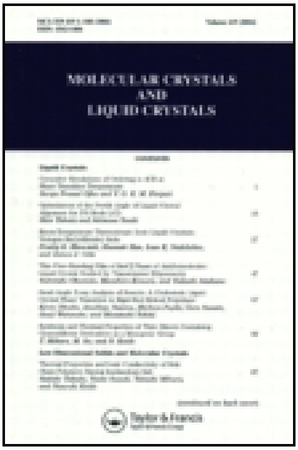

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Frontier Electronic Structures in Fluorinated Copper Phthalocyanine Thin Films Studied Using Ultraviolet and Inverse Photoemission Spectroscopies

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Ultraviolet photoemission and inverse photoemission spectroscopy was used to compare the electronic structure of copper phthalocyanine, copper octafluorophthalocyanine, and copper hexadecafluorophthalocyanine thin films. A rigid shift to lower energy was observed for both the occupied and unoccupied electronic states as the number of fluorine atoms around the phthalocyanine ring increased. The spectral features of the fluorine-substituted derivatives were otherwise very similar to copper phthalocyanine, and no change in the transport gap energy was observed. Vacuum level shifts were observed at the interface with polycrystalline gold substrates of sufficient magnitude to consistently pin the substrate Fermi level near the middle of the HOMO-LUMO gap. The calculated barrier heights for electron and hole injection across the interface were therefore equal, and no correlation with fluorine substitution was found.

Keywords: charge transport; CuPc; electron affinity; fluorination; ionization energy; IPES

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I. INTRODUCTION

Copper hexadecafluorophthalocyanine, Cu(F_{16}Pc), is one of the few organic semiconductors to combine usefully high electron transport with chemical stability in the presence of air [1]. Copper phthalocyanine (CuPc) is, in contrast, a hole transporting semiconductor noted for its chemical stability and ease of processing [2]. Cu(F_{16}Pc) and CuPc can, respectively, be used to make n-channel and p-channel FETs, building blocks for complementary logic circuits. Used together in a bilayer FET configuration, ambipolar behavior has recently been demonstrated [3].

In organic semiconductors two conditions must be met for effective charge transport: a low energy barrier to charge injection at the interface, and good orbital overlap in the bulk material [4]. Electron transport occurs through the LUMO-derived level, while hole transport occurs through the HOMO-derived level. The positions of both the occupied and unoccupied states must be known if charge injection barriers in CuPc and Cu(F_{16}Pc) are to be compared.

In this work we present the energies of the LUMO-derived and other unoccupied states of CuPc, copper octafluorophthalocyanine [Cu(F_8Pc)] and Cu(F_{16}Pc) (see molecular structures in Fig. 1), measured with inverse photoemission spectroscopy (IPES). The energies of the HOMO-derived and other valence levels were determined with ultraviolet photoemission spectroscopy (UPS). This combination of spectroscopic techniques provides us with a complete picture how frontier energy levels on either side of the transport energy gap change as a function of fluorine substitution.

Previous work on the same materials under comparable conditions include UPS data for CuPc and Cu(F_{16}Pc) [5], UPS-IPES data for CuPc [6], and IPES data for CuPc and similar transition metal phthalocyanines [7]. Although no spectroscopic data was presented, Cu(F_8Pc) has been reported before in the context of organic p-n devices [8].

II. EXPERIMENTAL

CuPc and Cu(F_{16}Pc) were purchased from Aldrich. Cu(F_8Pc) was synthesized in this work. All materials were purified by vacuum sublimation. Thin films were prepared by vacuum-deposition on polycrystalline gold substrates. Deposition rates, in the order of 0.5 nm min^{-1} and film thicknesses were measured with a quartz crystal microbalance. Both the gold substrates and organic films were prepared under UHV conditions. All measurements were made at room temperature.

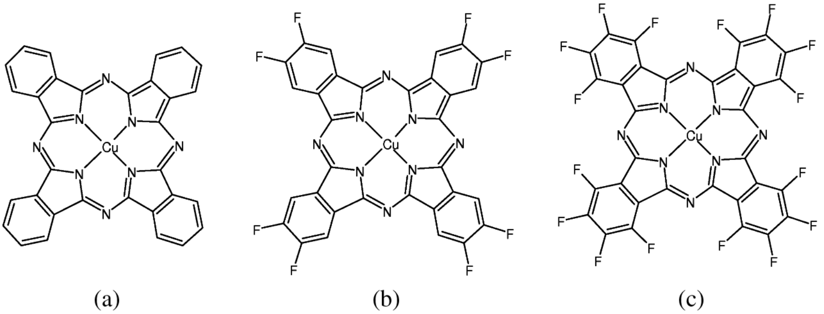


FIGURE 1 Molecular structure of (a) copper phthalocyanine, (b) copper octafluorophthalocyanine, and (c) copper hexadecafluorophthalocyanine.

The primary components of the UPS instrument are a commercial analyzer (SPECS Phoibos 150) operated in the constant analyzer energy (CAE) mode and an unmonochromatized He discharge lamp. Spectra were measured with the HeI line at 21.2 eV. The energy resolution was 150 meV, as judged from the Fermi edge of the gold substrate. A bias of –8 V was applied to the sample in order to clearly observe the secondary electron cutoff used to estimate the position of the vacuum level.

The IPES instrument with a bandpass photon detector is of our own design, described previously [9]. The energy resolution is approximately 0.6 eV, with an asymmetry that adds a distinct low-energy shoulder to spectral features. The spectra were acquired by scanning the retarding bias voltage applied to the sample while applying a constant bias of –20 V to the cathode of the electron source. Differentiating the current flowing through the target around the initial onset revealed a Maxwell-Boltzmann distribution of electron energies, the maximum position of which enabled us to determine the vacuum level of the sample. The position of the Fermi level was meanwhile calibrated from the leading edge of the IPES spectra of the gold substrates, as was the case for the UPS experiments.

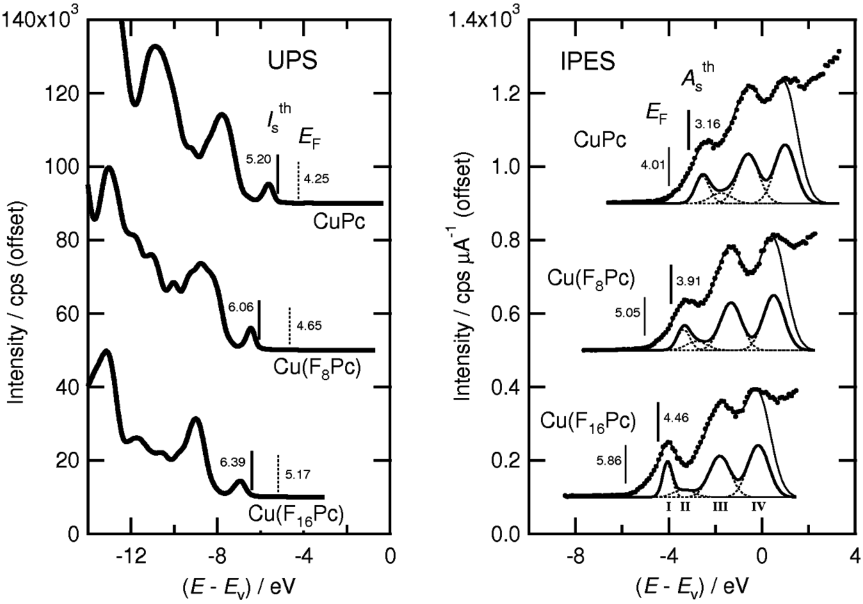
UPS and IPES experiments were performed in separate UHV chambers, with new samples prepared *in situ* for each experiment. The UPS chamber had a background pressure of 1×10^{-6} Pa with a maximum of 6×10^{-5} Pa during sample preparation. The comparable figures for the IPES instrument were 4×10^{-8} Pa and 6×10^{-6} Pa.

The (solid-state) threshold ionization energy of the phthalocyanine films, I_s^{th}, was calculated from the baseline intercept extrapolated from the half-maximum of the UPS HOMO-derived peak leading edge. The threshold electron affinity, A_s^{th}, was determined from the leading edge of the IPES LUMO-derived feature in a similar manner. Here, the LUMO feature used was the Gaussian component resulting from a peak fitting procedure where the trial lineshape was convolved with the instrument resolution before comparing with the experimental.

III. RESULTS AND DISCUSSION

A. Occupied and Unoccupied Electronic Structure

The UPS spectra for 8 nm-thick films of CuPc, Cu(F_8Pc) and Cu(F_{16}Pc) on polycrystalline gold are shown in Figure 2(a). The three spectra have very similar features. Fluorine substitution does not drastically alter the distribution of molecular orbitals, and the largest differences are mostly in lower energy states that are not likely to contribute to charge transport. Threshold ionization energies, I_s^{th}, are 5.2 eV, 6.1 eV and 6.4 eV, increasing with fluorine substitution.



(a) (b)

FIGURE 2 (a) UPS and (b) IPES spectra of copper phthalocyanine (CuPc), copper octafluorophthalocyanine [Cu(F_8Pc)] and copper hexadecafluorophthalocyanine [Cu(F_{16}Pc)] thin films on gold substrates. The average film thickness is 8 nm and the measurements were made at room temperature. The energy scale is plotted against the vacuum level of the organic film.

The IPES spectra are shown in Figure 2(b). Qualitatively, again, the spectral features are very similar. Threshold electron affinities, A_s^{th}, are 3.2 eV, 3.9 eV and 4.5 eV, increasing with fluorine substitution. The transport gap energy, $E_g = I_s^{th} - A_s^{th}$, is 2.0 ± 0.1 eV for all three films. As shown schematically in Figure 3, the net effect of fluorine substitution is a rigid shift of both the occupied and unoccupied states. Compared to CuPc, the states in Cu(F_8Pc) are on average 0.8 eV lower, while for Cu(F_8Pc) the shift increases to 1.3 eV on average.

The detailed curve fitting of the CuPc IPES data reveals four distinct peaks in the measured energy range. Peak II, a weak signal next to the LUMO, was not resolved in earlier studies. The whole number ratio of the four peak areas was estimated at 2:1:5:6. Based on the previous work of Rocco *et al.* [10], we have assigned the new peak II to a single b_{1g} state, derived primarily from the $3d_{x^2-y^2}$ orbital of the central Cu atom. Peak assignments are given in Table 1. The remaining features (peaks I, III and IV) originate from the molecular orbitals of the macrocyclic phthalocyanine ring. The uniquely metallic character of peak II can be confirmed by re-examining the IPES data for free base phthalocyanine (H_2Pc) and CuPc [7]: Peaks I, III and IV are common between the two spectra, with the same relative position and area ratio, whereas signal intensity corresponding to peak II is not found in the H_2Pc spectrum.

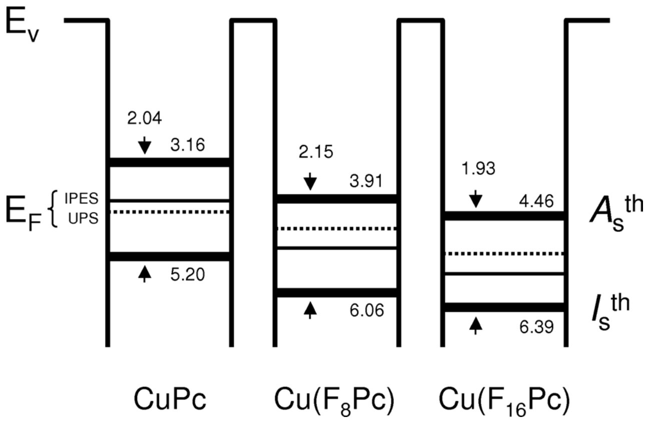


FIGURE 3 Schematic diagram of the energy levels. While the threshold ionization energy (I_s^{th}) and electron affinity (A_s^{th}) shift to lower energy with increasing fluorine substitution, the transport gap energy (E_g) remains constant. The Fermi level of the substrate (E_F) is pinned near the middle of the gap in each of the three films. All values are in eV.

TABLE 1 IPES Peak Assignment

Peak	Symmetry assignment for CuPc (after ref. [10])	Peak position/eV		
		CuPc	Cu(F_8Pc)	Cu(F_{16}Pc)
I	e_g	–2.56	–3.37	–4.06
II	b_{1g}	–1.76	–2.80	–3.36
III	$b_{1u}/b_{2u}/e_g/a_{2u}$	–0.59	–1.33	–1.81
IV	$a_{1u}/e_g\ldots$	0.99	0.50	–0.16

B. Vacuum Level Shifts and the Charge Injection Barrier Heights

For a metal electrode and a semiconducting organic film, the energy barrier to charge injection for holes can be defined as $B_h = I_s^{th} - \phi_m - \Delta$, while for electrons the equivalent expression is $B_e = \phi_m - A_s^{th} + \Delta$. ϕ_m is the work function of the bare metal measured prior to depositing the organic layer, while Δ is the magnitude of the vacuum level shift at the interface [11]. As shown in Figure 3, the substrate Fermi energies referenced to the vacuum level of the organic film, $E_F = \phi_m + \Delta$, do not exactly coincide for the UPS and IPES. The measurements were taken for different samples, with slightly different work functions. Unlike the bulk properties, A_s^{th} and I_s^{th}, the vacuum level shifts are sensitive to the specific conditions of the interface hence a certain amount of scatter is to be expected.

Charge injection barrier heights for each compound calculated taking the average of the IPES and UPS derived Fermi energies are shown in Table 2, together with the related energy level data. The general trend is clear: charge injection barriers for both hole and electron injection into CuPc, Cu(F_8Pc) and Cu(F_{16}Pc) remain essentially constant throughout, with the substrate Fermi level pinned to the center of the phthalocyanine transport gap in each case.

Figure 4 shows the progression of the vacuum level with respect to the substrate Fermi level as a function of film thickness. These results

TABLE 2 Energy Level Data (eV)

Compound	I_s^{th}	A_s^{th}	E_F	E_g	B_h	B_e
CuPc	5.20	3.16	4.13	2.04	1.07	0.97
Cu(F_8Pc)	6.06	3.91	4.85	2.15	1.21	0.94
Cu(F_{16}Pc)	6.39	4.46	5.52	1.93	0.88	1.06

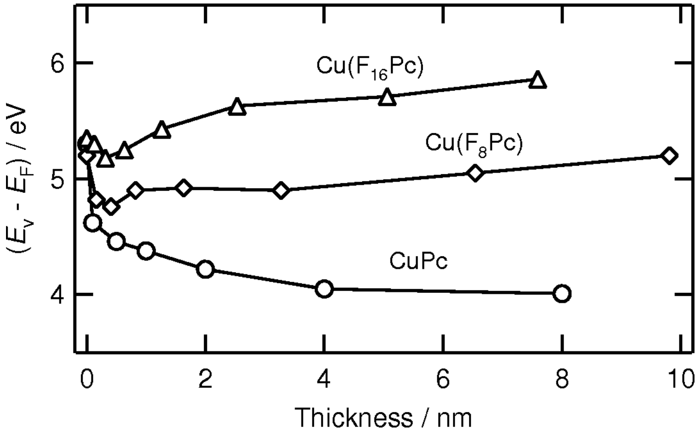


FIGURE 4 The position of the vacuum level relative to the substrate Fermi level of the gold substrate as a function of film thickness, calculated from IPES data. The vacuum level shift is positive for Cu(F_8Pc) and Cu(F_{16}Pc), indicating that both these materials are electron accepting.

are obtained on the basis of the IPES data. It can be seen that the vacuum level shifts for CuPc, Cu(F_8Pc) and Cu(F_{16}Pc) are clearly differentiated by fluorine content. The large negative shift (–1.3 eV) observed for CuPc is indicative of a strong surface dipole, most likely as the result of a charge transfer reaction with the CuPc acting as an electron donor. The vacuum levels of Cu(F_8Pc) and Cu(F_{16}Pc) exhibit positive shifts, indicating that they are electron accepting with Cu(F_{16}Pc) being the stronger electron acceptor of the two.

IV. CONCLUSION

Increasing the number of fluorine atoms in the phthalocyanine ring does not drastically alter the structure of either the occupied or unoccupied energy levels. It does, however, induce a rigid shift of those levels to lower energy. The ionization energy and the electron affinity of Cu(F_8Pc) increase by 0.8 eV, while for Cu(F_{16}Pc) the increase was 1.3 eV on average compared to CuPc. As the HOMO- and LUMO-derived states experienced an equal increase, the transport gap energy remained constant, at 2.0 ± 0.1 eV. At the gold-phthalocyanine interface, a negative vacuum level shift was observed for CuPc, while positive shifts were seen for Cu(F_8Pc) and Cu(F_{16}Pc). For all three films, however, the vacuum level shift tended to position the Fermi level of the gold substrate near the midpoint of the phthalocyanine

HOMO-LUMO gap. The barriers for electron and hole injection were therefore equal, and constant, for CuPc, Cu(F_8Pc), and Cu(F_{16}Pc).

These charge injection barrier heights are at odds with the complementary hole and electron transport behavior of CuPc and Cu(F_{16}Pc) in organic semiconductor devices. It is possible that charge transport in these materials may be limited not by the injection properties but rather the differences in spatial overlap of the frontier orbitals in the bulk film. No spectral evidence for this was detected, however. It is also possible that the surface dipole responsible for the observed vacuum level shift may not remain intact as the interface is subjected to an external electric field. If that were the case, charge injection in the device under operational conditions would change in favor of electron injection in the fluorinated phthalocyanine compounds.

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