exclusively dissolved in the WP.

The results of the quenching experiments are given in Table III. These quenching data seem to indicate that P which resides in the hydrocarbon medium is more efficiently quenched by quenchers which partition strongly into the hydrocarbon phase. On the other hand, PBA and PDA which are strongly bound to the water pool structure with their carboxylate groups anchored at the interface strongly interacting with the trimethyl ammonium groups of the surfactant molecules are more strongly quenched than P by quenchers that are associated with the water pool aggregate. However, PSA which is likely to be associated with the head groups of the surfactant molecules in the Stern-layer region is most efficiently quenched by I^- and CPC which are localized within the WP structure.

Photoinduced ET Reactions. P/DMA. In the CTAB-μE system (W_0 = 20.3), DMA quenches efficiently the fluorescence of P as well as that of PSA, PBA, and PDA (Table III). This quenching leads to very weak exciplex emission (lifetime 60 ns) in the case of P whereas no exciplex emission is observed for the P derivatives. However in a mixture of dodecane and hexanol having the same composition as in the μE system, DMA quenching of the fluorescence of P as well as its derivatives produces a strong exciplex emission with a measured lifetime of 110 to 120 ns. The much shorter lifetime of the P/DMA exciplex in the μE system seems to indicate that it is strongly quenched by the water pools. On the other hand, PSA, PBA, and PDA are expected to be bound to the water pool structure and therefore the absence of exciplex emission can be ascribed to static quenching by the water pools.

Laser flash photolysis studies on pyrene and its derivatives showed a very low yield of P^-, but a very high yield of anions for the pyrenyl derivatives. This result is in accord with the explanation given earlier for the low yield of P^- in the O/W CTAB-μE system, i.e., that high yields of ions in photoinduced ET reactions can only be achieved when the reactants are solubilized close to the micelle–water interface where escape of the photoproduced ions is most favorable. It is therefore suggested that quenching of the P/DMA exciplex by collision with the water pools does not lead to a separation of its constituent radical ions.

In CTAB-μE systems containing small water pools (W_0 = 20.3), the decay of the absorption of the anion of the pyrene derivatives (monitored at 493 nm) manifests itself in two fractions, a fast decay component (half-life 100 ns) attributed to first-order intra-water pool back ET reaction involving pairs of (P^-, DMA^+) residing in isolated water pools, and a slow second-order decay (half-life 2–3 μs) corresponding to an inter-WP back ET process.

Upon increasing the concentration of water in the μE system (W_0 = 60.9) the decay of P^- absorption no longer shows a distinct two-component feature but it remains nonexponential with a half-life of 2–3 μs. In the present μE system which contains larger water pools (see Table IV), the intra-WP back ET process is projected to occur within a few μs and therefore would be mixed in with the second-order inter-WP reaction which occurs within a comparable time period.

RuII/MV^{2+}/HV^{2+}. The laser flash photolysis technique was also applied to investigate the ET from photoexcited RuII to MV^{2+}, a reaction which is expected to take place inside the water pool, and to HV^{2+} which as indicated earlier is probably located at the interface boundary as a result of its amphiphilic structure. Results showed no yield of MV^+ (monitored at 395 nm) ions presumably due to a very fast back ET to RuIII, but a high yield of HV^+. The transient absorption of HV^+ decayed by two processes (similar to the case of P/DMA discussed above) intra- and inter-WP back ET reaction occuring in a time range of ca. 10 μs.

Attempts to intercept the back transfer of the electron from MV^+ to RuIII by addition of EDTA which would react with RuIII to regenerate RuII turned out not to be successful. However, in the case of RuII/HV^{2+} addition of EDTA increased the lifetime of HV^+ by more than an order of magnitude.

Conclusions

The data establish several important parameters such as water pool radius and hydrocarbon bubble radius for cationic W/O and O/W CTAB microemulsions, respectively. Photoinduced reactions, in particular electron-transfer reactions, point out the important role played by environment in controlling the nature of these reactions. Design of the microemulsion system provides factors that control the efficiency of electron transfer and the subsequent efficient separation of the ionic products. The data point out salient features to be obtained for optimum design of electron-transfer systems of interest to solar energy storage.

Highly Conducting Linear Stacked Polymers: Iodine-Doped Fluoroaluminum and Fluorogallium Phthalocyanines

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Abstract: Phthalocyanine–aluminum and phthalocyanine–gallium fluorides have been prepared and doped with iodine to give $(PcMFI_x)_n$ compositions, where $x = 0.012$–3.4 (M = Al) and $x = 0.048$–2.1 (M = Ga). Thermogravimetric analysis proved useful for iodine analysis as complete loss of I_2 is observed for these materials below 250 °C, leaving a PcMF residue. Both Raman and infrared spectroscopy were used to characterize the iodine-doped PcMF materials. The Raman spectra (ν_0 = 514.5 nm) of $(PcMFI_x)_n$ showed strong scattering attributable to I_3^- (106–108 cm^{-1}) and I_5^- (164–168 cm^{-1}). The pentaiodide band dominated the spectra of all samples with the exception of compositions prepared by heating $(PcAlFI_{3.4})_n$ to temperatures less than 200 °C for which the 107 cm^{-1} (I_3^-) transition was strongest. Conductivity of iodine-doped materials was studied by using linear four-probe (300 K) and variable temperature (77–300 K) van der Pauw methods on pressed pellets. Iodine doping results in increases in conductivity by factors as high as 10^9, with the highest conductivity (5 Ω^{-1} cm^{-1}) being observed for $(PcAlFI_{3.4})_n$ derived from sublimed $(PcAlF)_n$. The conductivity is thermally activated, with an apparent activation energy of 0.017 eV being measured for $(PcAlFI_{3.4})_n$.

Conducting and photoconducting organic and inorganic materials are of considerable interest as new candidates for optical, electronic, photoelectric, and electrochemical applications.[2] Because of their thermal and hydrolytic stability, intense color, and ready availability, phthalocyanines[3] have been the subject of study with regard to their photoconducting and semiconducting properties. Highly conducting doped phthalocyanines have been prepared,[4] and for one composition, $NiPcI_{1.0}$,[5] metallic behavior

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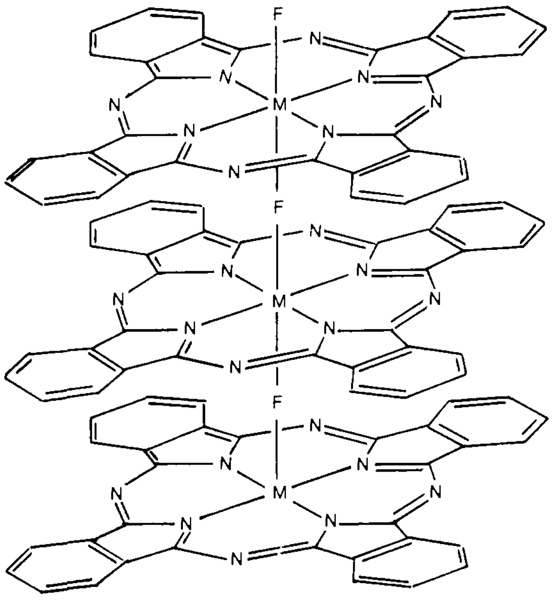

Figure 1. Proposed structure for $(PcMF)_n$, M = Al, Ga.

has been demonstrated. Conductive thin films of NiPc treated with iodine at elevated temperatures have also been examined with a view to their ultimate use as improved photosensitizers for optoelectronic devices.[6] In addition to investigations on stacked phthalocyanines, work on bridge-stacked phthalocyanines $[(MPcO)_n$, M = Si, Ge, Sn$]$[7] has shown that the presence of a central atom–oxygen bridge does not prevent high conductivity.

The novel polymeric fluoroaluminum and fluorogallium phthalocyanines, $(PcMF)_n$, M = Al, Ga were prepared and characterized by Kenney et al.[8,9] X-ray and microscopy studies as well as the physical properties of these compounds support the structure shown in Figure 1, where a linear $(MF)_n$ backbone is surrounded by a sheath of attached planar phthalocyanine rings. Our interest in these bridged-stacked fluoro phthalocyanines centered on whether iodine doping was feasible, as has been demonstrated for stacked phthalocyanines. We have communicated the preliminary results of our studies[10] and present the details of our investigation below.

Table I. Compositions and Conductivities for $(PcMFI_x)_n$

sample	I/Al[a]	conductivity,[b] Ω^{-1} cm^{-1}	E_a, eV
1^{c}	0	$<10^{7}$	
$2^{c,e}$	0.02 [0.04]	2.2×10^{-4}	
$3^{c,e}$	0.09 [0.09]	3.1×10^{-3}	
4^{f}	0.44	0.055	
$5^{d,g}$	0.65 [0.66]	0.20	
$6^{d,h}$	0.76	0.24 (0.20)	0.05
$7^{c,e}$	0.85	0.24	
$8^{c,f}$	0.9	0.23	
$9^{c,i-k}$	1.0 (0.87) [0.94]	0.70	
$10^{d,j,l}$	1.0	0.13	0.05
$11^{d,l}$	1.5	0.19	
$12^{c,e}$	1.9	1.1	
$13^{d,j,k}$	2.4 (2.2)	0.63	0.03
$14^{c,e}$	2.7	3.9	
15^{f}	2.7	4.5	
$16^{c,e}$	3.3	3.4	
$17^{c,m}$	3.3 [3.3]	3.4 (5.1)	0.017
$18^{d,k}$	3.4 (3.3) [3.2]	0.59 (0.51)	0.03
sample	**I/Ga**	**conductivity,[b] Ω^{-1} cm^{-1}**	**E_a, eV**
19^{c}	0	$<10^{-9}$ (4.6 × 10^{-10})	0.85
$20^{c,n}$	0.048	3.5×10^{-5}	
$21^{c,n}$	0.096	1.6×10^{-4}	
$22^{c,o}$	0.15	4.6×10^{-4}	
$23^{c,n}$	0.47	8.9×10^{-3}	
$24^{d,i}$	0.62 (0.62)	0.017	
$25^{d,j,l}$	0.77	0.044	
$26^{c,n}$	0.93 [0.94]	0.12	
$27^{d,j,k}$	0.97 (0.93)	0.072 (0.070)	0.03
$28^{d,l}$	0.98	0.086	
$29^{c,l}$	1.18	0.12	
$30^{d,k}$	2.1 (2.3)	0.15 (0.11)	0.04

[a] Iodine content from TGA; from independent weight uptake measurements in parentheses and from chemical analysis, in brackets. [b] Room temperature linear four-point probe van der Pauw measurements (295 K) in parentheses; all measurements on pressed disks at 295 K. [c] $(PcMF)_n$ purified by sublimation was used. [d] Unsublimed starting material. [e] Pentane slurry: saturated I_2 ($x > 3.3$) or I_2 limiting reagent ($x < 3.3$). [f] Prepared by heating $(PcAlFI_{3.3})_n$^{c,e} at $T < 200$ °C at ambient pressure. [g] 1,2-Dichlorobenzene slurry at 65 °C. [h] 1,2-Dichlorobenzene slurry at 103 °C. [i] Iodine uptake interrupted before maximum weight gain in vacuo. [j] Pumped to constant weight. [k] Solid-vapor reaction in vacuo. [l] Heptane slurry reaction. [m] Slurry reaction, I_2 saturated CCl_4. [n] Pentane slurry: saturated I_2 ($x > 1.18$) or I_2 limiting reagent ($x < 1.18$). [o] Prepared from 23 by heating at ambient pressure (N_2) for 4 min at 70 °C.

Experimental Section

$(PcAlF)_n$ and $(PcGaF)_n$. As described previously,[9] $PcAlOH{\cdot}xH_2O$ and $PcGaOH{\cdot}xH_2O$ were repeatedly evaporated to dryness with concentrated aqueous hydrofluoric acid. Heating the as-prepared fluorides to 300 °C in vacuum for several hours provided bulk quantities of suitable materials in a reasonable time period ("unsublimed starting material", Table I). The infrared spectra for PcAlF and PcGaF were identical with those reported for sublimed material.[8,9] PcAlF and PcGaF were sublimed (10^{-3}mmHg) by using an Ace Glass Inc. No. 8022 sublimation apparatus which was modified by replacing the lower portion of the sample holder tube (50 mm) with fused silica. The furnace temperature was monitored with a Fisher No. 20700 pyrometer. Approximate furnace temperatures for sublimation were 510–530 °C (Al) and 470–490 °C (Ga). The cold finger was cooled with water, which boiled vigorously under the sublimation conditions. Anal. Calcd for $C_{32}H_{16}N_8AlF$ (Galbraith Laboratories): C, 68.8; H, 2.89; N, 20.1; F, 3.40; Al, 4.83. Found (unsublimed sample): C, 65.7, 67.2; H, 2.90, 2.84; N, 19.2, 19.5; F, ---, 3.96. Found (sublimed sample): C, 68.7; H, 2.97; N, 20.0; F, 3.23; Al, 5.00. Calcd

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for $C_{32}H_{16}N_8GaF$: C, 63.9; H, 2.68; N, 18.7; Ga, 11.6; F, 3.16. Found (unsublimed sample): C, 65.3; H, 2.70; N, 18.5; Ga, 10.2; F, 3.33. Found (sublimed sample): C, 63.8; H, 2.80; N, 18.6; Ga, 11.4; F, 3.04.

Reactions with Iodine. (A) Slurry of $(PcMF)_n$ in Iodine Solution. Preliminary experiments with unsublimed PcAlF indicated rapid uptake of iodine when this compound was stirred with iodine solutions (pentane, heptane, carbon tetrachloride). Thus, unsublimed PcAlF (0.75 g) was treated with a clear solution of 0.5 g of iodine in 100 mL of heptane. The flask was stoppered with a septum and stirred magnetically. Iodine content was monitored by daily filtration and TGA. Virtually all iodine uptake occurred within the first 24 h. $(PcGaFI_x)_n$ was prepared similarly. The products are fine black (Al) or deep purple (Ga) powders. Samples prepared in this manner were subjected to pumping (10^{-3}mmHg) at ambient temperatures. Approximately one-third to one-half of the iodine originally present was eliminated in vacuo. Thus **11** (I/Al = 1.5) after removal of readily volatile iodine became **10** (I/Al = 1.0) (Table I).

Sublimed PcAlF was treated with a saturated solution of iodine in pentane. TGA showed that maximum iodine uptake ($x = 3.4$) occurred in less than 5 min. Iodine content could be controlled at any desired level by using iodine as a limiting reagent. Thus the data in Figure 3 are for $(PcAlFI_x)_n$ compositions prepared in this manner ($x = 0.012$–3.4). A complete analysis was obtained on one of these compositions (**14**, 43% I by TGA). Found: Al, 2.92; C, 38.30; F, 2.61; H, 1.60; I, 43.22; N, 11.13. Formula: $Al_{1.08}C_{31.9}F_{1.37}H_{16.0}I_{3.40}N_{7.95}$.

$(PcGaFI_x)_n$ compositions can be prepared similarly from sublimed starting material (Figure 3, $x = 0.048$–1.18). However, iodine uptake by sublimed PcGaF is much slower than for PcAlF. Thus **20**, $(PcGaFI_{0.096})_n$, is obtained by treatment of PcGaF with I_2/pentane after 5 min, while $(PcGaFI_{1.18})_n$ (**29**) is formed after 24 h. A complete analysis was obtained on one of these compositions (**26**, 16% I by TGA). Found: C, 52.26; F, 2.54; Ga, 8.95; H, 2.28; I, 16.15; N, 15.07. Formula: $C_{32.2}F_{0.993}Ga_{0.972}H_{16.9}I_{0.941}N_{8.00}$.

(B) $(PcMF)_n$ (Unsublimed) with Iodine Vapor. A reaction vessel was constructed by fusing a short piece (5 cm) of 22-mm tubing sealed at one end to that arm of a right-angle 8-mm Teflon needle valve collinear with the bore. An 18/9 o-joint was sealed to the other arm of the valve. After weighing the empty vessel (without the Teflon plug), a tube of glassine paper was inserted through the valve until it was in close proximity to the bottom of the tube. $(PcMF)_n$ (nominally 1 g) was then carefully transferred through the paper tube into the reaction vessel, the paper tube removed, the vessel reweighed, and the Teflon plug inserted. The vessel was then attached to a small manifold which provided iodine vapor from a tube filled with iodine crystals. Once assembled, the apparatus was evacuated, the valve to the main vacuum system was closed, and the system was allowed to equilibrate at ambient temperature. During the initial stage of iodine uptake a change in color occurred for $(PcAlF)_n$ from blue violet to dark violet black, while $(PcGaF)_n$ became a deeper violet. Iodine uptake was monitored periodically by removing the vessel containing $(PcMFI_x)_n$ and weighing it (no exposure to the atmosphere). After reaching constant weight (1–3 weeks), the reaction vessel was transferred to a glovebag (nitrogen atmosphere) where approximately half of the product was removed for characterization. The vessel was reattached to the vacuum line and pumped on for a few minutes for removal of readily volatile iodine from the remaining product before analysis. In a typical experiment, unsublimed $(PcAlF)_n$ (1.17 g, 2.10 mmol) was placed in the reaction vessel. After equilibration for 3 weeks, the I_2 uptake was 0.891 g (7.01 mmol of I), corresponding to an I/Al ratio of 3.34 (**18**).[11] The 43.1% I measured by weight uptake for this sample may be compared to 44% I by TGA (I/Al = 3.4, Table I). Anal. Found for **18**: C, 38.2; H, 1.62; N, 11.1; F, 2.42; I, 40.8. Formula: $C_{32}H_{16}N_{8.0}F_{1.3}I_{3.2}(Al_{1.0})$.[12]

A portion of the iodine-doped product was pumped to constant weight over a period of 2 weeks. The final composition (13) had I/Al equal to 2.37 (35% I).

(C) Slurry of $(PcAlF)_n$ in Iodine/1,2-Dichlorobenzene Solutions. Two reactions were carried out, one at 103 °C and the other at 65 °C. $(PcAlF)_n$ (1.0 g) was weighed and transferred into a round bottom flask containing 50 mL of 1,2-dichlorobenzene and a magnetic stir bar. A reflux condenser with drying tube was attached and heating and stirring begun. The temperature was maintained constant for 50 h (103 °C) for one reaction and 6 days (65 °C) for the other. The reaction mixture was then cooled to room temperature and filtered. The filter cake was washed with copious amounts of heptane until the filtrate was a pale pink. The powdery, nearly black material on the frit was allowed to air dry. Analytical and conductivity data for the products of these two reactions are in Table I.

Thermogravimetric Analysis. TGA data were obtained by using a Du Pont 990 thermal analyzer and 951 TGA module with a quartz furnace tube and platinum sample boat. A nitrogen flow rate of 50 mL/min and programmed heating rates of 5, 10, or 20 °C/min were employed. Scans were routinely made from room temperature to approximately 400 °C and occasionally to 900 °C. Initial sample mass was nominally 10 mg. Iodine analysis can be obtained directly from the thermograms; compositions containing from 2 to 43% iodine were analyzed in this manner. For confirmation of the TGA determinations, iodine analysis on a number of compositions was obtained. For ready comparison, TGA, weight uptake, and analytical data are listed in Table I.

Conductivity Measurements. Sample disks (13-mm diameter, about 1-mm thick) were formed by using an evacuable die and Carver press. The brittleness of the disks necessitated careful handling. Disk thickness was determined with the aid of a microscope. Disk colors ranged from highly reflective magenta for pure $(PcMF)_n$ to dark maroon for highly iodine-doped compositions.

(A) Linear Four-Probe Technique. Room temperature dc conductivities were obtained by using an Alessi Industries (Costa Mesa, CA) unit (1-mm probe spacings) connected to a Keithley Instruments (Cleveland, OH) Model 530 Type-All system. A model 616 electrometer was substituted for the Model 163 digital voltmeter. Resistivities were calculated as described by Valdes.[13]

(B) van der Pauw Measurements.[14] With the exception of manual selection of sample current input, data accumulation and processing were microprocessor controlled. Current to the sample was supplied by a Keithley Model 225 constant current source. Output dc voltages were detected by a Keithley Model 616 electrometer linked to a Tektronix 4051 computer via a Data Precision Model 3400 digital voltmeter and an IEEE 488 (1975) interface bus. Electrical contacts to the sample disks were made with either Du Pont No. 4817 silver paint or with a dispersion of carbon black and cellulose caprate in ethyl acetate. The latter proved essential for the highly iodinated samples as the silver paint contacts resulted in undesirable battery voltages up to ±600 mV with zero applied current. For provision of strain-free mounting, disks were secured to the anodized aluminum mount with a tuft of cotton over which was wrapped a strip of Teflon tape. The sample and holder were contained in a gas-tight brass can which fit into a liquid nitrogen Dewar centered between the poles of an electromagnet (0–5-kG magnetic field) for Hall voltage measurements. Thermal coupling to the sample mount was aided by providing a helium atmmosphere inside the can. A Eurotherm (Model 917) temperature controller (with computer-controlled set point) regulated the power input to the heating coil wrapped around the aluminum mount. A type E (Chromel-Constantan) thermocouple located ca. 1 mm from the sample monitored sample temperature (±0.1 °C).

The measurement procedure included (a) verification of electrical isolation between the sample and mount, (b) resistance measurements between all four electrodes as a function of current to check for nonohmic behavior, contact resistance, and sample integrity, and (c) measurements at zero current to the sample to check for stray voltages. Room temperature measurements were performed first. Sample temperature was then dropped to 77 K (66 K in one case) and data collection between 77 K and room temperature begun. Reproducibility of the initial room temperature data verified sample stability over the temperature range studied. At temperatures much above ambient, highly iodinated samples released iodine slowly and stable voltages could not be recorded.

Spectroscopy. Raman spectra were obtained with a Spex Ramalog 6 spectrometer employing 514.5-nm excitation (50-mW argon ion laser power). Sample disks were spun at 3000 rpm. Infrared spectra were recorded on samples contained in KBr disks with a Perkin-Elmer Model 267 spectrophotometer.

Mass Spectrometry. Mass spectra were obtained with a Hewlett-Packard 5985 quadrupole instrument (70-eV ionizing electrons). The samples, in glass capillaries, were introduced into the spectrometer via the variable temperature (30–300 °C) solid probe inlet system. A heating rate of 20 °C/min was employed. Both fragmentation patterns and profiles of I_2^+ (m/e 254) intensity as a function of temperature were generated.

Results and Discussion

The reaction of $(PcMF)_n$ with iodine produces highly conducting compositions as fine purple black (M = Al) or magenta to purple-black (M = Ga) powders. Due to the thermal and oxidative

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[11] Table I contains the key for sample numbers.

[12] Formula determined relative to C_{32}. The I/Al ratio is 3.2, assuming C/Al is 32.

[13] L. B. Valdes, *Proc. IRE*, **42**, 420 (1954).

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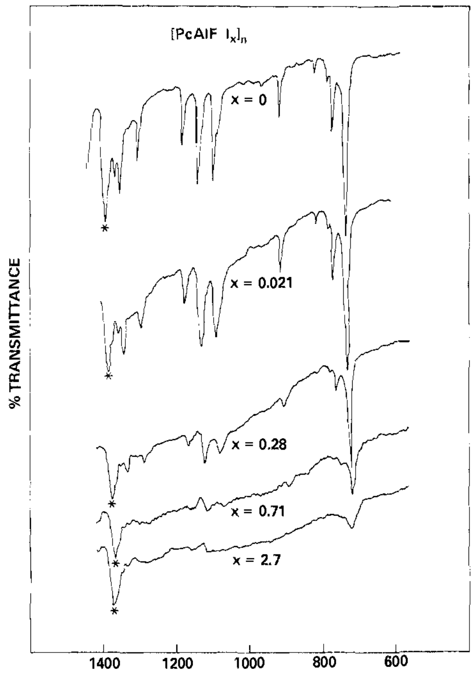

Figure 2. Infrared spectrum of $(PcAlFI_x)_n$ as a function of iodine content. Nujol absorption is marked with an asterisk; absorption at 722 cm^{-1} is partly due to Nujol. Samples prepared by iodine/solvent route.

stability of the $(PcMF)_n$ substrate, the iodine content was readily determined by TGA. This was accomplished in a manner similar to that used by Miller and Griffiths to study halogen oxidation of bis(diphenylglyoximato) complexes of nickel(II) and palladium(II).[15] TGA iodine analyses on $[PcMFI_x]_n$ compositions were checked in a number of cases by performing independent weight uptake experiments and elemental analyses (Table I).

The rate and extent of reaction of PcAlF and PcGaF with iodine are quite dependent on PcMF purity and reaction conditions. Sublimed PcAlF reacts with a saturated pentane/iodine solution to give $(PcAlFI_{3.3})_n$ (**16**) in less than 5 min, while with unsublimed PcAlF a maximum I/Al ratio of 1.5 (**11**) is obtained within 24 h. The reaction of unsublimed PcAlF with iodine vapor proceeds slowly, with $(PcAlFI_{3.4})_n$ (**18**) being obtained after 3 weeks. With sublimed PcGaF, **29** with I:Ga = 1.18 forms after 24 h by using iodine/pentane, while unsublimed PcGaF gives $(PcGaFI_{0.98})_n$ under similar conditions. Unsublimed PcGaF yields $(PcGaFI_{2.1})_n$ (**30**) on reaction with iodine vapor.

The $(PcMFI_x)_n$ compositions containing maximum iodine content are unstable in vacuo and slowly lose iodine over a period of days to weeks, finally giving stable compositions. Thus, the composition $(PcAlFI_{3.4})_n$ (**18**), initially obtained from the solid-vapor reaction, loses iodine to form $(PcAlFI_{2.4})_n$ (**13**) after 2 weeks in vacuo. $(PcAlFI_{1.5})_n$ (**11**), obtained from the iodine/heptane slurry reaction, is also unstable. The composition changes to $(PcAlF_{1.0})_n$ (**10**) after exposure to dynamic vacuum for two weeks. Despite pumping to constant weight, most samples evolved small quantities of iodine when stored at ambient temperature and pressure, as evidenced by the discoloration of the polyethylene caps of the storage vials. Compositions prepared by heating $(PcAlFI_x)_n$ were much more stable to loss of iodine. At elevated temperatures (ca. 250 °C) under dynamic vacuum complete removal of iodine is effected, leaving $(PcMF)_n$ which was identified by infrared spectroscopy, elemental analysis,[16] and TGA.

Infrared, Raman, TGA, and Mass Spectrometric Data. The infrared spectra for undoped and lightly iodine-doped $(PcMF)_n$ show characteristic phthalocyanine absorptions.[3,9,17] As iodine doping increases, the IR peaks become broadened and finally obscured due to the superposition of electronic excitation absorption.[18,19] The IR spectra for $(PcAlFI_x)_n$ (Figure 2) show that the intensity of the electronic excitation absorption increases markedly in the vicinity of 5–6% iodine content (curve $x = 0.28$). This correlates with the rapid rise in conductivity at this iodine doping level (Figure 3) and is consistent with a semiconductor to conductor transition. Similar IR and conductivity data were obtained for $(PcGaFI_x)_n$, although $(PcGaFI_x)_n$ compositions have

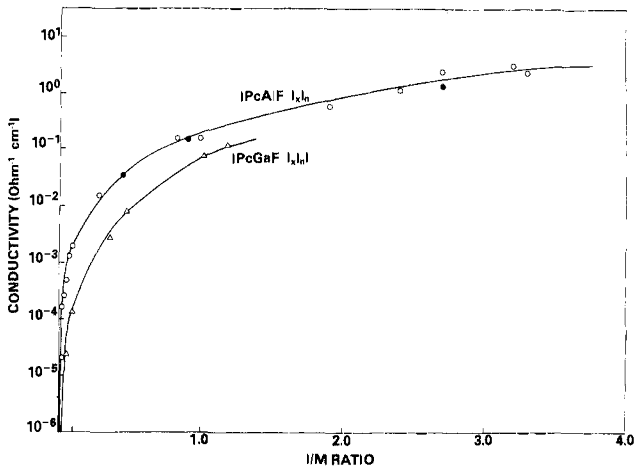

Figure 3. Ambient temperature electrical conductivity for $(PcMFI_x)_n$ as a function of iodine content. For $(PcAlFI_x)_n$ open circles represent compositions prepared by the iodine/solvent route; filled circles represent compositions prepared by heating highly iodine doped material.

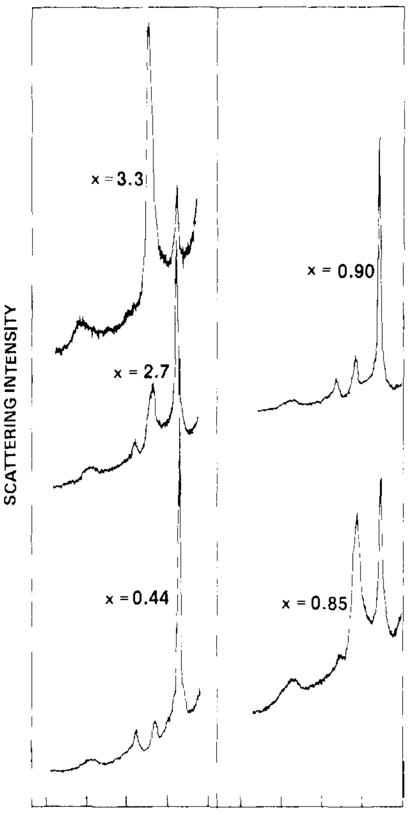

Figure 4. Raman spectra for $(PcAlFI_x)_n$ as a function of iodine content. Samples with $x = 2.7$, 0.90, and 0.44 were prepared by thermolysis of $x = 3.3$; samples with $x = 3.3$ and 0.85 were prepared by iodine/solvent route.

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[15] J. S. Miller and C. H. Griffiths, *J. Am. Chem. Soc.*, **99**, 749 (1977).

[16] Anal. Calcd. for $C_{32}H_{16}N_8AlF$: C, 68.8; H, 2.89; N, 20.1, F, 3.40. Found: C, 66.9, H, 2.78; N, 19.4; F, 3.69.

[17] J. E. Bloor, J. Schlabitz, C. C. Walden, and A. Demerdache, *Can. J. Chem.*, **42**, 2201 (1964).

[18] R. C. Wheland and J. L. Gilson, *J. Am. Chem. Soc.*, **98**, 3916 (1976).

[19] C. R. Fincher, Jr., M. Ozaki, A. J. Heeger, and A. G. MacDiarmid, *Phys. Rev. B*, **19**, 4140 (1979).

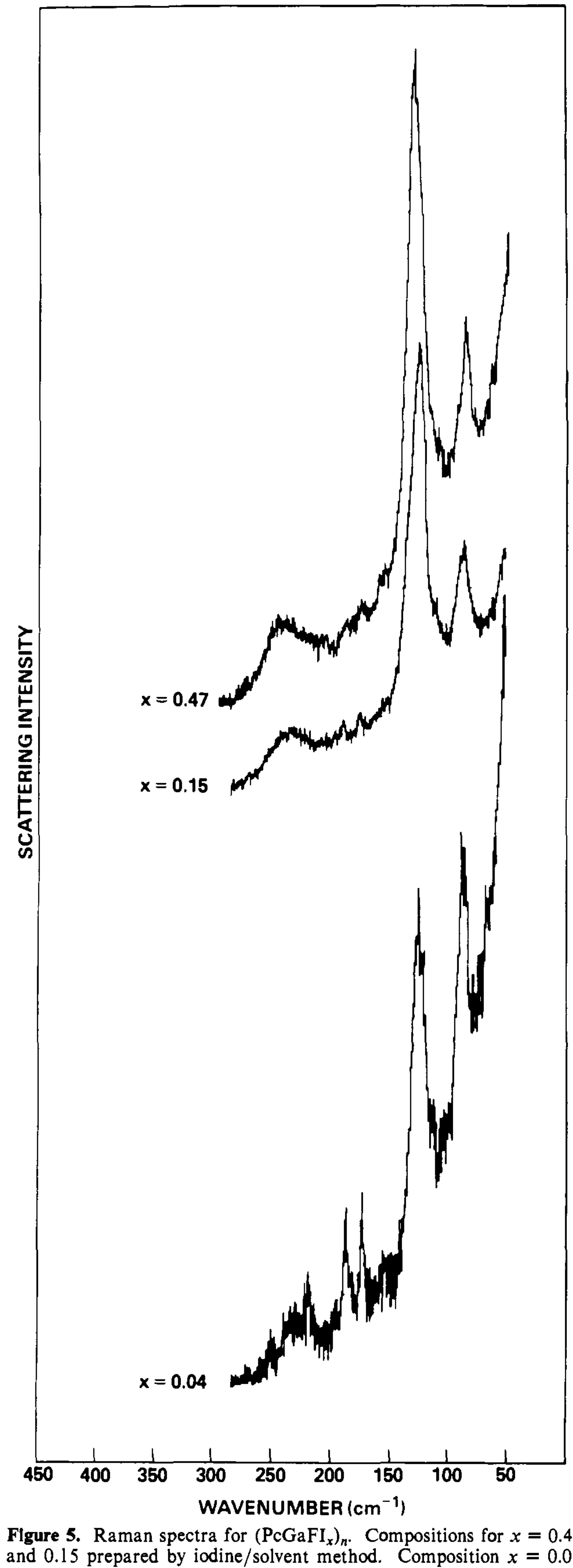

Figure 5. Raman spectra for $(PcGaFI_x)_n$. Compositions for $x = 0.47$ and 0.15 prepared by iodine/solvent method. Composition $x = 0.04$ obtained from $x = 0.47$ by thermolysis.

lower conductivities when compared to their Al analogues.

Raman spectra[20] (ca. 70–600 cm^{-1}) for $(PcAlFI_x)_n$ and $(PcGaFI_x)_n$ are shown in Figures 4 and 5, respectively. Contributions from $(PcMF)_n$ in this region are insignificant compared to the resonance enhanced polyiodide modes. All $(PcMFI_x)_n$ samples exhibit intense scattering between 105 and 108 cm^{-1}. In view of previous spectroscopic studies on iodine-doped transition-metal phthalocyanines,[4] porphyrins,[21,22] polyacetylene,[23] and triiodide salts,[20,24] this band is assigned to the I_3^- symmetric stretching fundamental. Overtones are also observed at 212 cm^{-1} (sharp, 2 × 106 cm^{-1}) and 315–330 cm^{-1} (broad, 3 × 106 cm^{-1} and 2 × 165 cm^{-1}). The very weak peak seen in some of the spectra at ca. 140 cm^{-1} is assigned to the antisymmetric I_3^- stretching mode.[20,24]

The moderately intense band at 164–168 cm^{-1} observed for most $(PcMFI_x)_n$ compositions is assigned to I_5^- in agreement with earlier work on iodine-doped macrocycles[22,25-28] and $(CH)_x$.[23] I_2 (207 cm^{-1}) could not be detected. Iodide cannot be detected by any of the spectroscopic techniques utilized in this study, but prior work on iodine-doped phthalocyanines[4-7] provides no precedent for the presence of I^-.

TGA thermograms for $(PcAlFI_x)_n$ are shown in Figure 6. Two weight loss processes are observed for most compositions between room temperature and the onset of the plateau at 260 °C which signals complete loss of iodine. Above 260 °C the thermograms are identical with that for pure $(PcAlF)_n$. For the latter, weight losses at ca. 550 (sublimation) and 700 °C (decomposition) are observed.

The nature of the two weight loss processes for $(PcAlFI_x)_n$ was investigated by a combination of TGA and Raman spectroscopy. $(PcAlFI_{3.3})_n$ (**16**) was heated at ambient pressure in a stream of dry nitrogen at 60 °C for 15 min to yield a composition with an I/Al ratio of 2.7 (**15**). Compositions with successively lower iodine content were prepared by increasing thermolysis temperature and time. In this way a number of $(PcAlFI_x)_n$ samples were prepared (Table I). Raman spectra and thermograms for representative compositions prepared in this manner (and by the solution method) are shown in Figures 4 and 6, respectively. A number of interesting features are apparent. The Raman spectrum of $(PcAlFI_{3.3})_n$ (**16**) shows intense I_5^- scattering (160 cm^{-1}) and a weaker I_3^- mode (107 cm^{-1}).[29] TGA of **16** (Figure 6) reveals two distinct iodine weight loss processes centered at 130 and 265 °C, with a less distinct process at ca. 145 °C. These temperatures refer to the point in the differential TGA (DTGA) mode (Figure 6, center section) where the rate of weight loss is maximum. The Raman spectrum of $(PcAlFI_{2.7})_n$, (Figure 4, $x = 2.7$), derived from thermolysis of **16** shows in marked contrast to **16** an intense I_3^- mode and an I_5^- peak of medium intensity. In addition, the absolute intensity of the I_3^- peak in **15** is much stronger (ca. ×2) than for **16**. Despite the contrasting Raman spectra, the thermograms of **15** and **16** (Figure 6) differ only in that a less prominent weight loss at 130 °C is observed for **15**. These results indicate that the first iodine weight loss process (130 °C) is due principally to decomposition of I_5^- to I_3^-.

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(20) W. Kiefer, *Appl. Spectrosc.*, **28**, 115 (1974) and references therein.

(21) T. E. Phillips and B. M. Hoffman, *J. Am. Chem. Soc.*, **99**, 7734 (1977).

(22) B. M. Hoffman, T. E. Phillips, C. J. Schram, and S. K. Wright, ref 2c, p 393.

(23) S. L. Hsu, A. J. Signorelli, G. P. Pez, and R. H., Baughman, *J. Chem. Phys.*, *69*, 106 (1978). We are grateful to Dr. P. S. Brant for calling our attention to this work.

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(26) T. J. Marks, ref 2f, p 594; M. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina, M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 2921 (1979).

(27) R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3215 (1978).

(28) Alternative explanations[23,26,27] considered "strongly electronically perturbed I_2"[23] or "unprecedentedly distorted I_3^-".[26]

(29) In support of this, resonance enhancement appears to be greater for I_5^- than for I_3^- when 514.5-nm excitation is used.[23]

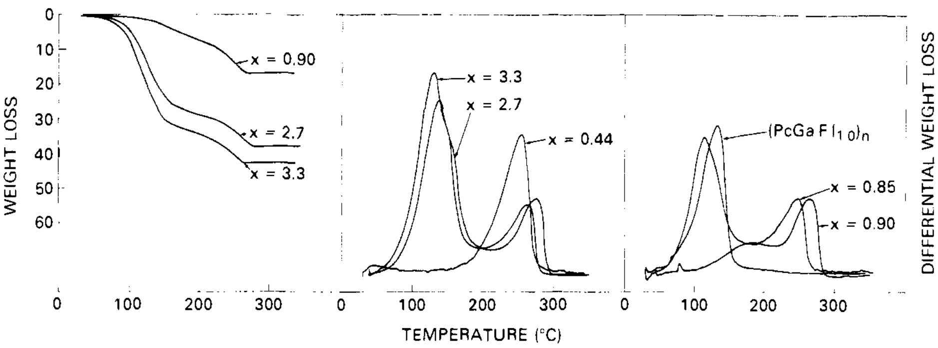

Figure 6. TGA and DTGA data for $(PcAlFI_x)_n$ and $(PcGaFI_{1.0})_n$.

Additional controlled thermolysis brings about lower iodine doping levels, e.g., **8** ($x = 0.9$), for which a much diminished low temperature iodine weight loss in seen. Examination of the DTGA curves shows that the peak corresponding to the temperature of maximum I_2 weight loss gradually broadens and shifts to higher temperature. The shoulder at 145 °C becomes obscured in the broad low temperature weight loss peak. In view of the growth of the I_3^- peak in the Raman Spectrum and the continued but shifted low temperature weight loss feature in the DTGA curves, it appears that two forms of I_3^- are present in compositions such as **8**. The low temperature forms would account for the shoulder at 145 °C observed for **16** and would account for the persistance of substantial low temperature iodine weight loss for compositions whose Raman spectra show weak I_5^- scattering.

Upon continued thermolysis below 200 °C, the Raman spectra for $(PcAlFI_x)_n$ compositions show progressively weaker I_5^- scattering which ultimately becomes very weak at the composition $(PcAlFI_{0.44})_n$. This composition is important in having the highest combined thermal stability (~180 °C) and conductivity (0.055 Ω^{-1} cm^{-1}) of any $(PcMFI_x)_n$ which we examined. Further thermolysis of $(PcAlFI_{0.44})_n$ results in monotonic loss of I_3^- and decreased conductivity.

An interesting kinetic feature is apparent on comparison of the DTGA and Raman data for $(PcAlFI_{0.85})_n$ (**7**) and $(PcAlFI_{0.9})_n$ (**8**). These are nominally similar compositions, but **7** was prepared by using iodine/pentane with iodine as a limiting reagent, while **8** was prepared via the thermolysis of **16**. The DTGA curves for **7** and **8** (Figure 6) reveal **7** has a prominent low temperature weight loss, while **8** shows only modest low tempearture weight loss. Comparing the Raman spectra of **7** and **8** (Figure 4) it is seen that **7** has a much more intense I_5^- peak than **8**. Despite these results which show considerable differences in the distribution of I_3^- and I_5^- for the two compositions, the conductivities of **7** and **8** are virtually identical (Table I, Figure 3). Additional conductivity data on compositions prepared by the limiting reagent method and thermolysis show that conductivity depends only on iodine content and not, within the variations observed, on relative amounts of I_3^- (low or high temperature forms) or I_5^-.

$(PcGaFI_x)_n$ compositions prepared from sublimed PcGaF and iodine/pentane solutions show by DTGA a single weight loss process centered at 130 °C. Raman spectra of samples prepared in this manner show strong I_5^- and I_3^- scattering. A comparison of curves for **20**, **22**, and **23** (Figure 5) reveals that heating these materials in a manner similar to that described above for $(PcAlFI_x)_n$ does not cause appreciable preferential loss of I_5^- vs. I_3^-. The limit of thermal stability of $(PcGaFI_x)_n$ compositions derived from sublimed PcGaF and I_2/solvent reactions is thus in the vicinity of 100 °C at ambient pressure under nitrogen.

Iodine-doped gallium compositions prepared from *unsublimed* PcGaF showed a two-stage weight loss pattern similar to that observed for the $(PcAlFI_x)_n$ compositions. Thus, **30** ($x = 2.1$), a composition resulting from the gas/solid reaction, and **27** ($x = 0.97$), obtained from **30** by pumping to constant weight in vacuo, exhibited two-stage weight losses in the same temperature regimes as the iodine-doped PcAlF compositions. An exception to this pattern was found for **24** ($x = 0.62$). This composition was prepared by the gas/solid route, but iodine uptake was unintentionally interrupted before maximum weight uptake occurred. It was found that this sample, which unlike **28** was exposed to ambient air during weighing after initial iodine uptake, did not take up additional iodine in vacuo. The reason for this is not clear. TGA showed a single broad weight loss beginning at ca. 60 °C. Nine percent by weight of iodine was lost below 100 °C while the remainder (~2.5%) was lost between 100 and 240 °C. The Raman spectrum showed a dominant peak at 166 cm^{-1} (I_5^-) relative to I_3^-. The predominance of the I_5^- band is consistent with the low temperature weight loss for this sample. These results offer a glimpse into an interesting kinetic feature of the gas/solid reaction, but this aspect was not pursued in detail.

$(PcSiOI_{1.3})_n$, prepared by the reaction of $(PcSiO)_n$, with iodine in heptane,[7c] was examined by TGA so that comparisons of the thermal stability of these highly conducting materials and their Al–F and Ga–F linked analogues could be made. A low temperature (~80 °C) and high temperature (300 °C) loss of iodine were observed for $(PcSiOI_{1.3})_n$. Raman spectroscopy confirmed earlier results[7c] which showed only the presence of I_3^-. Thus, as for certain $(PcAlFI_x)_n$ compositions, $(PcSiOI_x)_n$ compositions prepared by the solution method contain two thermally distinguishable forms of I_3^-. The "low temperature" I_3^- can be removed by thermolysis to give highly stable $(PcSiOI_x)_n$ compositions. If a comparison of thermal stability is made among the compositions with greatest thermal stability, i.e., those compositions where "low temperature weight loss" iodine has been removed, it is seen that Si–O linked systems are considerably more stable than those containing Al–F and Ga–F backbones.

Variable temperature mass spectral data were collected to confirm the nature of the volatile species. The fragmentation pattern for each sample showed a base peak at *m/e* 254 (I_2^+). Profiles of total ion current were nearly identical with the profiles of I_2^+ intensity vs. temperature, establishing iodine as the predominant volatile during thermolysis of $(PcMFI_x)_n$. The I_2^+ intensity/temperature profiles also displayed two maxima for $(PcMFI_x)_n$ compositions showing two-stage weight losses. A typical ion intensity/temperature profile [$(PcAlFI_{1.5})_n$, **11**] is shown in Figure 7. A sharp low temperature peak (~50 °C) and broad high temperature peak (90 °C) are seen. The temperatures for these ion intensity maxima are significantly lower than those for the TGA weight loss maxima due to the former data being obtained in vacuo. The higher temperature ion peak was seen to vary in shape and position of maximum intensity (up to 200 °C) from sample to sample depending on iodine content and kinetic effects (differing rates of transfer of thermal energy to particles of differing size at the relatively rapid heating rate employed). These mass spectrometric results were essential in demonstrating that I_2 was the only volatile product of significance. The data also provide independent support for the two-stage iodine weight loss process. It is interesting to note that low and high temperature maxima for I_2^+ intensity were also observed for iodine-doped polyacetylene.[30]

The ion intensity/temperature profile for the anomalous $PcGaFI_{0.62}$ (**22**) is shown in Figure 7 as an inset. A predominant

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[30] W. N. Allen, J. J. DeCorpo, F. E. Saalfeld, R. Wyatt, and D. C. Weber, ref 2b.

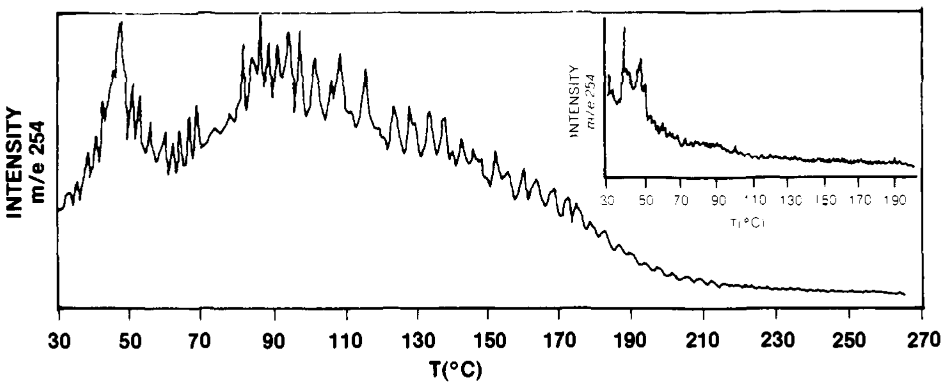

Figure 7. Mass spectrometric profiles of I_2^+ (*m/e* 254) ion intensity vs. temperature for $(PcAlFI_{1.5})_n$ and (inset) $(PcGaFI_{0.62})_n$.

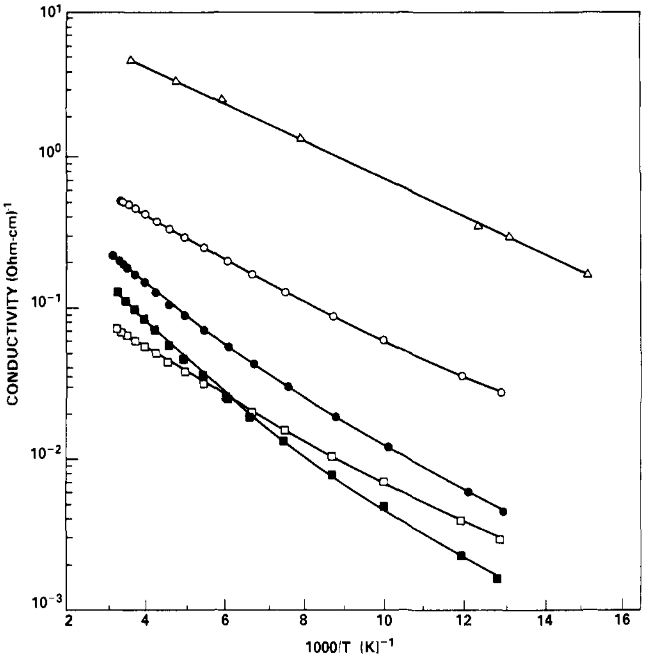

Figure 8. Electrical conductivity of pressed disks of $(PcMFI_x)_n$ vs. inverse temperature. $(PcAlFI_x)_n$: $x = 3.3$ (△), sublimed PcAlF; $x = 3.4$ (○), 0.76 (●) and 1.0 (■), unsublimed PcAlF. $(PcGaFI_{0.97})_n$ (□).

low temperature peak is observed with a long tail extending to higher temperatures, in accord with TGA and Raman data cited above.

Conductivity Studies. The room temperature pressed disk dc conductivities obtained by both the linear four-point probe and the four-probe van der Pauw methods are in excellent accord for all samples (Table I). The conductivity of unsublimed $(PcAlF)_n$ starting material was surprisingly high, as previously noted,[10] and is due to the presence of impurities; a linear four-probe conductivity value of $<10^{-6}\ \Omega^{-1}\ cm^{-1}$ was measured for sublimed $(PcAlF)_n$ and $(PcAlF)_n$ regenerated by heating $(PcAlFI_{2.4})_n$ to 180 °C in vacuum. Thus, striking increases in conductivity—as much as 10^9 for $(PcGaF)_n$—occur upon doping with iodine.

The variation of conductivity as a function of iodine content is plotted in Figure 3. For both the Al and Ga systems the conductivity rises rapidly with increasing iodine content until I/M equals 0.4–0.6 and then rises more slowly with increasing iodine content. The dependence of conductivity upon dopant level is not unexpected, as this behavior has been observed for other systems such as polyacetylene/AsF_5.[31] With $(PcMFI_x)_n$ the highest iodine dopant levels give higher conductivity for Al vs. Ga. This observation correlates with the greater interphthalocyanine ring spacing for Ga vs. Al[9] and provides evidence that the conductive pathway is through a conduction band generated by inter-ring π-orbital overlap. A similarly decreasing conductivity with larger E atoms has been observed for the series $(PcEOI_x)_n$, where E = Si, Ge, Sn.[7c]

Highest conductivities were observed for compositions where sublimed PcMF was utilized. Analytical data show an impurity level of ca. 2–4% in unsublimed PcMF samples. Differences in conductivity in going from unsublimed to sublimed substrate were factors of 5–10. This result may be due, over and above an effect expected from the rule of mixtures, to the presence of longer polymer chains in 7 due to the removal of species such as PcAlOH which could act as chain terminators. The most highly conducting composition prepared in this study ($5\ \Omega^{-1}\ cm^{-1}$) was $(PcAlFI_{3.3})_n$.

The variation of conductivity with temperature for several $(PcMFI_x)_n$ samples is shown in Figure 8. A fit of the linear high temperature portion of the curves to the relation $\sigma = \sigma_0 \exp(-E_a/kT)$ yields values for activation energies, E_a, given in Table I. The remarkably low activation energies[32] for the iodine-doped aluminum and gallium phthalocyanine fluorides are comparable to values reported for iodine-doped transition-metal phthalocyanines,[4] $(PcEOI_x)_n$[7] materials, and halogen-doped polyacetylene.[33,34] In the range of x values studied for $(PcMFI_x)$ compositions, E_a values are independent of iodine content. Thus the semiconductor-to-metal transition[35] seen at lower iodine doping levels for halogenated polyacetylene[33] was not observed for the $(PcMFI_x)_n$ compositions.

Efforts to determine the type and number of charge carriers and Hall mobility were hampered by a combination of low mobility and small sample inhomogenieties. At best, the carrier mobility at ambient temperature is estimated to be no greater than 10 cm^2/V s.

In summary we have shown that iodine-doped $(PcMF)_n$ compositions are highly conducting. They have lower thermal stability with regard to loss of iodine compared to iodine-doped $(PcSiO)_n$. But because the polymer chain is linked by coordinate covalent bonds in $(PcMF)_n$, these materials can likely be sublimed and doped to give conducting thin films. The conductivity of $(PcMFI_x)_n$ is equal to or greater than the SiO linked analogues. The improved conductivity of $(PcMFI_x)_n$ may be due in part to the capability of purification of $(PcMF)_n$ by sublimation vs. $(PcSiO)_n$ which is less tractable.

Acknowledgment. We thank the Office of Naval Research for partial support of this work. We are indebted to a number of NRL scientists, including Dr. F. J. Campbell and L. M. Johnson for use of their TGA instrument, Dr. J. E. Reardon for use of the linear four-point probe apparatus, Dr. W. N. Allen for obtaining the mass spectra, and Drs. Jj. R. Griffith, A. Snow, D. C. Weber, and P. S. Brant for many stimulating and useful discussions.

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(31) C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).

(32) For comparison, activation energies of 1.6 eV are recorded for both nickel and cobalt phthalocyanine. See F. Gutmann and L. E. Lyons, "Organic Semiconductors", Wiley, New York, 1967, p 718.

(33) A. G. MacDiarmid and A. J. Heeger, ref 2c, p 161.

(34) For true metallic behavior, E_a should be zero.

(35) N. F. Mott, *Adv. Phys.*, **21**, 785 (1972).