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Resonant inelastic x-ray scattering studies of the organic semiconductor copper phthalocyanine

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We report resonant inelastic x-ray scattering (RIXS) measurements on polycrystalline and single crystal samples of the organic semiconductor β-copper phthalocyanine (CuPc) as well as time dependent density functional theory calculations of the electronic properties of the CuPc molecule. Resonant and nonresonant excitations were measured along the three crystal axes with 120 meV resolution. We observe molecular excitations as well as charge-transfer excitons along certain crystal directions and compare our data with the calculations. Our results demonstrate that RIXS is a powerful tool for studying excitons and other electronic excitations in organic semiconductors.

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Organic molecular solids exhibit an enormous number of different properties, including quasi-one-dimensional (quasi-1D) or two-dimensional (2D) behavior, charge density wave formation, and exotic superconductivity. These solids are also potentially useful in novel opto- and microelectronic devices. Of great interest is the possibility of creating low cost alternatives to existing semiconductor technology. Some organic materials are capable of self-assembly, while others may be suitable for printing directly onto surfaces, thus opening up the possibility of inexpensive flat panel displays, smart cards, and sensors. Recent works have discussed the potential of these materials[1–3] and have mapped out the route to widespread applications.[4] One important reason that these materials may provide low cost devices is that properties of the molecules are believed to be only weakly influenced by being in the solid state. Thus, unlike conventional semiconductors, high quality single crystal materials are not believed to be critical. The extent to which this is true remains to be determined.

Optical applications such as displays and solar cells are some of the most important and exciting areas for development of organic materials. In these materials, the optical properties are mostly determined by the excitons. An understanding of the nature and properties of the exciton is therefore of great importance. Recently, Schuster *et al.*[5] carried out electron energy-loss spectroscopy (EELS) measurements on single crystal pentacene and found that the data did not fit the expected Frenkel model of excitons tightly bound on a single molecule. They hypothesized that the exciton could be of the charge-transfer type between molecules. Recently, Yang *et al.*[6] studied an open-ring form of spiro-oxazines (Py-SO) using nonresonant inelastic x-ray scattering. They found that they could reproduce the excitation spectrum using quantum chemical calculations within the Zerner's intermediate neglect of differential overlap/single configuration interaction formalism.[7]

We have used *resonant* inelastic x-ray scattering measurements near the copper *K* edge to study the bulk electronic excitations in copper phthalocyanine (CuPc), a small organic molecule used in organic solar cells,[8–11] organic transistors,[12,13] and gas sensors.[14] We carried out calculations of the single molecule excitations using time dependent density functional theory (TD-DFT).[15] Consistent with Schuster *et al.*,[5] we find that not all excitons are of the Frenkel kind. The excitation spectrum depends on the crystal orientation, indicating that a knowledge of individual molecular properties is inadequate to describe this system. In addition, by using resonant scattering, we couple strongly to excitations involving states on the central copper atom. This allows us to determine the electronic origin of at least some of the excitons. Knowing their origin may allow for choosing and even designing molecular structures that have excitons of desired energies.

The phthalocyanines are a durable and stable group of compounds that have been widely used as dyes and inks and in other applications ranging from compact disks to catalysis to chemotherapy. They are interesting examples of small molecular compounds with a more or less planar symmetry. The molecular symmetry of CuPc is close to planar D_{4h}, with small distortions out of the plane. Figure 1(a) shows the molecular structure of copper phthalocyanine (CuPc), $CuC_{32}H_{16}N_8$. In addition to copper, a large number of different metal atoms (including Li, Si, Ti, Fe, Co, Ni, Cu, Zn, Ag, Sn, Sb, and Pb) can be placed at the center of these materials. The hydrogen atoms on the outside of the molecule can be replaced by other atoms or functional groups.

The central ring, with a single metal atom surrounded by four nitrogen atoms, is similar to biologically important com-

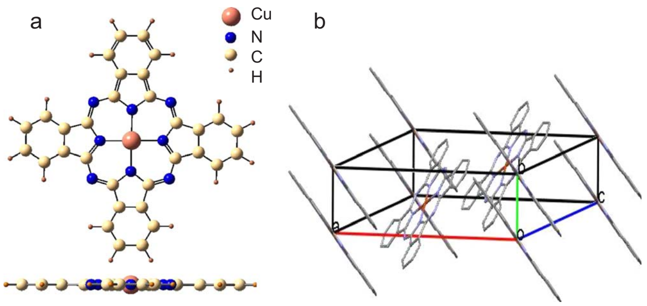

FIG. 1. (Color online) (a) CuPc molecule. (b) The β-CuPc unit cell. Molecules on the corners are parallel to each other, and molecules in the bases are parallel to each other.

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pounds such as chlorophyll and hemoglobin. The phthalocyanines therefore serve as model systems for understanding these more complicated molecules. In addition, the planar structure of CuPc with the fourfold coordination of the copper also has some similarity to the copper oxide planes in high temperature superconducting compounds.

The crystal structure of our samples, β-CuPc, is base centered monoclinic with dimensions $a=19.47$ Å, $b=4.80$ Å, $c=14.64$ Å, and $\beta=120.98°$ and is shown in Fig. 1(b). The molecular symmetry of CuPc is close to a planar D_{4h}, with small distortions out of the plane. The copper atoms form nearly ideal 1D metallic chains with very weak interchain interactions. At low temperatures, the systems act like a highly one-dimensional Heisenberg magnet.[16]

Crystals were grown from CuPc powder (Alfa Aesar) of $\sim$95% purity. The powder was sublimated in a temperature controlled tube furnace under slowly flowing (a few $\mathrm{cm}^3/\mathrm{min}$) CO_2. A large number of free standing needlelike single crystals were formed as found by earlier authors.[17] The largest crystals had dimensions of roughly $20\times 0.7\times 0.3$ mm^3. The long dimension of the crystals was found to be along the b axis.

Inelastic x-ray scattering measurements were taken at energies close to the copper K edge (8.9805 keV) at the Advanced Photon Source undulator beamline 9-ID-B. A double-bounce channel cut silicon (111) monochromator was used for the high resolution measurements. Energy analysis was provided by a diced Ge(733) analyzer. Overall energy and momentum resolution were 300 meV and 0.08 $\mathrm{Å}^{-1}$, respectively, or 120 meV and 0.04 $\mathrm{Å}^{-1}$ depending on the configuration.[18] Scattering took place in the vertical plane. The higher flux 300 meV setup was used to study excitations above 2 eV, while the 120 meV resolution allowed measurements down to about 1 eV. Data were mostly taken in a transmission geometry, which made it easier to study low momentum transfers ($\boldsymbol{Q}$). Measurements were taken on pressed raw powder as well as a stack of small crystals and finally on a single crystal with the incident beam perpendicular to the long axis b. There was no visible sign of sample degradation due to the beam, and single crystal scans remained unchanged during scans over several hours. For the single crystal data, the samples were translated to an untouched spot about every 2 h to minimize the radiation dose in one spot.

We carried out TD-DFT[19] calculations using GAUSSIAN 03 (Ref. 20) for a single CuPc molecule. Wachters+f (Ref. 21) basis set was used for copper. This was chosen since it has been found to be quite accurate for similar calculations.[22] For carbon, nitrogen, and hydrogen, atomic orbitals are given by double zeta valence polarized basis sets. All basis sets were obtained from Ref. 23. Two kinds of atomic coordinates were used: (1) using the atomic positions measured by Brown,[24] and (2) a completely 2D atomic structure. The atomic coordinates were optimized using the method B3LYP.[25] In both cases, stability checks confirmed that the geometric optimizations were stable points. The symmetric molecular calculations were significantly faster, but both calculations yielded similar results. Using B3LYP electronic excitations were calculated up to 5.6 eV. These calculations were carried out on the Jazz supercomputer at Argonne National Laboratory.

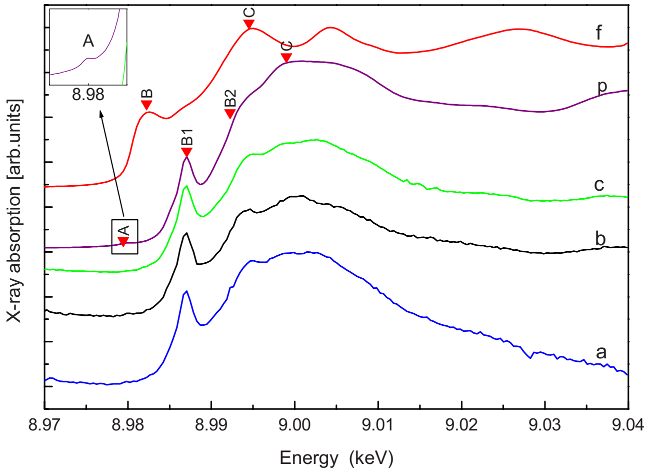

FIG. 2. (Color online) X-ray absorption spectra of f, 25 μm copper foil; p, CuPc powder; c, along the c^* direction; b, along the b^* direction; and a, along the a^* direction of a single crystal of CuPc.

Figure 2 shows the absorption spectrum near the Cu K edge for the CuPc powder and a CuPc single crystal along the three principal crystal directions. Peak A is due to a transition to a bound state, believed to be a dipole forbidden but quadrupole allowed $1s$ to $3d$ character.[26] Peaks B and B1 are due to a $1s$ to $4p$ transition plus shakeup.[27] Peak B2 is from a transition from $1s$ to $3d10L$, where L signifies a ligand hole.[28] Peak C is mostly $1s$ to $4p$, then into the continuum. The excitation from $1s$ to $4s$ is predicted to have essentially no intensity.[29]

Data were first taken using a moderate energy resolution (300 meV) on small stacked crystals, with the b axis oriented perpendicular to the scattering plane. The crystals were not individually oriented in this experiment. Energy scans as a function of $\boldsymbol{Q}$ are shown in Fig. 3 (left). Here, we see a feature near 3.1 eV whose energy is essentially independent of $\boldsymbol{Q}$. Based on our calculations, we identify this peak as the

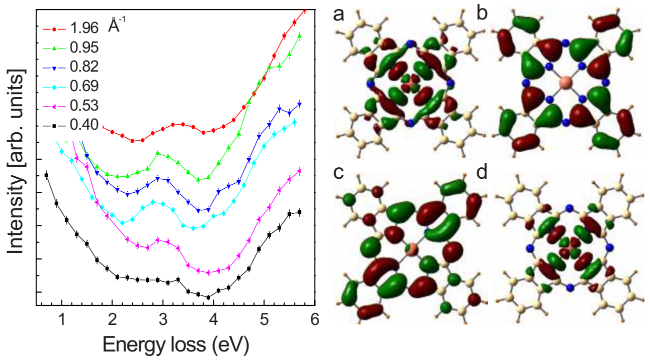

FIG. 3. (Color online) Left: IXS measurements of the HOMO-LUMO gap of a stacked crystal sample of β-CuPc (300 meV resolution). Right: Orbitals calculated using the B3LYP method. Different spins have different colors, and the surfaces shown have equal energy surfaces. (a) HOMO-1 (0), (b) HOMO (2), (c) LUMO (4), and (d) LUMO+1 (0); number of degenerate states are given in parentheses.

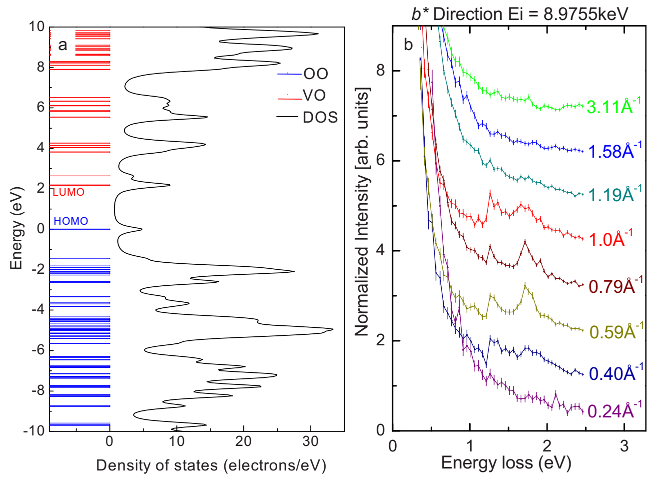

FIG. 4. (Color online) (a) Calculated density of states of CuPc using the B3LYP method. Red shows the VOs and blue shows the OOs. (b) Spectra of CuPc at constant incident energy. b^* is parallel to the momentum transfer ($\boldsymbol{Q}$).

highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) transition. This excitation begins at around 2.2 eV, which we call the band gap. Optical[30] and x-ray[22] absorption measurements show a peak beginning at about the same value, although their peaks are centered slightly higher than ours (near 3.4 rather than 3.1 eV). Our TD-DFT calculation finds a HOMO-LUMO gap at 2.2 eV. Figure 4(a) shows the calculated density of states (convoluted with a Lorentzian of 300 meV width) as well as virtual (unoccupied) orbitals (VOs) and occupied orbitals (OOs), which agrees reasonably well with the data. Thus, it seems likely that the MOs are relatively unchanged in the solid state compared to a single molecule. Since the oscillator strength only considers the dipole moment, any higher order excitations are not represented in the figure. These become important mostly at higher $\boldsymbol{Q}$ values.

The HOMO, LUMO, and adjacent states are shown in Fig. 3 (right). Here, the color of energy surfaces indicates the spin, while size beyond atomic indicates the contribution to the orbital. The calculations show that the outer atoms in the molecule contribute significantly to the HOMO-LUMO orbitals, which is also shown by STM measurements.[31] Earlier calculations that neglected the outer benzene rings for computational simplicity[22] are therefore less accurate. The central copper atom makes only a small contribution to the HOMO and LUMO. This is consistent with the fact that absorption in the phthalocyanines depends only weakly on the central species.[30]

Higher resolution (120 meV) measurements reveal excitations at 1.3 and 1.73 eV [see Fig. 4(b)]. The excitation at 1.3 eV is resonant (resonance behavior is discussed below) while the 1.73 eV excitation is nonresonant. They both have a strong directional dependence. These excitations are only visible when the momentum transfer is parallel to the b^* direction; no excitations appear with momentum transfer along the a^* or c^* axis. The effect is unlikely to result from the change in incident polarization. The molecules are tilted by approximately 45° with respect to the b axis [see Fig. 1(b)], so the component of the polarization along and perpendicular to a molecule remains essentially the same in or perpendicular to the b^* axis. The two excitations show little dispersion. The similar $\boldsymbol{Q}$ dependence of these two excitations implies that they have a similar origin. Previously, EELS was used to look at the excitations in these materials.[32] They find excitations at about 1.7, 1.8, 2, and 2.2 eV, consistent with optical absorption data.[30] The maximum in the Q dependence they observed for the 1.7 eV peak is likely due to the limited allowed Q range observed here.

The allowed $\boldsymbol{Q}$ range for these excitations is less than 1.0 Å^{-1}. Above this value (even at equivalent points in higher zones), no excitation was visible. At low $\boldsymbol{Q}$ (=0.24 Å^{-1}) along b^*, we also did not see the excitations clearly, probably due to the larger elastic background. The maximum momentum value 1.0 Å^{-1} corresponds to a real space distance of ~6 Å. Along the b^* direction, the molecules are tightly bound and the molecular spacing (center to center) is about 5 Å. Our interpretation is that these excitations involve charge transfer between two adjacent molecules. The excitations only occur along this direction since only along this direction are the molecules closely spaced. The 1.7 eV exciton lies about 0.5 eV below our calculated HOMO-LUMO gap. If we assume that the charge-transfer energy is close to the optical gap, then this energy would be the binding energy of the exciton. A 0.5 eV binding energy is a reasonable value for organic semiconductors of this size.[33] However, the HOMO-LUMO gap may well be quite different from the charge-transfer gap, so we cannot make any definitive statement about the exciton binding energy.

Next, we discuss the resonant scattering. Resonant scattering involves the transition of a copper 1s atom to an intermediate state, and then a subsequent decay from the intermediate state to the final state. The localized nature of the

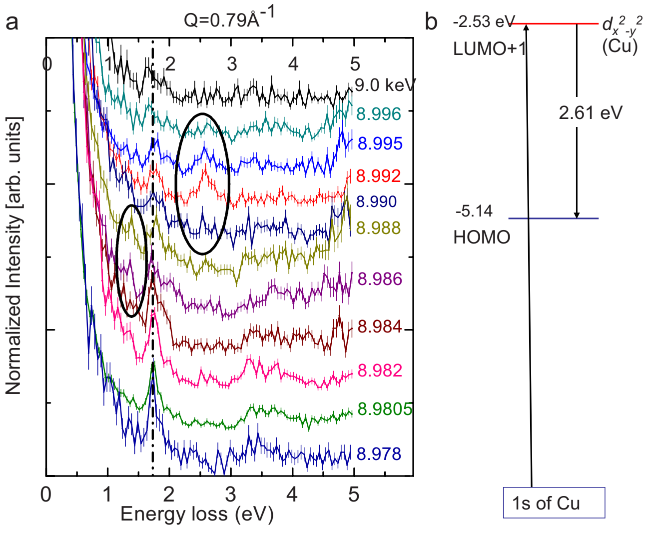

FIG. 5. (Color online) (a) Resonance scans with b^* parallel to the momentum transfer. The left oval in the plot shows the 1.3 eV excitation, and the right oval shows the resonant excitation at 2.6 eV. The dashed line shows that the exciton at 1.7 eV is nonresonant. The data are shifted vertically for clarity. (b) Possible states involved in 2.6 eV resonant excitations.

copper 1*s* level means that only intermediate states with significant contributions from the copper orbitals are likely to be resonantly enhanced. We observe a resonant excitation at an incident energy of 8.992 keV (Fig. 2, peak B2) with an energy loss of 2.6 eV [Fig. 5(a)]. This excitation has no directional dependence and is therefore mostly likely a localized molecular excitation. Our calculations indicate the following picture for this excitation [Fig. 5(b)]: At resonance, a 1*s* electron of the copper atom is excited into one of the $d_{x^2-y^2}$ orbitals (−2.53 eV [LUMO+1]) of the copper atom. Then, the HOMO electron (−5.14 eV) will fall into the 1*s* state of the copper atom.

The excitation at 1.3 eV is also resonant and is visible with the incident energy of 8.9775 keV (Fig. 2, peak A) corresponding to a quadrupolar transition. It also resonates near the incident energy of 8.987 keV (Fig. 2, peak B1), which is a 1*s* to 4*p* transition. The resonant nature indicates that the excitation involves states on the copper atoms, and its directional dependence argues for an intermolecular excitation. The fact that this state is visible neither in our nonresonant data nor in the EELS or the optical data indicates that it is only weakly excited. It could be a more strongly bound exciton, or the proximity of the two molecules along this crystal direction may result in alterations of the electronic states from the molecular states we calculate.

In conclusion, we have carried out inelastic x-ray scattering (RIXS) studies on the organic semiconductor CuPc and have observed four separate electronic excitations. Peaks at 1.3 and 2.6 eV are resonant excitations, while the exciton at 1.7 and the band gap at 2.2 eV are nonresonant. The excitations at 1.3 and 1.7 eV involve intermolecular excitations and only occur along the crystal direction where the intermolecular distance is smallest. The other excitations are consistent with single molecule excitations.

Combining RIXS and TD-DFT allows the determination of the atoms and states involved in many of the electronic excitations. This combination will be a useful tool for understanding the excitations in a large number of organometallic compounds.

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