Chemically modified thin organic films supported on polished silica substrates

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Organic films, of thickness up to *ca.* 1000 nm, derived from polycyclic aromatic hydrocarbons containing 3–15 rings, have been grown on highly polished silica glass supports by vacuum sublimation. The quality of the films, as judged by their electronic spectra, is very dependent on achieving a near subnanometre surface finish on the silica. Exposure of the films to MoF_6 at room temperature results in irreversible adsorption of the latter, as demonstrated by electronic spectroscopy. The fluorides WF_6 and AsF_5 show similar behaviour, although in many cases their interactions with the films are less marked.

The reactions of organic molecules have been studied traditionally in solution but there is increasing emphasis on selectivity in syntheses and by the use of an ordered, structurally well characterized environment it is often possible to obtain more information than would be the case in solution. Our interest in the chemistry involved in the chemical–mechanical polishing of silica glass and silicon,[1] led us to investigate the use of these materials as supports for organic films that could then be modified by interaction with volatile inorganic reagents, silica supports being particularly useful for investigations of reactions between the films and high oxidation state fluorides by electronic spectroscopy.

Polycyclic aromatic hydrocarbons are potential π donors and an obvious way of modifying their electronic properties is *via* the formation of charge-transfer complexes with volatile Lewis-acid halides adsorbed on the surface of the film. Interactions between π-donor aromatic hydrocarbons and high oxidation state metal halides have been studied in solution for many years.[2] In contrast to n-donor molecules, where the formation of insoluble adducts with acceptor molecules is well documented,[3] studies involving π-donor aromatic hydrocarbons indicate that the interactions are very much weaker, for example in systems exhibiting 'contact charge transfer' behaviour.[4]

In this initial survey study, fourteen polycyclic aromatic compounds possessing 3–15 aromatic rings and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) were investigated. Although intrinsically related, there are important differences between series of structurally comparable compounds, for example the *cata*- and *peri*-condensed systems. In the former, all the carbon atoms participate in a conjugated system in contrast to the latter, which often possess individual discrete cycles of π-electron conjugation, with *peri* bonds having bond lengths approaching those of a C–C single bond.[5] The effect of substituents on thin film formation has been examined in, for example, rubrene, which is a non-planar *cata*-condensed hydrocarbon by virtue of the four phenyl groups attached to the tetracene backbone, decacyclene, a non-planar *peri*-condensed hydrocarbon and coronene tetracarboxylic acid.

The structures and optical properties of thin films derived from polycyclic hydrocarbons and their derivatives on various supports have been widely reported.[6–15] Structural information has been obtained usually by transmission electron microscopy[9,10,12,15] or by electronic spectra recorded at low temperatures.[6–8,11] Particularly relevant to the present work are studies of tetracene and pentacene films supported on glass[6–8,11] or carbon[10] from which it has been concluded that amorphous structures are formed when films of these hydrocarbons are formed by condensation of the vapour at low temperature. Although long-range order is absent, short-range order, to the extent of a few lattice parameters, is present. Annealing processes observed at higher substrate temperature can lead to greater alignment of molecules with the substrate[12–14] and interactions with a polar substrate such as cleaved single-crystal KCl can be important in determining the structure of the film, a notable example being films derived from a polymeric μ-fluoroaluminium(III) phthalocyanine.[15]

Experimental

Wafers of silica (2 × 1 cm; Spectrosil B, Multilab Ltd) or silicon (2 × 1 cm; (100) p-type, MCP Wafer Technology Ltd), chemomechanically polished (surface roughness $R_A \leqslant 1$ nm over 250 μm) using a procedure described elsewhere,[1] were degreased and cleaned carefully by ultrasonic agitation for 5 min in 68% nitric acid (GPR, Rhône Poulenc), Genklene (ICI) and isopropyl alcohol (GPR, M & B). High-purity (Gold Label, Aldrich) organic compounds were employed without further purification wherever possible for the preparation of thin films, otherwise starting materials were purified by recrystallisation. Owing to the hygroscopic nature of many of the materials employed, reactions were conducted *in vacuo* (10^{-4} Torr) using a flamed-out Pyrex glass vacuum system. Molybdenum hexafluoride, tungsten hexafluoride, phosphorus pentafluoride (all Fluorochem) and arsenic pentafluoride (Matheson) were purified by repeated trap-to-trap vacuum distillation over activated NaF at 77 K. They were transferred finally to Pyrex breakseal vessels containing activated NaF and stored at 77 K until required. Instrumentation was as follows: electronic spectra PE Lambda 9, IR Nicolet 5DXC with a SpectraTech collector for diffuse reflectance and an MTEC 100 cell for PAS, IR microscopy Nicolet Nic-Plan with ZnSe ATR accessory.

Preparation of organic thin films

Since this was a survey study, films were synthesised using a straightforward thermal evaporation procedure *in vacuo* based on previous work in this Department.[9,12,15] The apparatus consisted of an Edwards 306 coating unit, capable of 10^{-7} Torr with a liquid-nitrogen cooled cold trap. A copper–constantan thermocouple was employed to measure the substrate temperature. Cooling the silica support below ambient temperature was not possible with the equipment used. A measured quantity (*ca.* 10 mg) of material was placed in a cleaned molybdenum or stainless-steel boat at a measured distance from the substrate. The substrate was heated to 493 K at 10^{-5}–10^{-6} Torr and allowed to equilibrate for 30 min. This procedure ensured clean and dry substrates were obtained. The substrate was allowed to cool to the required temperature, whereupon the organic material was evaporated by heating resistively the boat for 1 min. The substrate was allowed to cool to ambient temperature before being removed for spectroscopic analysis at room temperature. Film thicknesses were estimated assuming a sticking coefficient of unity, which has been demonstrated to yield values correct to within an order of magnitude.[16]

Preparation of chemically modified thin organic films

A thin film supported on silica was loaded into an evacuable Pyrex cylindrical cell fitted with Spectrosil B windows and a Pyrex/PTFE (J. Young) stopcock. Its electronic spectra was then obtained. The cell was attached to a reaction manifold which incorporated a breakseal vessel containing the fluoride and the entire system evacuated, pumped out for 24 h and repeatedly flamed out thoroughly to remove residual moisture. The breakseal vessel was cracked open, the fluoride transferred by vacuum distillation to a second vessel containing activated NaF and vapour allowed to fill the cell and manifold. When the reaction cell containing the thin film was supplied with sufficient fluoride to achieve a stoichiometry fluoride: film $>1:1$, the cell was isolated from the manifold and allowed to equilibrate for *ca.* 30 s. Volatile material was removed and the cell pumped for 5 min to remove any volatile material remaining. The evacuated cell was removed from the line and the electronic spectrum of the chemically modified film recorded at room temperature.

Results

Determination of experimental conditions for film growth

The room-temperature electronic spectra of films deposited on commercially polished silica wafers were characterised by very broad absorption bands from which little information could be extracted, since the new bands formed on the subsequent addition of a high-oxidation state fluoride could hardly be discerned. However using wafers polished by the method described previously,[1] satisfactory electronic spectra were obtained in all cases with the exceptions of pyrene and to some extent, rubrene where the spectra, irrespective of film thickness, were dominated by interference patterns. Films, up to an estimated thickness of *ca.* 1000 nm were stable *in vacuo* over long time periods apart from anthracene and fluoranthrene films which fractured readily. In all cases films were annealled at the temperature at which the substrate was heated during evaporation, the most satisfactory temperatures being those approaching or slightly greater than, half the melting point of the hydrocarbon, Table 1. The observations are consistent with those made previously using this procedure, the annealing process being significant only above a temperature of half the mp of the compound being evaporated.[12] The ratios, substrate temperature : mp for the low-melting pyrene and fluoranthrene were somewhat larger than the optimal (Table 1) owing to experimental limitations.

Table 1 Optimum temperature range for thin film growth on polished silica glass

compound	substrate temperature T_S/K	T_S/mp
anthracene	288–298	0.6
tetracene	333–353	0.54
pentacene	333–353	0.60
chrysene	293–303	0.56
rubrene	293–303	0.49
perylene	313–333	0.60
ovalene	333–353	0.46
decacyclene	313–333	0.46
pyrene	288–298	0.68
fluoranthene	288–298	0.76
PTCDA[a]	313–333	0.56
CTCDA[b]	333–353	0.48
CTCA[c]	333–353	0.48
violanthrone	333–353	0.49
BEDT-TTF[d]	293–303	0.59

[a] PTCDA = perylene tetracarboxylic dianhydride. [b] CTCDA = coronene tetracarboxylic dianhydride. [c] CTCA = coronene tetracarboxylic acid. [d] BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene.

FTIR spectra of the silica and silicon supported films, although restricted in the information available using silica, were indistinguishable from the spectra of the parent hydrocarbons, strongly suggesting that no chemical change, for example decomposition or decarboxylation, occurred during evaporation. Well resolved transmission electronic spectra which resembled closely those obtained from solutions, were obtained from silica-supported films derived from tetracene and perylene over a range of thickness *ca.* 30–800 nm. All the bands expected in the 600–200 nm region of the spectra were resolved easily. However there was no evidence for solid-state splittings which might have been expected from previous work,[6,7,11] possibly because spectra were recorded only at room temperature. The situation for ovalene films was similar except that thick films, *ca.* 900 nm, showed some loss of resolution particularly below 300 nm. Of the other *cata*-condensed hydrocarbon films examined, anthracene gave well resolved spectra from films up to *ca.* 100 nm thickness, thick pentacene films gave rather poorly resolved spectra at wavelengths $\leqslant 400$ nm, chrysene spectra were virtually unaffected by increasing the film thickness while the information obtained from rubrene films was limited by interference effects. Similar practical limitations were apparent in the spectra of *peri*-hydrocarbon films. Reasonably resolved bands from violanthrene, decacyclene and fluoranthrene were obtained only from very thin films, thickness $\leqslant$ *ca.* 50 nm. Perylene tetracarboxylic dianhydride produced well resolved spectra at all film thicknesses whereas for coronene tetracarboxylic dianhydride, spectra were satisfactory only for thin films. The situation was similar for coronene tetracarboxylic acid.

Despite their limited nature, the electronic spectra enabled the experimental suitability of a supported film for further study to be assessed, the operational criterion being a comparison with the appropriate solution electronic spectrum.

Chemically modified supported hydrocarbon films

Exposure of films derived from the hydrocarbons listed in Table 1 to either boron trifluoride or phosphorus pentafluoride at room temperature resulted in no observable changes in electronic spectra. In contrast, spectral changes were substantial in many cases on exposure to molybdenum or tungsten hexafluoride vapours or to arsenic pentafluoride under similar conditions. The most detailed studies were undertaken for tetracene, perylene and ovalene silica-supported films since high quality spectra could be obtained readily from a range of films of different thicknesses, *ca.* 50–1000 nm.

Modified tetracene, perylene and ovalene films. Admission of MoF_6 or AsF_5 to tetracene films at room temperature led to immediate colour changes, orange–yellow to blue–green with MoF_6 and to emerald-green in the case of AsF_5. No colour change was observed using WF_6. The electronic spectra of the three modified films, recorded after removal of any unchanged volatile materials by pumping at room temperature, are compared with the unmodified film spectrum in Table 2. In all cases high-energy bands due to tetracene were observed and in the WF_6-treated film there was no evidence for any significant change throughout. In the spectrum of AsF_5-treated tetracene additional weak bands at low energy, $\lambda_{max} > 600$ nm were apparent. The striking features of the spectrum obtained from MoF_6-treated tetracene films were strong bands, λ_{max} 350 and 670 nm, and its general appearance is reminiscent of the spectrum of tetracene in dimethyl sulfate after oxidation with

Table 2 Electronic spectra, λ_{max}/nm (absorption coefficient/cm^{-1}),[a] of supported tetracene films before and after exposure to MoF_6, WF_6 or AsF_5

λ_{max}/nm(α/cm^{-1}) before exposure	λ_{max}/nm(α/cm^{-1}) after exposure to MoF_6	WF_6	AsF_5
206(22.7)	205(sh)		
213(45.9)		215(45.9)	
225(sh)	225(sh)	230(sh)	225(sh)
275(11.6)	280(10.6)	275(11.7)	275(sh)
305(sh)		305(sh)	305(sh)
	338(sh)		
	350(26.8)		
387(4.1)	387(4.7)	385(sh)	385(5.7)
412(sh)	412(5.9)	412(sh)	
438(7.4)		438(7.2)	438(3.8)
	460(4.4)		
472(1.1)	478(sh)	472(11.0)	472(3.4)
503(14.0)		503(13.9)	505(2.5)
525(7.3)		520(13.6)	525(2.4)
	605(sh)		625(0.8)
	670(25.0)		675(1.0)
	725(sh)		
	775(4.1)		765(1.8)
			1010(3.1)

[a] Defined by: absorbance = $10^4\alpha \times$ film thickness(cm); sh = shoulder.

Table 3 Electronic spectra, λ_{max}/nm (absorption coefficient/cm^{-1}),[a] of supported perylene films before and after exposure to MoF_6, WF_6 or AsF_5

λ_{max}/nm(α/cm^{-1}) before exposure	(λ_{max}/nm(α/cm^{-1}) after exposure to MoF_6	WF_6	AsF_5
		225(sh)	
260(13.8)	270(sh)	270(sh)	
330(8.9)	330(sh)		
340(8.4)	360(sh)	358(sh)	365(sh)
435(sh)		407(17.7)	
470(sh)	495(5.6)	479(13.3)	490(4.8)
		505(sh)	
	660(4.4)	623(13.3)	650(4.4)
	1000(3.8)		1230(5.5)

[a] See footnote to Table 2.

SO_3. The latter spectrum has been attributed to a mixture of mono- and di-positive tetracene cations.[17]

Perylene films darkened immediately on exposure to MoF_6, WF_6 or AsF_5 at room temperature, the colour change being most marked with MoF_6 where the sequence golden–yellow→red→crimson→violet→black was observed over 1 h. The electronic spectra obtained after removal of volatile material (Table 3) were all similar and, as in the tetracene–AsF_5 case (Table 2) new bands at low energies were observed, λ_{max} *ca.* 650 and $\geqslant$1000 nm with MoF_6 and AsF_5 and λ_{max} *ca.* 623 nm with WF_6.

The behaviour of supported ovalene films was similar. Blue–green colouration of the orange films was immediately apparent on their exposure to MoF_6 or AsF_5 and although no change in colour was apparent when WF_6 was admitted, the electronic spectra in all cases showed several new bands at $\lambda_{max} > 500$ nm (Table 4).

Table 4 Electronic spectra, λ_{max}/nm (absorption coefficient/cm^{-1}),[a] of supported ovalene films before and after exposure to MoF_6, WF_6 or AsF_5

λ_{max}/nm(α/cm^{-1}) before exposure	λ_{max}/nm(α/cm^{-1}) after exposure to MoF_6	WF_6	AsF_5
225(sh)		235(sh)	
255(sh)	260(sh)		
285(sh)		285(sh)	
	310(6.5)		
350(49.5)	325(sh)	337(sh)	350(sh)
		385(8.3)	385(13.2)
413(sh)	413(6.2)		
438(31.2)			437(11.7)
475(sh)	462(sh)	465(6.9)	465(12.0)
505(30.3)	495(sh)		500(11.7)
	525(sh)		530(10.5)
		550(5.5)	550(10.2)
	620(sh)		
	670(3.9)		
		750(2.6)	750(9.1)
	850(2.9)		
	962(3.6)	1000(0.9)	1000(9.1)

[a] See footnote to Table 2.

Table 5 New, low-energy bands, λ_{max}/nm (absorption coefficient/cm^{-1}),[a] of some *cata*-condensed hydrocarbons after exposure to MoF_6, WF_6 or AsF_5

hydrocarbon	new bands λ_{max}/nm(α/cm^{-1}) after exposure to MoF_6	WF_6	AsF_5
anthracene	920(0.5)[b]	460(2.3)	430(2.5)
pentacene	785(4.9)	—[c]	—[c]
	975(0.8)		
chrysene	455(sh)		433(sh), 480(sh)
	533(sh)	500(1.4)	560(0.7)
	680(1.5)	680(1.1)	
rubrene	615(10.1)	—[c]	—[d]

[a] See footnote to Table 2. [b] Loss of resolution at higher energies. [c] No significant change. [d] Not examined.

Table 6 New, low-energy bands, λ_{max}/nm (absorption coefficient/cm^{-1}),[a] of some *peri*-hydrocarbon derivatives after exposure to MoF_6

hydrocarbon derivative	λ_{max}/nm(α/cm^{-1})
perylene tetracarboxylic dianhydride	620(sh) 770(4.4)
coronene tetracarboxylic dianhydride	500(14.5)
violanthrone[b]	725(6.3) 920(12.4)
decacyclene	770(3.2)

[a] See footnote to Table 2. [b] Exposure to AsF_5 resulted in a new weak band at λ_{max} 690(3.7).

Other modified films. New spectral bands observed after modification of four *cata*-condensed hydrocarbon films and four films derived from *peri*-hydrocarbon derivatives are summarised in Tables 5 and 6. New low-energy bands after MoF_6 treatment were observed in all cases, after AsF_5 treatment in three cases but only for anthracene and chrysene was there any evidence for modification by WF_6. Films derived from bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) developed a blue colouration on exposure to MoF_6 and the spectra of modified films had two prominent new features, λ_{max} = 775 and 895 nm. Fluoranthrene films showed no change in their spectra after MoF_6 treatment and those derived from coronene tetracarboxylic acid (CTCA) lost spectral resolution.

Discussion

The most striking finding from this work is the strong adsorption of molybdenum and tungsten hexafluorides and of arsenic pentafluoride on many of the supported organic films as demonstrated by the appearance of new bands at low energies that may generally be described as being due to charge transfer between the organic molecules and the adsorbed fluorides.

Monocyclic π donors such as benzene or hexafluorobenzene, interact only weakly with high oxidation state halides and in these latter cases isolable complexes are not formed.[2] Apart from the reaction between tetracene and MoF_6, where the spectrum of the modified film (Table 2) provides some evidence for formation of tetracene radical cations,[17] there is no compelling evidence that electron transfer is complete. The presence of multiple charge-transfer transitions in the spectra of many of the modified films is not unexpected and has been reported for numerous solid complexes.[3]

There have been many studies of charge-transfer complexes in which attempts have been made to correlate the energy of the charge-transfer absorption band(s) with intrinsic properties of the donor or acceptor species.[18,19] However the results obtained suggest that in the systems studied here the appearance or otherwise of charge-transfer absorption bands cannot be correlated with any single property of a given molecule. This may reflect the diversity of polycyclic aromatic compounds investigated; differences in chemical behaviour and spectroscopic characteristics between series of structurally related polycyclic aromatic hydrocarbons (PAHs) have been widely reported.[20] Correlations within any given series, for example *cata*-condensed PAHs, are expected and often found.[21] For example, the linear acene series exhibits most clearly the effect of annelation, the three main absorption bands α, *para* and β, (characteristic to all PAHs) are progressively red-shifted with each additional aromatic ring, representing a dilution of the aromaticity; hence anthracene is colourless, tetracene is golden–yellow and pentacene violet–blue. These compounds (D_{2h} symmetry) provide a sample group for which it would be expected that for a series of donor–acceptor complexes, the intermolecular repulsion and relative orientations of donor and acceptor molecules would be similar. However, no simple conclusions can be drawn from a comparison of the lowest energy CT band observed after exposure to MoF_6 with the MO coefficient χ_i[19] or E_i[22] of the donor PAH for the acene series anthracene, tetracene and pentacene.

In principle CT bands might be correlated with the Lewis-acid strengths or oxidizing abilities of the binary fluorides. The former appear not to be relevant, at least using gas-phase F^- affinities as the indicator of Lewis acidity. Thermochemical estimates of gas-phase F^- affinities are in the order $AsF_5 > PF_5 > BF_3$,[23] however gas-phase F^- transfer reactions observed by ICR[24] and F^- ion displacement reactions in MeCN[25] both point to WF_6 being a weaker Lewis acid than BF_3. The existence of the $[MF_7]^-$, M = Mo and W, anions in equilibrium with the hexafluorides MF_6 in MeCN at room temperature, suggests that WF_6 and MoF_6 have comparable F^- ion affinities.[26] It appears therefore that although Lewis acidity may be a necessary criterion, it is not a sufficient criterion for modification of PAH films observed here.

The superior one-electron oxidizing ability of MoF_6 compared with WF_6 is well established both in the gas phase[27] and in solution, anhydrous HF[28] or MeCN,[29] and studies of the behaviour of these and other fluorides with respect to the oxidative intercalation of graphite[30–33] make an interesting comparison with the present work. Bartlett and co-workers have established that a thermodynamic threshold exists for the intercalation of fluoroanions derived from binary fluorides, MF_x.[30] The fluorides MoF_6 and AsF_5 are sufficiently oxidizing for spontaneous intercalation to occur at room temperature,[30–32] the estimated changes in ΔG_{298}^0 for $MoF_6(g) + e^- \rightarrow [MoF_6]^-(g)$ and for $\frac{3}{2}AsF_5(g) + e^- \rightarrow [AsF_6]^-(g) + \frac{1}{2}AsF_3(g)$ being similar. Tungsten hexafluoride and phosphorus pentafluoride are insufficiently strong oxidizing agents to initiate spontaneous intercalation of $[WF_6]^-$ or $[PF_6]^-$,[30] although PF_5 or BF_3 do react with graphite in the presence of HF and with Cl_2 as the oxidizing agent.[32]

In the present work modification of the supported polycyclic hydrocarbon films by MoF_6 has been demonstrated in all cases and by AsF_5 in a substantial number. Adsorption of BF_3 and PF_5 on the films, if it occurs, does not result in any change in electronic properties of the hydrocarbons, while WF_6 occupies an intermediate position. A more detailed consideration requires structural information to be obtained on the precise nature of the surface layer but the importance of the oxidizing ability of the fluoride is clear.

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