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David Wisbey
University of Nebraska-Lincoln

Ning Wu
University of Nebraska-Lincoln

Yaroslav B. Losovyj
Louisiana State University at Baton Rouge, ylozovyy@indiana.edu

Ihor Ketsman
University of Nebraska-Lincoln, iketsman2@unlnotes.unl.edu

A. N. Caruso
University of Missouri - Kansas City, carusoan@umkc.edu

See next page for additional authors

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Authors

David Wisbey, Ning Wu, Yaroslav B. Losovyj, Ihor Ketsman, A. N. Caruso, Danqin Feng, John Belot, Elio Vescovo, and Peter A. Dowben

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David Wisbey [a], Ning Wu [a], Yaroslav Losovyj [b], Ihor Ketsman [a], A.N. Caruso [c], Danqin Feng [a], John Belot [d], Elio Vescovo [e], Peter A. Dowben [a,*]

[a] Department of Physics and Astronomy and the Nebraska Center for Materials and Nanoscience, 116 Brace Lab, University of Nebraska-Lincoln, Lincoln, NE 68588-0111, USA
[b] The J. Bennett Johnston Sr. Center for Advanced Microstructures and Devices, 6980 Jefferson Highway, Baton Rouge, LA 70806, USA
[c] Department of Physics, 257 Flarsheim Hall, University of Missouri - Kansas City, 5110 Rockhill Road, Kansas City KS 64110, USA
[d] Department of Chemistry and the Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE 68588-0304, USA
[e] Brookhaven National Laboratory, National Synchrotron Light Source, Upton, NY, 11973, USA

ABSTRACT

The effects of vacuum ultraviolet radiation on the adsorbed copper center molecule bis(4-cyano-2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) (or Cu(CNdpm)$_2$), (C$_{24}$H$_{36}$N$_2$O$_4$Cu, Cu(II)) was studied by photoemission spectroscopy. Changes in the ultraviolet photoemission spectra (UPS) of Cu(CNdpm)$_2$, adsorbed on Co(1 1 1), indicate that the ultraviolet radiation leads to decomposition of Cu(CNdpm)$_2$ and this decomposition is initially dominated by loss of peripheral hydrogen.

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1. Introduction

Metal organic molecules are very promising because it is possible to customize their electronic properties by changing metal centers or functional groups. Modification of a layer of large organometallic and metal-organic molecules, by way of radiation exposure, is not only very possible, but common also. For example, the decomposition of a number of metallocenes, as a result of ultraviolet radiation has been investigated including nickelocene [1], cobaltocene [2] and ferrocene [3,4]. Photochemical decomposition of cobalt phthalocyanine (CoPc) [5] and tris-(8-hydroxy quinoline aluminum (Alq$_3$) [6] has also been investigated, among many other species.

Such photodecomposition can lead to some valuable modifications of the molecular adlayer. In the case of monomolecular insulator [1,1′;4′,1″-terphenyl]-4,4″-dimethanethiol films, irradiation-induced modifications lead to cross-linking of the terphenyldimethanethiol molecules within the film, which results in a quasi-polymeric material with improved dielectric properties [7–10]. While irradiation-induced modifications tend to lead to decomposition and desorption processes in aliphatic organic adlayers, cross-linking is the dominant effect in the aromatic ones, resulting in a quasi-polymerization of the monomolecular film [11–13]. Such polymer-like but ordered layers provide the possibility of using the organic self assembled monolayers as ultrathin insulating layers in electronic and spintronic devices [7–13].

Here, we investigate the irradiation-induced modification of adsorbed copper metal center molecule bis(4-cyano-2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) (or Cu(CNdpm)$_2$). This is a copper metal center molecule, schematically illustrated in the inset to Fig. 1, where N1' and N2'' represent the nitrogen atoms from the nearest neighbors. Like the metal
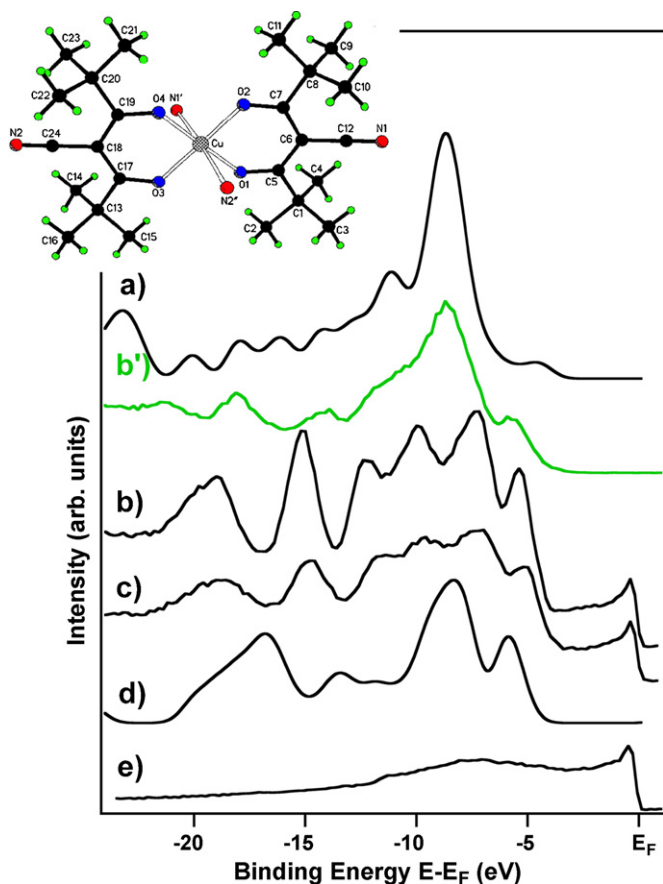
Fig. 1. The experimental photoemission spectra of adsorbed Cu(CNdpm)$_2$, and the changes resulting from irradiation-induced modifications. Spectrum (a) shows a model density of states for the occupied molecular orbitals of Cu(CNdpm)$_2$, with all the hydrogen atoms attached. Spectra (b and b′) are of the pristine molecular thin films of Cu(CNdpm)$_2$ on Co(1 1 1) at 100 K or less, prior to any photo-degradation. The spectrum (b), taken at a photon energy of 49 eV, tends to emphasize the ligand contributions while (b′), taken at 79 eV photon energy (of a 50 molecular monolayer thick film) tends to emphasize the molecular orbitals with copper weight. Decomposition of Cu(CNdpm)$_2$ is evident in photoemission after exposure to roughly 1.2×10^{17} photons/cm^2 of about 50 eV photon energy (c), while (e) is after roughly an additional 10^{18} photons/cm^2 of about 50 eV photon energy. For comparison, a model density of states for the occupied molecular orbitals of Cu(CNdpm)$_2$, with all the peripheral hydrogen atoms removed is illustrated in (d). Spectra (b, c, and e) were taken at 49 eV photon energy and at a substrate temperature of 40 K. The inset shows the single-crystal structure of Cu(CNdpm)$_2$ adapted from reference [14,19].

phthalocyanines, Cu(CNdpm)$_2$ has large ligands surrounding a metal core. Ultraviolet radiation enhanced decomposition of CoPc may possibly be a means for fabrication of nanostructured metal oxide films [5], and this might apply to Cu(CNdpm)$_2$ as well. The photodecomposition of Cu(CNdpm)$_2$, on the other hand, if restricted to the loss of peripheral hydrogens, could be used for enhancing the cross linking in the molecular film and fabrication of a copper atom containing polymer, without copper atom clustering.

2. Experimental

Synthesis of bis(4-cyano-2,2,6,6-tetramethyl-3,5-heptanedionato)copper(II) (or Cu(CNdpm)$_2$), (C$_{24}$H$_{36}$N$_2$O$_4$Cu, Cu(II)) was described previously [14]. Cu(CNdpm)$_2$ was adsorbed molecularly, from the vapor, onto the surface of epitaxial Co(1 1 1). The Cu(CNdpm)$_2$ molecules were deposited on Co(1 1 1) at about 40 K, diminishing the possibility of any thermal degradation.

The epitaxial Co(1 1 1) substrate films were grown prior to each experiment on Cu(1 1 1) single crystals, to a cobalt thickness of 20 Å or about 7 monolayers (ML), as described in prior work [15,16]. The clean Cu(1 1 1) surfaces were prepared by repeated cycles of Ar + ion sputtering and annealing of a Cu single crystal, prior to Co deposition.

Ultraviolet photoemission spectra (ARPES) of the adsorbed molecular layers on Co(1 1 1) were acquired at the U5UA undulator spherical grating monochromator (SGM) beamline at the National Synchrotron Light Source (NSLS) [17,18], as described elsewhere [15]. The ultrahigh vacuum photoemission end-station at the SGM beamline was equipped with a hemispherical electron energy analyzer (EA125, Omicron GmbH) [17,18]. The analyzer had a ±2° angular resolution while the combined energy resolution of the analyzer and the light source was approximately 150 meV or less. The photoemission spectra were taken at a 45° light incidence angle, with the photoelectrons collected normal to the surface.

The irradiation-induced decomposition was the result of continual exposure to light from the undulator beam line at photon energies in the region of 49 eV, similar to the studies of nickelocene decomposition, as described in [1], carried out with vacuum ultraviolet radiation at 50 eV.

3. Irradiation and photo-degradation of adsorbed Cu(CNdpm)$_2$ on Co(1 1 1)

Cu(CNdpm)$_2$ is close to being a copper spin 1/2 system [19] and adsorbs molecularly with a strong preferential molecular orientation [15]. As demonstrated in previous work [15,19], Cu(CNdpm)$_2$ adsorbed onto the surface of Co(1 1 1) provides photoemission spectra very similar to adsorption on Cu(1 1 1), in spite of expected differences in substrate reactivity. For the thicker molecular films (50 molecular layers), the photoemission spectra taken at higher photon energies of 79 eV (Fig. 1b′) closely resemble expectation (Fig. 1a), obtained from semiempirical NDO-PM3 (neglect of differential diatomic overlap, parametric model number 3) model calculations based on Hartree–Fock formalism [20]. Although PM3 is a simplistic semiempirical calculation it is preferable here to density functional theory (DFT), which is notorious for underestimating the band gap sometimes by a factor 2 or more [21], particularly for molecular systems. DFT must be rescaled for comparison with experiment [22], particularly with final state spectroscopies like photoemission and inverse photoemission. To compare the model calculations with experiment (Fig. 1), we applied Gaussian envelopes of 1.2 eV width to each calculated molecular orbital energy (Eigen value) to account for the solid state broadening in photoemission and then summed. The orbital energies for this model density of states calculations has been rigidly shifted in energy by 4.4 eV and then compared to the photoemission data.

As described in [15], the spectrum taken at a photon energy of 49 eV (Fig. 1b) tends to emphasize the ligand contributions, while that in Fig. 1b′, taken at 79 eV photon energy, tends to emphasize the molecular orbitals with copper weight. It is the latter that shows the better agreement with expectation.

To study possible ligand fragmentation as a result of irradiation, a sequence of photoemission spectra was taken with a photon energy of 49 eV. Fig. 2 illustrates the gradual change in the photoemission spectra of 7 molecular monolayers films of Cu(CNdpm)$_2$ deposited on Co(1 1 1), after exposure to radiation for increasing amounts of time, up to an exposure of roughly 10^{17} photons/cm^2 of about 50 eV photon energy. The peak closest to the Fermi energy level in all the spectra in Fig. 2 originates from the Co 3d bands of the underlying Co(1 1 1) substrate. All the spectra were aligned with the substrate Fermi level.
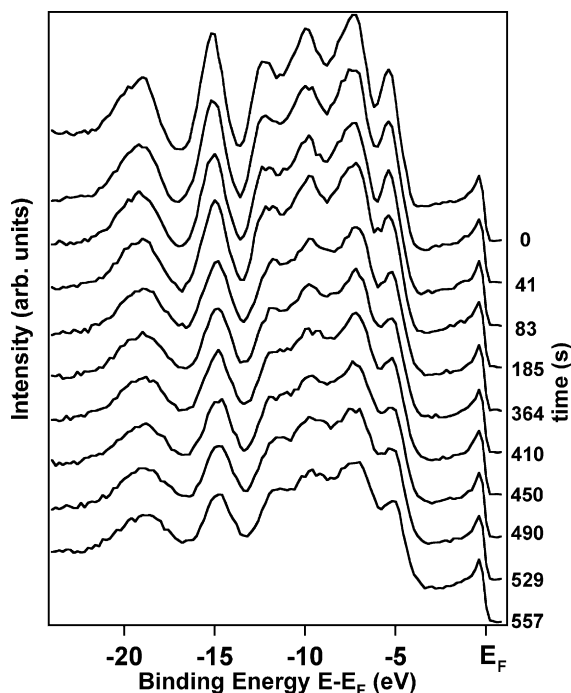
Fig. 2. The photoemission spectra of Cu(CNdpm)$_2$ deposited on Co(1 1 1) at about 40 K, as a function of increasing exposure to radiation. The spectra were taken at a photon energy of 49 eV. The numbers on the right indicate exposure time to radiation at the beginning of each spectrum, with the last spectrum corresponding to an exposure of roughly 10^{17} photons/cm^2. All spectra were taken using Cu(CNdpm)$_2$ molecular thin films 7 ML thick on Co(1 1 1) at substrate temperatures of ∼40 K.

The photoemission spectra (Fig. 2) do not provide indications of ligand decomposition occurring with photo-irradiation in the vacuum ultraviolet. The first three peaks attributable to the Cu(CNdpm)$_2$, in the photoemission spectra of Fig. 2, occur at binding energies of 5 eV and greater. After about 500–600 s of exposure to low intensity UV radiation corresponding to exposure of roughly 10^{17} photons/cm^2 or less, the main peaks between 5 eV and 12 eV binding energy, Fig. 1(c), are much less distinct when compared with the pristine film (Fig. 1(b)). This is summarized in Fig. 3, where a significant increase in the full width, at half maximum, of the photoemission features attributable to molecular Cu(CNdpm)$_2$ deposited on Co(1 1 1) is indicated. This significant increase in photoemission peak width is less profound for the feature resulting from the highest lying occupied molecular orbitals, and in fact is not observed for that feature (feature 'A' in Fig. 3). The feature derived from the highest lying occupied molecular orbitals exhibits a dramatic decrease in intensity above 500 s of exposure to synchrotron radiation at a photon energy of about 50 eV. In fact, as indicated in Fig. 4, there is a shift of intensity from the highest lying occupied molecular orbitals (feature 'A', as labeled in the inset to Fig. 3) to high binding energies features (feature 'B', as labeled in the inset to Fig. 3). Thus the photoemission feature resulting from the highest lying occupied molecular orbitals, differs from the other Cu(CNdpm)$_2$ molecular orbital derived photoemission features.

After exposure to low intensity UV radiation corresponding to exposure of roughly 10^{17} photons/cm^2, the main photoemission features, attributable to the Cu(CNdpm)$_2$ molecular orbitals, are still present (Fig. 2). The small decreases in the binding energies of some of the molecular orbital derived photoemission features, leading to shifts towards the Fermi level, are consistent with changes caused by loss of hydrogen atoms. With modest amounts

of UV radiation (roughly 10^{17} photons/cm^2) these photoemission features of molecular origin decrease in binding energy, shifting by about 0.2 ± 0.1 eV towards the Fermi level, and become much less distinct. Also, the photoemission peak at 15 eV binding energy, nearly solely of ligand origin, is seen to shift by around 0.4 ± 0.1 eV towards the Fermi level. The photoemission peak around 18 eV does not shift in energy position with exposure to very modest radiation (Fig. 2).

While ligand fragmentation probably does not occur until exposure to low intensity UV radiation corresponding to exposure of roughly 10^{17} photons/cm^2 (at about 50 eV photon energy), hydrogen loss may occur with very little radiation exposure as indicated by the loss in peak intensities, in Fig. 4. Intensity loss in the photoemission features due to the Cu(CNdpm)$_2$ molecular orbitals at less than 50 s exposure is accompanied by an enhancement of the substrate Co 3d bands nearest to the Fermi level. These changes in the spectra could well be the result of simple photo-induced desorption. Generally, except possibly at the very initial exposures to radiation, since enhancement of the substrate Co 3d bands nearest to the Fermi level, with radiation exposure, is not apparent in Fig. 2, the irradiation modification is not a result of significant molecular desorption, as may be the case with similar experiments of nickelocene adsorbed on Ag(1 0 0) [1].

Okudaira et al. [23] also observed small shifts towards the Fermi level with irradiation-induced decomposition of poly(methyl methacrylate), and as in the case of adsorbed [1,1';4',1''-terphenyl]-4,4''-dimethanethiol films [7–10], some dehydrogenation is implicated. These binding energy shifts of the photoemission features could indicate a formation of a smaller band gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. This would be consistent with a loss of H atoms [10,24,25]. In practice, inverse photoemission studies
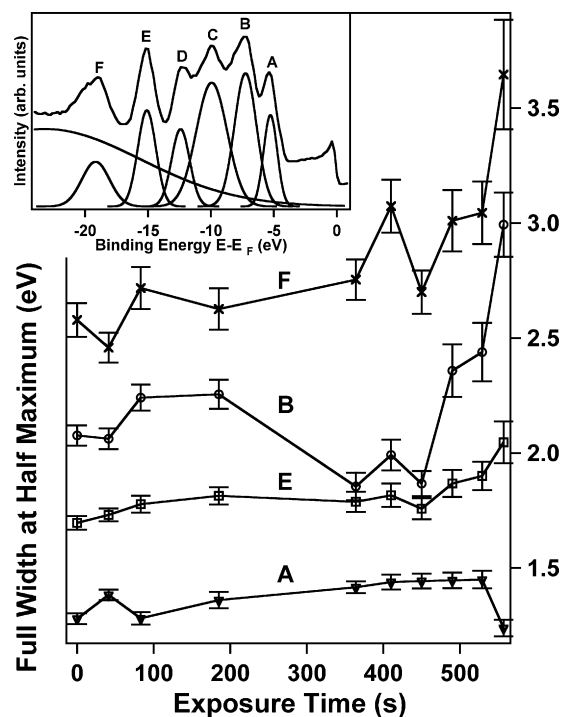
Fig. 3. The full width at half maximum of select photoemission features attributable to the molecular Cu(CNdpm)$_2$, as a function of increasing exposure to radiation. The data were obtained from spectra taken at a photon energy of 49 eV, as in Fig. 2. The assignment of the various curves follows the assignment of the features for molecular Cu(CNdpm)$_2$, as indicated in the spectrum in the inset at the upper left. Data here are for Cu(CNdpm)$_2$ molecular thin films 7 ML thick on Co(1 1 1) at substrate temperatures of ∼40 K.
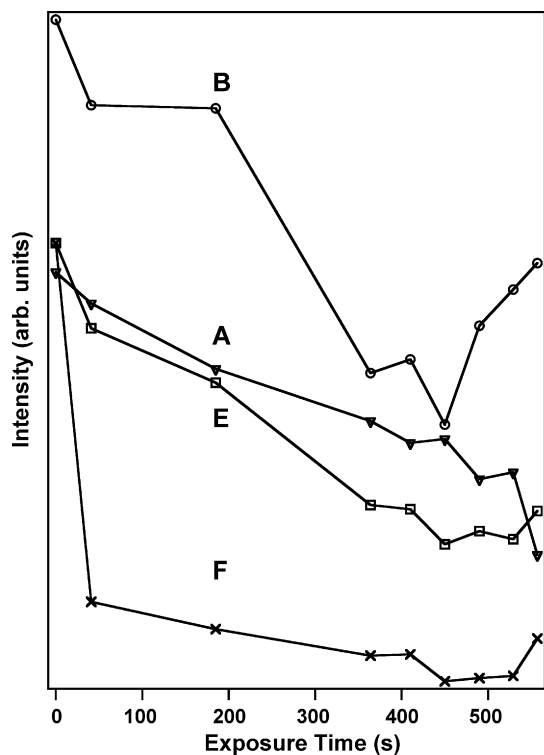
Fig. 4. The integral peak intensities for select photoemission features attributable to the molecular $Cu(CNdpm)_2$, as a function of increasing exposure to radiation. The data were obtained from spectra taken at a photon energy of 49 eV, as in Fig. 2. The assignment of the various curves follows the assignment of the features for molecular $Cu(CNdpm)_2$, as indicated in the spectrum in the inset at the upper left to Fig. 3. Data here are for $Cu(CNdpm)_2$ molecular thin films 7 ML thick on Co(1 1 1) at substrate temperatures of ~40 K.

Fig. 5. The Cu $2p_{1/2}$ and $2p_{3/2}$ X-ray photoelectron spectra for $Cu(CNdpm)_2$ following deposition (a), and irradiation (b). The decomposition of $Cu(CNdpm)_2$, due to irradiation leads to a species with greater binding energy (b). All binding energies are referenced to the Fermi level.

would be necessary to determine if the HOMO–LUMO gap decreased.

To support the contention that initially dehydrogenation dominates irradiation-induced fragmentation, a number of model calculations were undertaken. Fig. 1(a) shows the $Cu(CNdpm)_2$ molecular orbital density of states with all the hydrogen atoms attached. While our model calculations do not take into account the change in the photoemission cross sections with photon energy, nor any matrix element effects, the shifts in binding energies seen in photoemission resemble the changes expected for dehydrogenation (Fig. 1d).

While the decomposition and desorption processes prevail in aliphatic self-assembled monolayers, Caruso et al. [24] pointed out that for the *closo*-carborane, the main photoemission features are preserved with exposure to synchrotron white light. As is the case here, this indicates that a heterogeneous mixture of carbon species is not formed. Rather, the structure of the molecule is preserved while decomposition is dominated by the loss of hydrogen [26,27]. The absence of shifts in the photoemission feature at around 18 eV, while the ligand derived molecular orbital features do shift towards smaller binding energies, with exposure to radiation, also supports the postulate that initial irradiation leads to hydrogen loss for $Cu(CNdpm)_2$ deposited on Co(1 1 1) at about 40 K. While irradiation-induced fragmentation of the ligand -C-C- backbone cannot be excluded by either the data or model calculations, and remains quite likely, this does not appear to be the dominant fragmentation process with initial irradiation.

As with the case of adsorbed [1,1′;4′,1″-terphenyl]-4,4″-dimethanethiol films [7–10], and other molecular adlayers, extensive irradiation leads to fragmentation beyond simple
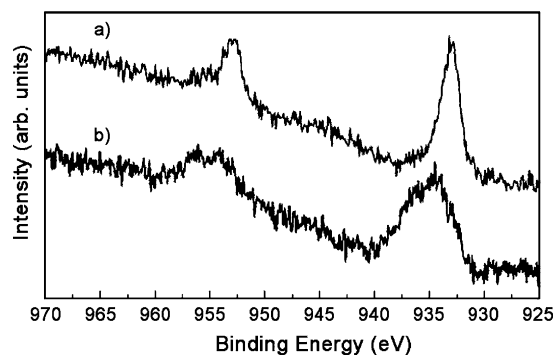
dehydrogenation of peripheral hydrogens. As seen in Fig. 1d, high irradiation levels lead to the loss of all of the molecular orbital features, and as noted elsewhere [19], to a large shift in the core level binding energies. The XPS Cu 2p photoemission for adsorbed $Cu(CNdpm)_2$ is shown in Fig. 5. The Cu $2p_{3/2}$ binding energy for $Cu(CNdpm)_2$ (932.8 ± 0.2 eV), is a slightly higher binding energy than for copper metal (932.3–932.5 eV [28–30] for the Cu $2p_{3/2}$) but less than the value expected for copper in CuO (933.4 eV [28] to 933.6 eV [29] to 933.7 eV [30–32]). Thus our values for the Cu $2p_{3/2}$ binding energy for $Cu(CNdpm)_2$ (932.8 ± 0.2 eV) are somewhat smaller than expected, even compared to a similar copper compartmental complex 6,11-dimethyl-7, 10 diazahexadeca-5, 11-diene-2,4,13,15-tetraene [Cu(H$_2$daaen)] (934.1 eV [33]), which should have a similar (or even smaller) charge transfer from the Cu metal center. By way of comparison, we find that the Cu $2p_{3/2}$ core level binding energies for $Cu(CNdpm)_2$ exhibit increase to 935 eV or more after molecular decomposition initiated by either photon or electron irradiation. The greater binding energies are more in line with values indicative of a copper oxide insulator, with a weakly screened final state.

4. Summary

In conclusion, we have shown that $Cu(CNdpm)_2$ is affected by radiation. With ultraviolet radiation, the initial decomposition appears to lead to the loss of peripheral hydrogen from the molecule, but with much of the molecular backbone preserved. As seen in the photoemission spectra of adsorbed $Cu(CNdpm)_2$, irradiation leads to binding energy shifts of the occupied molecular orbitals towards the Fermi level. If cross-linking of this or similar species could be demonstrated, then a route to the formation of a widely dispersed copper metallized polymer may be possible. For large amounts of radiation, in the region of 10^{18} photons/cm^2, the loss of the features associated with adsorbed $Cu(CNdpm)_2$ is evident. With such extreme photodecomposition it is hard to see how the decomposition of $Cu(CNdpm)_2$ will differ substantively from photochemical decomposition of cobalt phthalocyanine (CoPc) reported previously [5].

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