Low-Energy Electron-Induced Processes in Fluorinated Copper Phthalocyanine Films Observed by F$^-$ Desorption: Why So Little Damage?[†]

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Received: June 1, 2007; In Final Form: August 14, 2007

As an indication of damage induced by hot electrons in an organic electronic material, the desorption of F$^-$ ions from a thin perfluorinated copper phthalocyanide film on SiO$_2$ under low-energy (0−25 eV) electron impact has been recorded mass spectrometrically. Yields and damage cross sections are very low. No strong features due to negative ion resonances are found in the electron energy dependence of the desorption yield; rather the yield function rises from a threshold at about 5−6 eV continuously (with some weak structure) throughout the measured range. We discuss these findings in terms of the electronic structure of the film, as well as parameters influencing the relevant bond breaking process. We emphasize the strong influence of energy redistribution, which quenches normally long-lived negative ion resonances and selects localized and strongly repulsive excitations, as often observed in electronically induced bond breaking at surfaces. The improved understanding should be helpful in the selection of low-damage materials for organic semiconductor devices and for selection of operation parameters.

I. Introduction

Fluorine-substituted organic materials can be used as active elements in FET (field effect transistor) circuits.[1,2] One such material is perfluorinated copper phthalocyanine, FCuPc ($C_{32}F_{16}N_8Cu$), a quasi square-planar molecule with a Cu atom in the center and C−F bonds at the perimeter. Its utility as an n-channel semiconductor in condensed films is based on high carrier mobility due to strong $\pi-\pi$ overlap of the stacked molecules in the FCuPc layers.[3,4] In model devices, loss of contact near the polymer/metal interface leads to failure after prolonged operation.[2,5,6] In test cases, it is reported that gate voltages of 100 V and bias potentials of ∼100 V between source and drain are often employed.[3−6] This means that in principle electrons can gain energies of several electronvolts before suffering important inelastic losses in the film. Under such conditions, these hot electrons can cause electronic excitations that may lead to degradation of the material. In this low-energy region, below the threshold for dipolar dissociation (DD), the potentially bond-breaking excitations with the highest cross sections usually occur via the formation of negative ion resonances.

One possible way to investigate these destructive excitations is to detect the expulsion of negatively charged ions from the surface under controlled electron irradiation. For materials with high electron affinities, such as perfluorinated aromatic molecules, irradiation by low-energy electrons (<10 eV) can lead to temporary electron capture by the target molecule with very high cross sections. The transient negative ions thus formed can dissociate, resulting in the production of negative ions (F$^-$ and others),[7,8] a process called dissociative electron attachment (DEA). In the present work, we examine the electron-stimulated desorption of F$^-$ ions from thin films of FCuPc, focusing on low electron energies (<15 eV), well below the thresholds expected for F$^+$ formation. The desorption of F$^-$ ions from films of FCuPc is proposed as a useful indicator of electronically induced dissociation processes, which can lead to degradation of the desired electronic coupling between molecules, and thus of the functionality of devices. Also, we hope to clarify the important aspects and parameters of this process in terms of excitations and subsequent processes.

Ion desorption as an indicator of damage is most useful if this damage occurs at or near the surface. There could be destructive processes deep below the surface, in particular at the interface of film and support, which would not lead to desorption. Although in dielectric films electronic excitations originating in the bulk can be transported to the surface, dissociative events following electronic excitations in a condensate are likely to be localized. Also, dissociation events in which neutral fragments are expelled, and after which ions remain trapped, are not detected. So, when fragment desorption occurs there is certainly some damage; but if no desorption is observed, freedom from damage is not assured. On the other hand, because the films appear to be electronically quite uniform throughout their thickness (except for the monolayer in contact with the substrate), the observed desorption events—even if mainly stemming from the surface region—indicate the suspected presence of similar processes occurring inside the films. This will lead to deteriorating performance, even though these events are not observable through desorption. Therefore we believe that our detection method is indicative of processes detrimental to device functionality.

[†] Part of the “Giacinto Scoles Festschrift”.

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10.1021/jp074269h CCC: $37.00

The main experimental results of this investigation are as follows. The yields of F^- and cross sections of bombardment-induced changes are very low compared to expectations from gas-phase values. The threshold electron energy for desorption of F^- ions from FCuPc is ∼5−6 eV, and the yield function (i.e., the electron energy dependence of the ion yield) exhibits an atypical behavior. Strong peaks due to DEA, as observed in the yield functions of fluorocarbons, are not observed; rather the F^- energy dependence exhibits only a slightly structured increase with energy between 5 and 9 eV. Above 9 eV, the yield function increases more rapidly, which is likely due to the onset of dipolar dissociation (DD) through excitations localized on the C−F bonds, possibly overlaying broad resonances involving σ^*(C−F) derived orbitals, partly of many body nature. The low overall damage seen and its behavior with energy is due to the suppression of the high cross section negative ion resonances.

The bulk of the present work is concerned with a detailed analysis of these results, which are taken as representative for a larger class of molecules useful for electronic devices, those containing large aromatic systems. In these, considerable intramolecular and intermolecular energy redistribution appears to affect the desorption yield and to quench excitations that may be observable in isolated molecules and are observable in smaller molecules. The rather high primary excitation energies found suggest that damage in electronic devices can be minimized by using low voltages to suppress electron-induced bond breaking. Also, the strong tendency of energy redistribution in coupled π-electron systems explains the particular suitability of the present and similar systems for such devices.

II. Experimental Procedures

The samples consisted of 10 cm Si wafers with native oxide, which were cleaned by rinsing with acetone, methanol, and finally 2-propanol, and dried by blowing with a N_2 gun. The films of FCuPc were vacuum evaporated at room temperature. The film thickness (2.5 nm) was verified using Rutherford backscattering spectroscopy (RBS). Samples 1 cm × 1 cm were cut from the wafers and transported in air to a vacuum interlock, for insertion in the ultrahigh vacuum measurement system held at a base pressure of 2×10^{-10} Torr. No sample heating or cleaning was attempted. Separate experiments on similar films with XPS showed very good agreement with published *in-situ* XPS of vacuum-deposited films.[9] This suggests that these films are quite inert and clean, so no important contamination is expected; this is corroborated by the low-impurity signals in electron-induced ion desorption (see below). No structural investigations on these samples have been done; although NEXAFS would have been valuable, this would have required synchrotron radiation, which was not available. XRD of similar films indicated that the majority of the molecules were oriented edge-on which suggests that at least a large part of the surface molecules is oriented nonparallel.[10]

The apparatus used to measure electron-stimulated desorption of anions has been described in detail elsewhere.[10,11] Only a brief description of the procedure and experimental arrangement is provided here. Each sample was irradiated at an incident angle of 70° from the surface normal by an electron beam from a commercial electron gun (Kimball Physics Inc.). The gun provides a beam with a spot diameter of 2 mm^2, a current density of 0.5 $\mu A/cm^2$ (i.e., 10 nA in a 2 mm^2 spot) and an energy resolution of 0.4 eV full width at half-maximum. The zero of electron energy was obtained from the onset of the electron transmission curve to the sample.[12] A representative transmission curve is shown in Figure 1, where variations up to 20% were recorded for the current transmitted through the film between 4 and 19 eV. The incident current was constant within 5% for electron energies above 4 eV. Negative ions desorbed from the surface were collected by an ion lens and detected by a quadrupole mass spectrometer (Extrel 150-QC). The lens is covered by a grounded shield held at the same potential as the sample. However, the first element of the lens is held at +10 V with respect to the sample and thus provides a draw-in potential for anions. Considering the effective collection angle from this potential and the detection efficiency of the quadrupole for F^-, we roughly estimate that about 30% of the desorbed F^- ions are measured in our experiments. In the latter, F^- was the dominant species; the H^-, and Cl^- impurity ion signals were lower in intensity by more than a factor 50, as seen from the mass spectrum of Figure 2. This suggests that the samples were quite clean, with only traces of contamination. Measurements of ion yields vs electron energy were made by sweeping the beam energy while monitoring the ion signal.

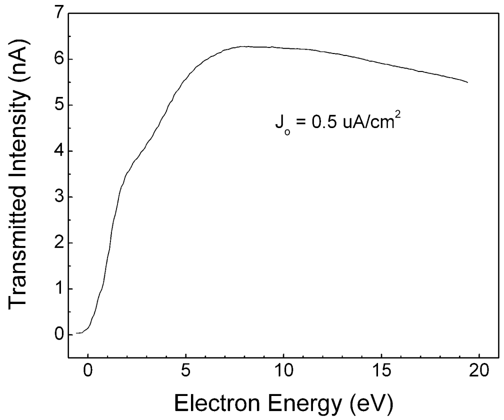

Figure 1. Current to sample as a function of incident electron energy.

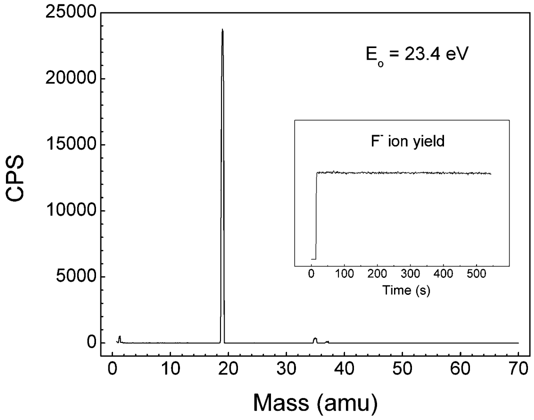

Figure 2. Electron-stimulated desorption (ESD) of negative ions from a FCuPc film. Inset: stability of the F^- signal as a function of time of electron irradiation.

III. Experimental Observations

The maxima of the observed F^- yields were about 10^6/(s cm^2); this value corresponds to about 10^{-7} ions/electron, which approximates to a desorption probability of 3×10^{-7} ions/electron. The F^- yield was roughly stable with time at 23 eV and 0.5 $\mu A/cm^2$ (corresponding to $\sim 3 \times 10^{12}$ electron/(s cm^2) or ∼0.1 electron/s per surface molecule) over times necessary for experiments. The change of about 2% in 500 s shown in the inset of Figure 2 corresponds to a cross section of about 10^{-17} cm^{-2} for the electron-induced change in the layer

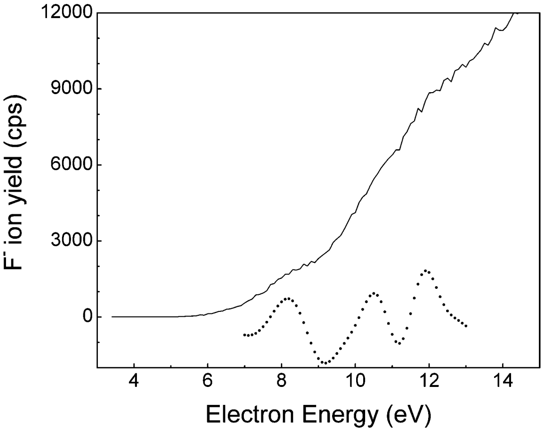

Figure 3. Solid curve: F$^-$ ESD signal from a FCuPc film as function of electron energy. Dotted curve: Negative second energy derivative of the F$^-$ yield emphasizing structure of the yield curve.

connected with F$^-$ desorption. This cross section represents a lower limit for electron damage because the product resulting from degradation can also emit F$^-$. If this decrease scales with electron energy as the anion desorption, then the cross section at 10 eV is about 10^{-18} cm^2. Compared to DEA of fluorocarbons at lower energies in the gas phase, these cross sections are lower by at least 2 orders of magnitude.

The main result concerns the electron energy dependence of the F$^-$ yield, which is displayed in Figure 3. The threshold of F$^-$ desorption lies around 5−6 eV, depending on the way extrapolation is done. A gradual, slightly structured rise, without clear indication of resonances, follows up to 25 eV where the measurements were terminated. The negative second energy derivative of the yield function has peaks at 8.2, 10.5, and 11.9 eV. The curve is displayed at the bottom of Figure 3. Even if these peaks can be interpreted as resonances, they are very broad and/or are covered by a superimposed gradual increase. For the yield of a negative ion, this is a quite unusual behavior.

IV. Discussion

i. Negative Ion Formation. The resonant formation of atomic or molecular anions at the surface or in the bulk of physisorbed molecular layers[7,12,13] is initiated, as in the gas phase,[14] by the capture of a low-energy electron into a transient anion state (i.e., a resonance) of an adsorbate molecule, e.g., $e^- + ABC \rightarrow ABC^{(*)-}$, where the transient anion $ABC^{(*)-}$ can be formed by temporary electron attachment into a shape resonance (one-electron, 1e, state) or a core-excited resonance (one-hole two-electron, 1h 2e, state). This process may occur whenever a low-energy electron ($E < 20$ eV), created near a surface as a photoelectron or secondary electron or incident from a vacuum source, impinges onto a condensed molecular solid. The ground- or excited-state $ABC^{(*)-}$ may decay via (a) electron autodetachment to a molecular ground or excited state, (b) dissociation into an anion and ground- or excited-state neutral fragments, or (c) stabilization of the molecular anion. Process c may in practice only occur if the internal excitation energy of the intermediate $ABC^{(*)-}$ can be transferred to the solid. Fragmentation also occurs if in process (a) a dissociative electronic state is produced. Depending on the energy of the electronic state, the fragments can be either neutral (e.g., A + BC) or charged (e.g., $A^- + BC^+$). The latter process is termed resonant DD.[15] The only other channel, which can lead to molecular damage, is nonresonant DD of an ABC* state into positive and negative fragments, e.g., $A^- + BC^+$. Of course, for stable negative ion fragments to be formed, at least one of the fragments must have a positive electron affinity.

For isolated fluorine-containing hydrocarbons there are clear low-energy resonances corresponding to DEA. The frequently observed negative ion at vanishing electron energy is due to a shape resonance for electrons captured into the LUMO. With increasing electron energy, F$^-$ as well as larger fragments are found. For F$^-$ ion production, resonance peaks found mostly in the range 4−10 eV dominate the spectra.[7] These peaks were interpreted as due to shape resonances as well as core-induced resonances of considerable lifetime; their energy content is sufficient to break the C−F bond, albeit possibly after energy redistribution. For instance, for C_6F_6, the simplest perfluorinated aromatic, which is a building block of FPc molecules, the F$^-$ yield for the isolated molecule shows peaks at electron energies of ∼4.5, and 9−11 eV, and then becomes very small at higher energies.[16] Electron capture into the LUMO of π*-type near 0 eV leads to a transient negative ion state with energy below the anion−neutral fragment dissociation limit, which therefore cannot dissociate. The 4.5 eV resonance (which also yields $C_6F_5^-$ fragments) is explained by electron capture into the second unoccupied MO, also of π*-type, or by a core-induced resonance (1h 2e state) involving a hole in the π HOMO and two electrons in the π* LUMO and possibly another UMO. We note that the σ*(C−F) orbital of C_6F_6 condensed on gold has been determined at 3 eV above the Fermi level,[17] so that this orbital could well participate. The higher resonances are ascribed to core-induced resonances; they certainly contain some C−F antibonding nature. Above 15 eV the intensity vanishes. In general, above approximately 12−15 eV there is seldom strong anion intensity for isolated molecules, which means that, compared to the (resonant) cross sections of DEA, those for (nonresonant) DD are small for molecules. For clustered and condensed species the initial transient negative ion cannot leave the surface because polarization leads to an increased binding energy in addition to the ground-state condensation energy. Similarly, large fragment desorption is mostly quenched, because high-mass fragments cannot escape the induced polarization potential; in addition, their share of acceleration is small compared to a small fragment. In other words, conservation of energy and momentum in molecular dissociation have the effect that the low-mass fragments have higher kinetic energy and are more likely to escape the surface than the slowly moving higher mass fragments, which are more efficiently trapped by the polarization potential. Nevertheless, in the F$^-$ yield function strong resonances frequently appear, which are usually separated from intensity increases above ∼12−15 eV (examples include F$^-$ from $CFCl_3$, C_2F_4, and C_6F_5Cl (ref 7, pp 58−61).

Again looking at C_6F_6, its condensate (here on a xenon or krypton spacer layer) shows an F$^-$ yield curve in which the 4.5 eV resonance is almost invisible[18] but exhibits a broad structured peak starting at ∼5 eV and a maximum at ∼11 eV; above this energy the yield intensity declines.[7] Bigger anionic fragments, which exist for the isolated molecule, disappear for the condensate; indeed, in essentially all *condensed* fluorinated aromatics (as well as in Freon-type molecules) no larger negative ionic fragments are observed to leave the surface at any electron energies. Though the threshold for DD is expected around 10−12 eV, the similarity of the 8−10 eV peaks for the isolated and the condensed species suggest that their origin is mainly DEA via core-induced resonances. These are usually assumed to be a $\pi \rightarrow \pi^*$ transition with 2 electrons in the LUMO as the strongest excitations. So the π*-type resonance at 4.5 eV can lead to F$^-$ production only after some energy redistribution within the molecule to produce some σ^*(C−F) character, i.e., to localize the excitation on the C−F bond. This would require that the resonance concerned is rather long-lived. In the condensate, however, rapid delocalization of the excitation energy and/or the additional electron should occur and make this reshuffling, which can lead to F^- desorption, improbable. Complex excitations such as core-induced resonances (1h 2e excitations) are more strongly localized by correlation and should therefore have longer lifetimes than shape resonances. Furthermore, they usually possess a larger gradient of the potential energy curve in the Franck−Condon region (i.e., are more repulsive). Both these properties increase the success rate for fragmentation. These interacting effects are well-known for bond breaking in adsorbates and condensates at higher energies (above the ionization or multiple ionization limit) by excitonic and ionic excitations (see, e.g., refs 19−21). There the general rule has been derived that complexity and repulsiveness of excitations conspire to make bond breaking more successful under circumstances of competing delocalization.

We now apply this general knowledge to our case. For CuPc and FCuPc films there is agreement that at most the first monolayer of molecules on a conducting support shows stronger binding; thicker condensed layers interact only weakly by Van der Waals forces and $\pi-\pi$ overlap. Therefore it appears justified to approach the problem mainly from a molecular viewpoint, albeit taking the mentioned condensation influences into account. As no data on electron-induced fragmentation of isolated Pc molecules exist, we cannot make a similar comparison as was possible for C_6F_6.

The discussion above has explained two of the main characteristics of our findings, the absence of any anion production at very low energies (0−5 eV), and the rather high threshold. It has not explained why the energy dependence of the yield curve is so different from other condensed fluoroaromatics, such as C_6F_6: the relatively low ion intensity in the range of negative ion resonances (below 10 eV) and the high increases above that range, continuing to 25 eV (and likely above). The most similar case is F^- desorption from condensed C_2F_4,[16] also a π-system.

One possible explanation could be that the observed behavior is not due to any specific excitations but to the action of secondary electrons in a condensed layer. The low-energy part of these secondaries could again be attached to produce transient negative ions, or—if they have sufficient energy—could produce DD or ionic excitations. However, the secondaries involved would have to possess energies above 6 eV to become effective. Secondary yields are known to be low below 30 eV, and to contain their main weight at very low energies.[22] Although the secondary yield of our sample has not been measured, it appears extremely unlikely that the yield of such secondaries would rise sufficiently within the relevant span to produce the observed behavior. We therefore exclude this as an explanation for the range up to about 15 eV. Secondaries might contribute to the continuing rise above that energy and explain why in general the negative ion yield from condensates does not drop drastically above the resonance region.

It makes sense, then, to discuss the possible excitations responsible for the (structured) increase in the range 6−15 eV, and the absence of resonances. The overall cross sections observed here are small on the scale of negative ion resonances. So, though these resonances will still exist, their contributions to F^- production must be strongly quenched; already for C_6F_6 the lowest resonance is quenched by condensation. We are now concerned with a molecule with a much larger and correlated π-electron system. We therefore suggest that for a Pc-like system already *intra*molecular delocalization of excitations can lead to strong quenching of fragmentation for all nondirect dissociation paths. *Inter*molecular delocalization, coming into play as the effect of the condensates, might even not be necessary for the observed quenching of fragmentation induced by such transient negative ions. Here fragmentation can only be successful for excitations that lead to bond breaking in the first pass, i.e., impulsively. Consequently, the relevant excitation itself must have a strong component on the C−F bond, and be very repulsive; then a long lifetime is not necessary. It is interesting to ask whether more can be concluded about the orbitals and transitions involved under such conditions.

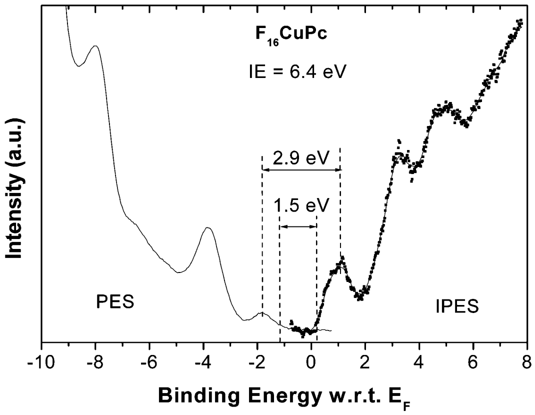

Figure 4. Spectral features of a film of FCuPc on Au in the ranges of occupied electronic states (photoemission spectroscopy, PES) and the empty states (inverse photoemission spectroscopy, IPES) (courtesy of A. Kahn, unpublished data[23]).

ii. Electronic Structure of FCuPc: Filled and Empty Orbitals. A few spectroscopic papers exist on the filled and empty levels of FCuPc. As an example we show in Figure 4 data from photoemission (UPS; filled states) and inverse photoemission (IPE; empty states).[23] Other work has reported data from UPS and XPS[24−26] and from XES.[27] Although there is some variation of the derived level energies with thickness and preparation of the films, a set of energy values (relative to E_F) can be derived for occupied states (at −1.3/−1.8/−3.7/−6.2/−7.6 to −8 eV) and for unoccupied states (at 0.2/1.1/3.5/5.0/>8). We note that the corresponding data for CuPc[28,29] and for other metal−Pcs such as ZnPc[4] are not very different.[30]

For further conclusions we need information on the nature of these orbitals. Although most authors who have been working on this have been mainly concerned with the mobility gap, i.e., with HOMO1 and LUMO1, some theoretical analyses of the full range exist, in particular for CuPc and other metal Pc's.[27,31−33] The comparison of Liao and Scheiner[31] is particularly helpful in pinpointing the metal participation in the various orbitals. These calculations clearly show that the HOMO in CuPc is Cu-dominated and the "ring-derived" HOMO lies below it; Cu participation extends into the valence band. Though there is strong metal character in the LUMO for early transition metal Pc's, for CuPc the LUMOs 1+2 are found to be π-type ring orbitals. Carniato et al.[32] state that the HOMO is a Cu−N hybrid and the LUMO is a π-type ring orbital with little Cu character.

The only work that directly addresses FCuPc orbital assignments is that of Kurmaev et al.[27] From the combination of XES data and calculations, the authors arrive at the conclusion that the main σ(C−F) character should be in the OMOs at 8−10 eV below E_F. This agrees with the conclusion of ref 26, which compares UPS data of CuPc and FCuPc and concludes that although most peaks essentially stay rigid with respect to each other (the observed shift relative to E_F is mainly due to the change of interface dipole moment[30]), the peak at about −8 eV shifting against the others should be due to σ(C−F). Their observation agrees with the general expectation from the well-known perfluoro effect, which for aromatic molecules states that upon substitution of all H atoms by F the σ-levels are stabilized relative to the π-levels and the latter stay rigid;[34] for a discussion related to C_6F_6, see ref 35. Calculations of Liao et al.[36] on the effects of fluorination for the case of FePc show a rigid shift by about 1.5 eV to higher binding energy of all examined orbitals, which may suggest that the σ-orbitals supposed to become stabilized lie below their range of calculation (from E_V to −8 eV relative to E_V[30]).

So, unfortunately, the cited papers do not give a clear answer about the energetic position of the σ*(C−F) level. An interesting argument about its location derives from a paper on X-ray absorption (NEXAFS) in the F1s excitation range, monitored by F^+ ion desorption.[37] From the high F^+ desorption in the lowest energy F1s NEXAFS peak it was concluded that this peak corresponds to the F1s → σ*(C−F) transition (the results have recently been corroborated by ion-Auger electron coincidence measurements[38]). This means that the LUMO of the F-*core ionized* system is the σ*(C−F). Although the core hole introduced in the F atom will pull down the empty states in energy relative to the ground state, this still suggests that even in the latter the σ*(C−F) level cannot be too high in energy.

iii. Correlation of Electronic Structure with F^- Yield. If we scrutinize these results for possible excitations that could lead directly to a strongly repulsive state localized on the C−F bond, there are several candidates. The weakness of resonant structure in the yield suggests that we should not concentrate on negatively charged states. The strongest dissociative effect would occur for a neutral excitation from a σ(C−F) to a σ*(C−F) orbital followed by DD because this would introduce a hole into the bonding and an electron into the antibonding state localized on C−F. The corresponding high repulsiveness would lead to the required direct dissociation, and the negative charge on the F fragment would be due to its high electronegativity. Because any energy above threshold can go into the fragments and the scattered electron, the excitation need not be resonant and would result in a monotonically increasing yield with increasing energy, as observed experimentally. The large positive fragment would stay on the surface and disperse its energy (a small share as a consequence of momentum conservation) and charge in the layer. Pure energetics show that desorption from DD is possible for electron energies greater than about 10 eV (we recall that a σ(C−F)-type filled orbital appears to lie around −8 eV below E_F), whereas core resonances may lie above 5 eV (see Appendix).

The discussion above has not given a clear answer as to where a σ*(C−F)-like empty orbital would lie in the ground state—it could be the 3.5 or the 5 eV peak of Figure 4. This would lead to an energetic distance between the two orbitals of at least 12 eV. However, due to the hole−electron interaction, the transition energy is smaller than this energy difference. Actually, this Coulomb interaction should not be too much larger for the core electron excitation[36] than for this valence excitation because the latter is also localized on the same atoms as the receiving orbital. For the σ*-orbital to become the LUMO in the F1s-ionized system[38] the Coulomb stabilization has to be at least 4 eV; so the proposed σ → σ* transition should then have a threshold around 10 eV. This is well compatible with the main increase in the F^- yield seen in Figure 3. The signal below 10 eV can be ascribed to decay of a resonance at ∼8 eV into the DEA channel, which overlaps with the onset of DD. Energetically, this resonance could correspond to the $\pi \rightarrow (\pi^*)^2$ resonance mentioned above. However, this excitation does not possess the required localization on the C−F bond and therefore is expected to be ineffective for F^- production even if its lifetime against delocalization is increased by correlation. It is more likely that there exists also a 1h 2e excitation in this range, which involves a π−p* excitation coupled to electron capture into the σ*(C−F) orbital. Similar excitations may play a role in the threshold range below that.

So we propose that the observed unusual F^- yield curve is due to fast intra- as well as intermolecular energy redistribution in this condensed layer of a strongly coupled π-ring system, which has the effect that only excitations directly localized on the C−F bonds and being highly repulsive for these bonds are successful in fragment production, because they can lead to impulsive dissociation. The excitations with the highest cross sections, the π* as well as the $\pi \rightarrow (\pi^*)^2$ resonances, do not appear in the F^- yield function. Therefore, our observations can be understood in terms of the superposition of one (or several) core-induced resonance with some σ* character and the onset of DD through σ → σ* excitations localized on the C−F bonds. This competition of delocalization and localization and the additional influence of high repulsive nature to select the successful excitations is well-known from the body of work on electronically induced fragmentation of adsorbates at higher energies.[20,21]

Above 10 eV, the oscillatory structures in the F^- yield function may arise from two possible sources superimposed on a direct DD background. The latter may be due to an increase with electron energy of the number of electronically excited states that dissociate via DD. The structures may arise from DEA via transient anions formed at higher energies with a small cross section. However, above the threshold for DD, DEA is not the only process that can produce peaks in anion yield functions. As explained in the beginning of this section, transient anions decaying via autoionization can leave the molecular target in dissociative electronic excited states. Such states can dissociate via DD if the process is energetically possible. There could also be a contribution from secondary electrons leading to excitations at lower energies.

In conclusion, we note that the high stability of FCuPc in devices derives from the discussed rapid intra- and intermolecular energy redistribution after electronic excitation. This leads to efficient quenching of most of the strongest excitations. The remaining processes leading to potential damage most likely involve loss of F from the ring periphery. The resulting asymmetric molecules are certainly not planar any more, and the energy injected into the layer will enhance disorder and reduce π−π overlap between molecules. This phenomenon will lead to deterioration of device functionality.

We have derived these conclusions from the observation of F^- desorption. This must be accompanied by the formation of neutral radicals and positive ions; at higher electron energies dissociative ionization contributes to the formation of these species. The main practical conclusion for stability of electronic devices that utilize FCuPc is to try and limit as much as possible the energy of electrons that could arise from acceleration in regions of high-voltage drops. If these can be limited to voltages below 5 V, then film stability could be considerably improved. Because the processes showing up by F^- desorption should occur throughout the film, albeit without being observable by anion desorption, and because in the range up to 10−15 eV the described mechanisms should be dominant, our probe can be considered as an adequate indicator of destructive processes in high electric field devices.

V. Summary

We have used the desorption of F^- ions from FCuPc films under low-energy electron irradiation to monitor damaging processes and access their nature. The main experimental result is related to electron resonances, or rather their absence. Generally, these dominate the F^- yield functions from F-containing molecules, but with FCuPc films the yield function is low and exhibits essentially a continuous rise from a threshold around 5−6 eV. The main conclusion is that the negative ion resonances normally dominating fragmentation of fluorinated hydrocarbons at electron energies up to 15 eV are inefficient in these films due to fast energy redistribution, in the big correlated π-system of the molecule and in addition among the coupled molecules. Their contribution to the production of negative fragment ions is lowered by several orders of magnitude. Therefore, most of the fragmentation occurs by direct impulsive dissociation via strongly repulsive excitations localized on the C−F bond. Below 10 eV, contributions to the F^- yield arise from core-excited negative ion resonances involving σ^*(C−F) participation, and at higher energies dipolar dissociation via $\sigma \rightarrow \sigma^*$(C−F) excitations is the main contribution to the F^- yield.

We believe that the results of our detailed analysis of this test case have led to improved understanding of the processes relevant for radiation damage in molecular electronics materials. Materials with large coupled π-systems will be particularly suitable for low-damage devices due to their ability of efficient redistribution of excitation energy for all but the most localized excitations leading to direct, impulsive dissociation. To further improve device stability, measures should be taken to minimize the energy to which electrons are accelerated in electronic devices due to high local fields. Inhomogeneities, which have a tendency to increase the magnitude of local electric fields should therefore be reduced to a minimum. Generally, devices constructed from systems highly capable of energy redistribution, both intra- and intermolecularly, should be considerably more stable toward the destructive action of low-energy electrons.

Acknowledgment. We are grateful to Dr. Zhenan Bao for providing the FCuPc samples, and to Prof. A. Kahn for supplying Figure 4. D.M. acknowledges the hospitality of Rutgers University, during an extended visit when this project was initiated. This work was supported in part by the National Science Foundation, Grant No. CHE-0315209, the Fonds der Chemischen Industrie (DM) and the Canadian Institutes of Health Research.

Appendix

The thermodynamic minimum excitation energies, E_{exc}(min), for the various dissociation channels can be estimated at least roughly from known energy contributions. Because we aim at an estimate, the fact that the individual values are not known very accurately is not important.

E_{exc} is the excitation energy put into the molecule by the incoming electron; its scale must be connected to the energy of the incoming electron. Because our electron energy scale has been calibrated by the sample current, we can equate its zero to that of the measured electron energy. For the minimum excitation energy, the amounts of kinetic and internal energies of the fragments are set to zero, so also no need to consider the partitioning of excess energy over the fragments (generally governed by momentum conservation) arises. However, the final state attractive interactions between the separating fragments have to be taken into account.

Dissociative Electron Attachment (DEA). For the minimum energy E_{exc}(min) for DEA of F^- from F_{16}CuPc, i.e., for the reaction

$$e^- + F_{16}\mathrm{CuPc} \rightarrow (F_{16}\mathrm{CuPc})^{*-} \rightarrow F_{15}\mathrm{CuPc} + F^-$$

we have

$$E_{exc}(\mathrm{min}) = E(\mathrm{C-F}) + E(\mathrm{pol}) - \mathrm{EA(F)}$$

Here E(C−F), the energy necessary to break the bond of one F to the remaining F_{15}CuPc fragment, and E(pol), the attractive polarization energy between the two fragments (or between the F^- and the film), have to be expended, and EA(F), the electron affinity of F, is gained.

A web search for the values of E(C−F) yields an estimate of about 4.8 eV;[39] EA(F) is about 3.4 eV.[40] With an estimate of E(pol) of 0.5−1 eV we arrive at a minimum energy of 2−2.5 eV. Our measured threshold value is considerably higher, which corroborates our conclusion gained independently by the discussion of the likely mechanism: that the lowest anionic excitation with enough energy does not lead to DEA in our case.

Dipolar Dissociation (DD). For the minimum excitation energy for DD of F^- from F_{16}CuPc, i.e., for the reaction

$$e^- + F_{16}\mathrm{CuPc} \rightarrow F_{15}\mathrm{CuPc}^+ + F^- + e^-$$

we estimate

$$E_{exc}(\mathrm{min}) = \mathrm{IP}(F_{15}\mathrm{CuPc}) + E(\mathrm{C-F}) + E(\mathrm{attr}) - \mathrm{EA(F)}$$

Here, IP is the ionization potential of the F_{15}CuPc fragment, and E(attr) is the energy required to separate the negative F^- from the positive fragment ion (F_{15}CuPc), or from the film. In view of the large size of F_{15}CuPc, we assume that its ionization potential is about equal to that of the parent molecule (IP(F_{16}CuPc) ~ 6.1−6.3 eV[23]). The C−F bond energy (now for F_{15}CuPc) is assumed to be the same as for F_{16}CuPc, i.e., 4.8 eV; the electron affinity of F is about 3.4 eV (see above). The two ions attract each other; however, the interaction is not modeled well by a simple Coulomb interaction because the positive charge is spread over the molecular ion or even the film, for the lowest excitation. The attraction then scales roughly like that of an ion with its image charge on a metal surface, i.e., $\sim 1/r^2$. Separating the F^- from the layer, starting at the C−F bond distance of about 0.14 nm, to infinity needs about 2 eV.

The estimate then results in an absolute threshold of about 9.5 eV. Because it is unlikely that the lowest possible final state carries much weight, the actual threshold should be somewhat higher. This agrees well with our interpretations.

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