metal–phthalocyanine derivatives with peripheral functional groups and the polymers derived from them.[4–7] Quite recently, we have synthesized metal–2,9,16,23-tetracarboxyphthalocyanines (M–tapc) (M = Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II}) covalently bound to poly(2- or 4-vinylpyridine–CO–styrene) [P2 (or 4) VP–CO–St] (**1**) by Friedel–Crafts reaction of the styrene units of the copolymer with M–tapc tetra-acid chlorides.[6,7] We show here that the films can be doped with various gases to yield highly conducting materials.

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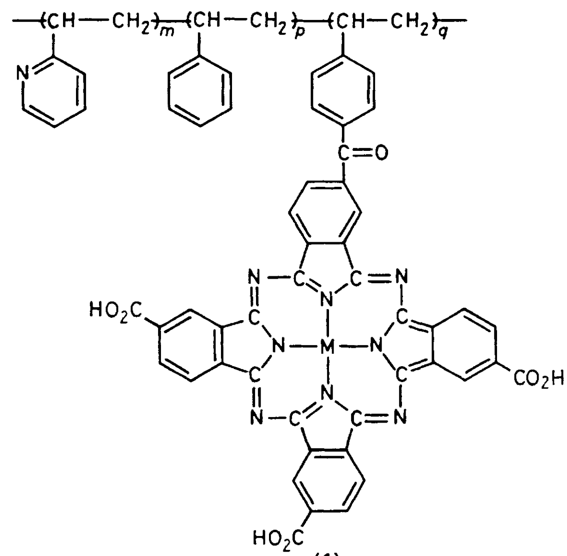

(1)

(**1**); m = 0.50, p = *ca.* 0.48—0.39, q = *ca.* 0.02—0.11.

The bound phthalocyanines M–tapc–P2VP–CO–St [M = Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II}] were prepared and purified as before.[6,7] The copolymer films containing M–tapc were made by spreading a 20% methanolic solution on a polyethylene plate and heating to dryness for *ca.* 10 h at *ca.* 40 °C. The films were peeled off the plate, put into test samples (1.5 × 1.5 cm^2), and dried further at room temperature for 12 h under vacuum. *X*-Ray diffraction data showed that the M–pc rings were randomly oriented in the films. The doping of the samples was carried out at room temperature. The films were exposed to various gases including iodine, using grease-free vacuum line techniques until constant weight was attained (2 days). The samples thus modified with different dopants were stored over silica gel in a desiccator. The conductivities of these films were measured using a standard technique described previously which employs gold electrodes.[5]

The room temperature conductivity data for P2VP–CO–St as well as the M-tapc bound to the copolymer are listed in Table 1. The conductivities of the M-tapc copolymer-bound films were 10^6—10^9 greater than those of the parent copolymer alone. As shown in Table 1, further increases in electrical conductivity for the M-tapc–P2VP–CO–St films resulted from their doping. Doped M-tapc–P2VP–CO–St films have σ_{RT} values of *ca.* 10^{-5}—10^{1} ohm^{-1} cm^{-1}. In the absence of M–tapc, P2VP–CO–St–I_2 had a conductivity of less than *ca.* 10^{-9}—10^{-10} ohm^{-1} cm^{-1}. With increasing metal–phthalocyanine concentration the conductivities rose steeply by 2—3 orders of magnitude. This suggests that the conductive pathway involves significant π–π overlap between phthalocyanine rings.

The Raman spectrum of the iodinated Ni^{II}–tapc–P2VP–CO–St film shows strong scattering attributable to I_3^- (*ca.* 106—108 cm^{-1}), and the e.s.r. spectrum at 25 °C contains a sharp signal at g = 2.000. These data indicate that there are free electrons in the iodine-doped Ni^{II}–tapc polymer. The conductive mechanism of the iodine-doped Ni^{II}–tapc polymer may be explained as follows. The free electrons are formed by charge transfer from a phthalocyanine ring or a pyridine group in the parent polymer to a di-iodine molecule to give I_3^-. Charge transport can be envisaged by a process in which 'free electrons' (or 'holes') move between isoenergetic configurations.[8]

The doped films are stable in air and could be heated to *ca.* 80 °C with little effect on their conductive properties. The bridge-stacked metallophthalocyanines are powders.[2,3] The films obtained here may be practically useful in various electronic devices, because of the flexibility and easy processing of the films.

Table 1. Conductivities[a] for doped M–tapc–P2VP–CO–St[b] films.

M	Amount of M (mol%)	Dopant	σ_{RT} (ohm^{-1} cm^{-1})[c]
—	—	HCl[d]	10^{-12}
—	—	I_2[d,e]	10^{-10} [f]
[g]	1.8	—	10^{-10} [f]
[g]	3.6	—	10^{-9} [f]
[g]	10.3	—	10^{-8} [f]
[g]	3.6	HCl[d]	*ca.* 10^{-1}—10^{-2}
[g]	10.3	HCl[d]	*ca.* 10^{0}—10^{-1}
[g]	3.6	H_2SO_4[d]	10^{-3}
[g]	10.3	H_2SO_4[d]	10^{-2}
[g]	1.8	I_2[d,e]	10^{-6} [f]
[g]	3.6	I_2[d,e]	10^{-4} [f]
[g]	10.3	I_2[d,e]	10^{-3} [f]
Co^{II}	7.2	—	10^{-9} [f]
Co^{II}	7.2	HCl[d]	10^{-3}
Ni^{II}	10.9	—	10^{-8} [f]
Ni^{II}	10.9	HCl[d]	10^{-2}
Ni^{II}	10.9	I_2[d,e]	10^{-3} [f]
[h]	9.0	—	10^{-7} [f]
[h]	9.0	HCl[d]	10^{-2}
[h]	7.3	H_2SO_4[d]	*ca.* 10^{-2}—10^{-4}
[h]	7.3	SO_3[d]	*ca.* 10^{1}—10^{0} [f]
[h]	7.3	I_2[d,e]	*ca.* 10^{0}—10^{-2} [f]
[h]	7.3	BF_3–phenol[i]	*ca.* 10^{0}—10^{-1}
[h]	7.3	$CuBr_2$[i]	*ca.* 10^{-2}—10^{-3}
[h]	7.3	TCNE[i]	*ca.* 10^{-4}—10^{-5}
[h]	7.3	TCNQ[i]	*ca.* 10^{-4}—10^{-5}

[a] A three point terminal electrode (ref. 8) was used at room temperature. [b] 2VP/St = 1.13, 2VP/St was assumed to be identical with the monomer molar ratio. [c] The values reported are averages of five repeated measurements on each sample. [d] Solid–vapour reaction under vacuum. [e] Films were doped to constant weight. [f] 10^{-5} Torr. [g] M = Fe^{III}. [h] M = Cu^{II}. [i] Reaction in heptane slurry. TCNE = Tetracyanoethylene and TCNQ = tetracyanoquinodimethane.

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