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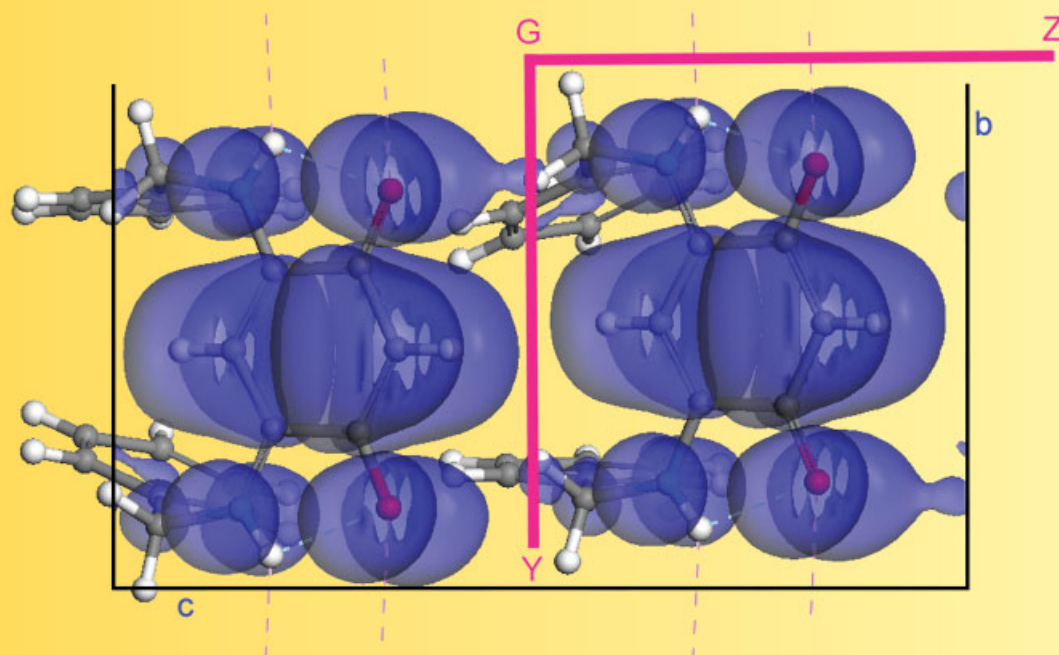University of Strasbourg
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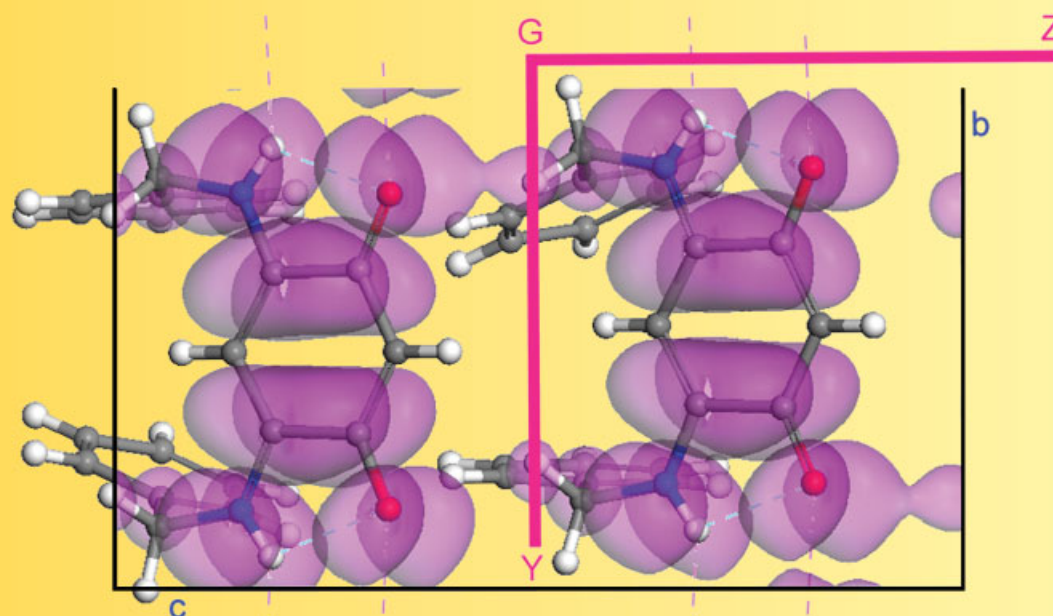SEE PROFILE

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Approaching an organic semimetal:
Electron pockets at the Fermi level for a *p*-benzoquinonemonoimine zwitterion

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Approaching an organic semimetal: Electron pockets at the Fermi level for a *p*-benzoquinonemonoimine zwitterion

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There is compelling evidence of electron pockets, at the Fermi level, in the band structure for an organic zwitterion molecule of the *p*-benzoquinonemonoimine type. The electronic structure of the zwitterion molecular film has a definite, although small, density of states evident at the Fermi level as well as a nonzero inner potential and thus is very different from a true insulator. In spite of a small Brillouin zone, significant band width is observed in the intermolecular band dispersion. The results demonstrate that Bloch's theorem applies to the wave vector dependence of the electronic band structure formed from the molecular orbitals of adjacent molecules in a molecular thin film of a *p*-benzoquinonemonoimine type zwitterion.
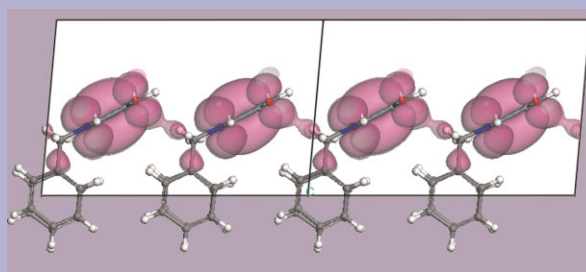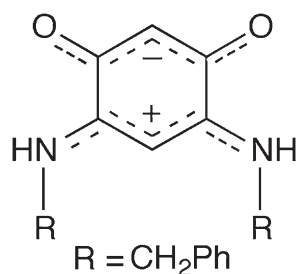
1 Introduction Most organic materials are insulators or semiconductors and few explicitly exhibit a density of states at the Fermi level. Stable charge neutral organic molecules do not usually behave as metals because the interatomic hybridization causes the conduction and valence bands to be completely unfilled and filled, respectively. This is to say that for most stable completely organic systems, the chemical potential resides well within the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) gap. There are exceptions, notably the tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) system [1, 2], and since 1973, over 400 organic conductors have been synthesized of which about 50 are superconducting, like the Bechgaard salts. Yet a single component organic conductor remains a Holy Grail of organic chemistry.

One of the general issues in molecular conductors is the hybridization of molecular orbitals to form a well-defined band structure; an issue studied for nearly three decades [3–5]. Molecular orbital band structure is fairly well established experimentally and theoretically. With larger molecular species, an intramolecular band structure is far more likely and commonly observed [3, 6–10]. Intramolecular band dispersion has been documented in self-assembled monolayers [3, 9, 10, 11, 12], including polyphenyl species [10, 11]. In contrast, because of the very small effective Brillouin zone (requiring exceptionally good wave vector resolution) and the generally much smaller intermolecular interactions, experimental evidence of band structure resulting from intermolecular interactions is seldom observed for ordered assemblies of large molecules (larger than ethylene, benzene, and CO), with only a few exceptions [3, 9, 10, 11, 12]. Measuring an intermolecular band structure relevant to the conduction properties thus continues to remain a technical challenge for larger molecular species. In spite of the wide acceptance of band structure for molecular systems, when it comes to organic conductors, even for TTF–TCNQ [13–17], and related compounds [18], and for Bechgaard salts [16, 19], the density of states directly observed at the Fermi level is quite low.

Recently, we reported fabrication and characterization of well-packed ultra-thin films made of dipolar molecules [20, 21]. Large dipole molecules tend to be good dielectrics, but obviously molecular packing and orientation can enhance or suppress the dielectric properties. Quinonoid zwitterions of the type A in Fig. 1, electrically neutral as a whole, carrying positive and negative charges on different parts of the molecule, remain a single component system. Their positive charge is delocalized between the nitrogen groups over four bonds involving the 6π electrons, while the negative charge is spread likewise between the oxygen atoms involving 6π electrons [22–24]. In these potentially antiaromatic molecules, the two 6π electron systems are connected by carbon–carbon single bonds but remain electronically isolated. The result is a large electric dipole that is formed across the C_6-plane of the benzoquinonemonoimine "core," which makes these zwitterionic compounds fascinating candidates for the study of their electronic structure. These molecules have not only a very strong local dipole, but the π system of the zwitterion "core" loses aromatic character due

to the large charge separation. The crystalline packing of these molecules often involves rather short distances between the "cores," suggesting that they represent an original system with possible $\pi{-}\pi$ stacking involving non-aromatic cycles. In this paper we report on the experimental and calculated band structure that reveal a significant density of molecular states at the Fermi level, related to the occurrence of electron pockets in thin films of (6Z)-4-(benzylamino)-6-(benzyliminio)-3-oxocyclohexa-1,4-dien-1-olate, a member of this family of benzoquinonemonoimine zwitterions (Fig. 1, with R = CH$_2$–C$_6$H$_5$).

2 Experimental The zwitterion (6Z)-4-(benzylamino)-6-(benzyliminio)-3-oxocyclohexa-1,4-dien-1-olate, of formula C$_6$H$_2$($\cdots$NH–CH$_2$–C$_6$H$_5$)$_2$($\cdots$O)$_2$, was synthesized according to established procedures [22–25]. The zwitterions were deposited from a CH$_2$Cl$_2$ solution on freshly deposited gold substrate, with Au(111) texture growth, 500 nm thick over 50 nm WTi on Si(111). The 4–5 nm thick zwitterion samples were dried under nitrogen flow and kept under nitrogen atmosphere.

Combined ultraviolet photoemission (UPS) and inverse photoemission (IPES) spectra were taken in a single ultrahigh vacuum chamber to study the placement of both occupied and unoccupied molecular orbitals of the zwitterions, as has been done elsewhere for other p-benzoquinone-monoimine zwitterion molecular films [20, 21]. The IPES were obtained by using variable kinetic energy incident energy electrons while detecting the emitted photons at fixed energy (9.7 eV) using a Geiger–Müller detector. The IPES was limited by an instrumental line width of approximately 400 meV, as described elsewhere [20, 21]. Key to this work, however, are the angle resolved photoemission spectroscopy (ARPES) measurements that employed plane polarized synchrotron radiation dispersed by a 3 m toroidal grating monochromator [26, 27], at the Center for Advanced Microstructures and Devices (CAMD) [28–30]. The measurements were made in a UHV chamber employing a hemispherical electron analyzer with an angular acceptance of ±1°, as described elsewhere [26, 27]. The combined resolution of the electron energy analyzer and monochromator was 70–120 meV. The angle-resolved photoemission experiments were undertaken as a function of photon energy, and with the photoelectrons collected along the surface normal, to preserve the highest point group symmetry and eliminate any wave vector component parallel with the surface. This normal emission photoemission collection geometry or normal incident (IPES) electrons was preserved throughout these studies. In both photoemission and inverse photoemission measurements, the binding energies are referenced with respect to the Fermi edge ($E_F = 0$ eV) of gold in intimate contact with the sample surface and the photoemitted (UPS, ARPES, IPES, and XPS), in terms of $E - E_F$ (thus making occupied state energies negative).

Figure 1 Schematic of the zwitterion (6Z)-4-(benzylamino)-6-(benzylliminio)-3-oxocyclohexa-1,4-dien-1-olate.

3 Theoretical approach The zwitterion (6Z)-4-(benzylamino)-6-(benzylliminio)-3-oxocyclohexa-1,4-dien-1-olate

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molecular electronic structure calculations were performed for both bulk molecular crystals and single molecules. Using a plane-wave-based density functional theory (DFT) method within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation [31], the bulk molecular electronic structure was calculated as a function of wave vector (the molecular crystal Brillouin zone) which was implemented in the CASTEP computer code (Accelrys Inc. San Diego, CA) [32]. The wave functions were expanded in terms of a plane-wave basis set with a kinetic energy cutoff of 300 eV, which with adopted ultra-soft pseudopotentials provided good convergence of calculated total energies and atomic forces [33]. The supercell had dimensions $a_x = 8.446$ Å, $b_y = 14.996$ Å, $c_z = 12.728$ Å, as illustrated in Fig. 2, based on the known molecular crystal structure as measured by X-ray diffraction (XRD) [34].

Semiempirical (PM3) calculations of two identical (6Z)-4-(benzylamino)-6-(benzyliminio)-3-oxocyclohexa-1,4-dien-1-olate zwitterion molecules were also performed as well as a check. There were differences between the two molecules (PM3) and the solid state DFT calculations, as expected. In all cases, the molecular orbital energies were rescaled by aligning the HOMO of the calculated spectra to the -2.4 eV HOMO features of the experimental photoemission spectra.

## 4 Electron pockets at the Fermi level and band structure

4.1 The electronic structure of molecular film

The combined occupied and unoccupied electronic structure, measured by photoemission and inverse photoemission, of the zwitterion (6Z)-4-(benzylamino)-6-(benzyliminio)-3-oxocyclohexa-1,4-dien-1-olate shows that the LUMO is placed just above the Fermi level or chemical potential, as shown in Fig. 3a. The calculated density of states for this zwitterion is shown in Fig. 3b.

As part of the analysis of the electronic structure, a band gap for the zwitterion, packed in the molecular film, was deduced from the combined photoemission and inverse photoemission and found to be 1.7 ± 0.2 eV based on the conduction and valence band edges in Fig. 3a and 1.63 eV from DFT. Although the vertical energy gap is much larger than the DFT calculated band gap, this remains much smaller than for other similar zwitterions [20, 21], and this is in better agreement than previously observed for any DFT calculation for a zwitterion of this class of molecules. It is more typical that the HOMO to LUMO shows far better agreement with the larger gap calculated through semiempirical modeling [20, 21].
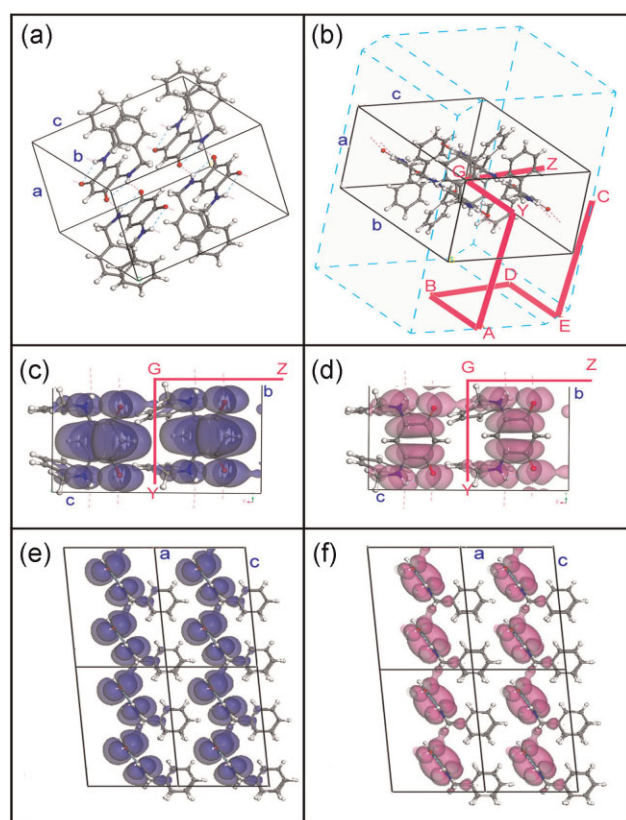
Figure 2 (online color at: www.pss-b.com) Views of the calculated crystal structure of zwitterion (6Z)-4-(benzylamino)-6-(benzylimini-nio)-3-oxocyclohexa-1,4-dien-1-olate. While the crystal structure (a) is shown alone, on this we have overlaid the reciprocal lattice directions (b) and the highest occupied molecular orbital (HOMO) electron density (c and e) as well as the lowest unoccupied molecular orbital (LUMO) state density (d and f) to provide different views of the frontier orbitals.
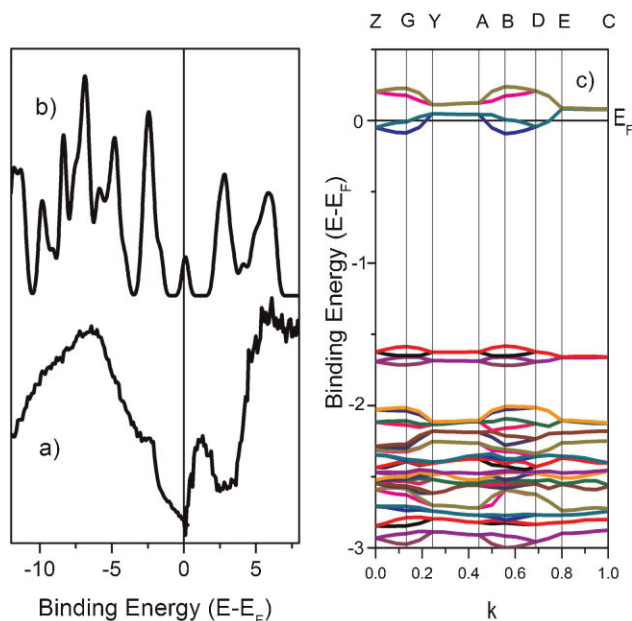
Figure 3 (online color at: www.pss-b.com) (a) Combined photoemission and inverse photoemission of the zwitterion zwitterion (6Z)-4-(benzylamino)-6-(benzyliminio)-3-oxocyclohexa-1,4-dien-1-olate. These data are compared to occupied and unoccupied DFT density state calculations of the $C_6H_2(\cdots NH-CH_2-C_6H_5)_2(\cdots O)_2$ (b). The actual calculated band structure is plotted in (c), with the individual molecular orbitals distinguished through the use of different color coding.
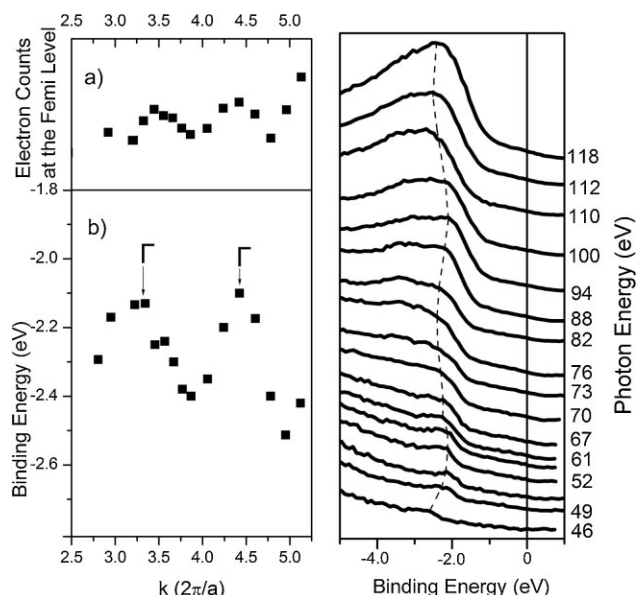
Figure 4 (a) Evidence of electron pockets, electron were collected normal to the surface at the Fermi level, (b) band structure dispersion as a function of wave vector $k_\perp$, providing an experimental lattice of 5.9 Å along the surface normal, and (c) energy-dependent photoemission spectra of zwitterion (6Z)-4-(benzylamino)-6-(benzylimi-nio)-3-oxocyclohexa-1,4-dien-1-olate on gold, showing evidence of band dispersion. The photoelectrons were collected along the surface normal.

4.2 Electron pockets at the Fermi level As shown in Fig. 4, energy-dependent photoemission spectra were taken for the zwitterion molecular films grown on gold substrates. In the particular experimental setup used here, the photon energy dependence of the photoemission spectra (relative to the Fermi level) can be exploited to determine the dispersion (change in binding energy) as a function of wave vector $k_\perp$ (along the surface normal). Such dispersion, as observed here (Fig. 4a and b), is a consequence of the hybridization, as shown in Fig. 2, of molecular orbitals of adjacent zwitterion molecules fulfilling the criteria of Bloch's theorem [3–5, 11].

The wave vector difference between the Brillouin zone center and edge according to the value of $k_\perp$ (the wave vector along the surface normal) can be estimated using Eq. (1) and the photoelectron kinetic energy (E_{kin}),

$$k_\perp = \sqrt{\frac{2m}{h^2}\left(E_{kin}\cos\theta^2 + U_{in}\right)}, \tag{1}$$

since the emission angle (θ) relative to the surface normal is 0, and where U_{in} is the inner potential. As shown in Fig. 4b, the photoemission peak binding energies exhibit oscillatory behavior as a function of electron wave vector (proportional to the square root of electron kinetic energy).

This is summarized in Fig. 4b, where the peak position for the $-2.4\,eV$ ($E - E_F$) binding energy band is plotted against wave vector along the surface normal, $k_\perp$. Band

dispersion in binding energy with amplitude of 200 meV, is evident. This band structure confirms that the zwitterion molecular films have crystallinity along this direction (the normal direction) and are sufficiently thick (at least four to five molecules thick) to establish a bulk band structure. The density of states at the Fermi level was also found to follow the same wave vector dependence, as illustrated by the variation in counts obtained within 90 meV about the Fermi level, as illustrated in Fig. 4a. This is key evidence of electron pockets formed by a placement of the Fermi level at energy above the bottom of the nominal conduction band. What would normally be considered the bottom of the conduction band is no longer unoccupied: the filling of the bottom of the nominal conduction band leads to the formation of electron pockets in the vicinity of the Fermi level.

A lattice parameter along the surface normal can be derived from the critical points established by the experimental band dispersion and the changing density of states with wave vector at the Fermi level. From these experimentally derived reciprocal lattice critical point values, we find that the zwitterion crystal grown on the gold substrate has a crystal layer spacing of 5.9 ± 0.2 Å along the surface normal. This lattice parameter derived from the band dispersion can be assigned to the bulk crystal value of 6.4 Å, along the Z to G direction expected from the molecule to molecule real space O–O distances in the roughly tetragonal zwitterion crystal structure, as determined by XRD as shown in Fig. 2a–f [22–25]. This 8% contraction along one axis could reflect distortions to the molecular lattice as a result of crystallization in a thin film and has been observed in other molecular systems [3]. Complications due to the limited molecular film thickness also cannot be excluded.

We find some evidence for a small inner potential of $5 \pm 1\,eV$ from the experimental band dispersion. This implies bandwidth and is certainly much larger than the value expected for a molecular insulator (where the value for the inner potential U_{in} should be close to 0). This nonzero inner potential energy correction and the oscillating density of states at the Fermi level suggests a molecular thin film that is in fact more semi-metallic than insulating; i.e., there exist electron pockets formed from the conduction band (the LUMO) in the vicinity of the Fermi level.

As shown in Fig. 3c, the DFT band structure calculations also indicate that the conduction band does cross the Fermi level and shows dispersion, with appreciable band width along the Z–G direction consistent with experiments. The conduction band wave function density is plotted in Fig. 2d and f to illustrate how the overlap of electron density between adjacent zwitterion molecules through the oxygen and the nitrogen weighted groups along the Z–G direction might occur. The calculated occupied bandwidths are in fact much smaller than experimentally observed and plotted in Fig. 4. This limited band width in the calculated band structure, a band width much smaller than observed in experiment, can be understood by the fact that the intermolecular spacing from XRD, using molecular crystals [34], is much larger than the value we derive from the experimental band structure.

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Interactions with the gold substrate could alter crystal structure, and a closer proximity of adjacent molecules would only serve to increase the dispersion and band widths, more consistent with the experimental observations. There is no *a priori* reason why the crystal structure of the free standing molecular crystal need be identical to the crystallography adopted in the molecular film grown from solution on gold. What is needed at this point is careful crystallography of these zwitterion thin films, so as to improve the preliminary calculations and obtain more realistic band-widths.

5 Summary There is a distinct wave vector dependence of the electronic band structure formed from the molecular orbitals of adjacent molecules in a thin film of the zwitterion (6Z)-4-(benzylamino)-6-(benzyliminio)-3-oxo-cyclohexa-1,4-dien-1-olate deposited from solution on gold. Inter-molecular band dispersion has been previously observed for small adsorbates (like the molecular CO and N_2) and for large adsorbate molecular layers like pentacene, thione 2-mercatobenzoxazole, and a few other examples [3–5, 34–39], but this zwitterion molecular system is a somewhat larger molecule that has a large intrinsic dipole and there is evidence of a finite density of states at the Fermi level.

This zwitterion molecular film is very different from a true insulator. The nonzero inner potential and the evidence of electron pockets, observed in the photoemission spectra, can be associated with electronic states which appear to be slightly filled or occupied in the solid state (i.e., for the solid thin films deposited on gold) but normally would be completely unoccupied in the single molecule. Our model calculations confirm that there is an electronic density shared inter-molecularly through the oxygen to nitrogen groups of the zwitterion crystal at least along the *Z–G* direction of the zwitterion crystalline structure, consistent with experiment. One can therefore expect significant intrinsic conductivity of such films, making them of interest for organic electronics buffer layers.

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