

SUPPORTING MATERIALS

Mesoscopic Donor-Acceptor Multilayer by Ultra-High-Vacuum Co-deposition of Zn-Tetraphenyl-Porphyrin and C₇₀

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S.1 UPS Valence Bands.

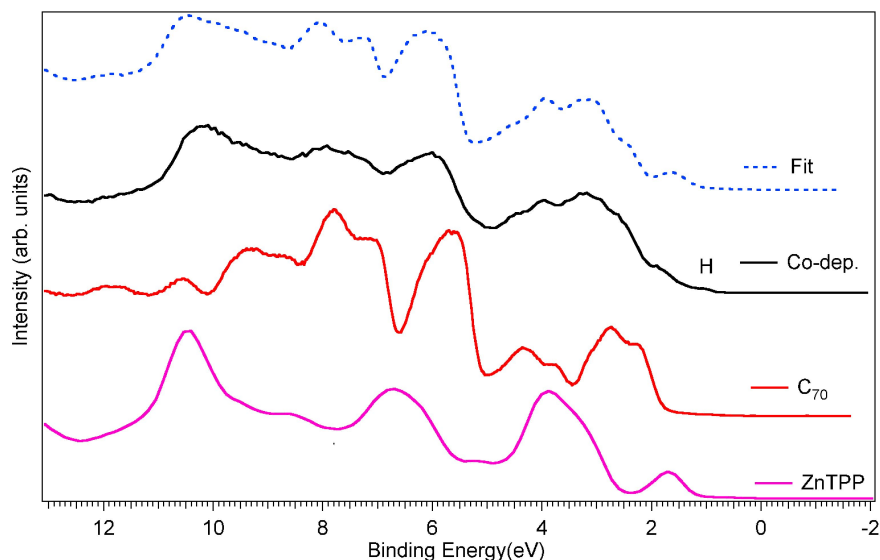


Fig. S.1.1: Valence band of the co-deposited system, of ZnTPP and C₇₀ multilayer and the sum of these two pristine spectra (fit). The spectra were measured at $h\nu=90$ eV.

In Fig. S.1.1 are plotted the valence band spectra of the pristine molecular multilayers (ZnTPP and fullerene C₇₀), the co-deposited system, and a linear combination of the former two. To linearly combine the two pristine spectra the porphyrin spectrum has been shifted toward the Fermi level by 100 meV, while the C₇₀ spectrum has been shifted in the opposite direction by 200 meV. Although a simple rigid shift and superposition of the two spectra is probably not adequate to describe the complex system because some states should hybridize (for example between 6 eV and 10 eV the C₇₀ features appear quite stronger than in reality), this superposition captures the main features of the co-deposited spectrum. The first peak H near the Fermi level comes from the HOMO, HOMO-1 and HOMO-2 of porphyrin and confirms that the HOMO states of the co-deposited system stem from the HOMO states of porphyrin.

S.2 Calculation of the π^* features in the N1s NEXAFS spectrum

In order to understand the origin of the peaks in the experimentally measured the N1s edge NEXAFS spectrum, we also calculated the above peaks theoretically. Within dipole approximation, the spectral intensity ($I_{N1s \rightarrow f}$) is given by:

$$I_{N1s \rightarrow f}(\varepsilon) \propto \sum_f \left| \langle \psi_{N1s} | \vec{r} | \psi_f \rangle \right|^2 \delta(\varepsilon_f - \varepsilon_{N1s} - \varepsilon),$$

where $\vec{r}$ is the position operator, ε is the energy of the incident X-ray, ε_f and ψ_f are the KS eigenvalue and eigenfunction respectively of the f^{th} conduction band of the excited ZnTPP+C₇₀ complex, ε_{N1s} and ψ_{N1s} are the eigenvalue and eigenfunction of the N1s state of the complex respectively. Since we are using a pseudopotential based technique for the calculations, in which the core electrons and the strong nuclear potential has been replaced with a pseudopotential, we cannot obtain the eigenvalues of the N1s core state of the complex, which is the initial state for the transition. However, based on the assumption that the core states of an atom are the least affected one when it interacts with another atom, we approximate the N1s state of the complex with that of a N atom obtained from an all-electron calculation. The excited system is simulated by replacing the pseudopotential for the N atom (whose core level spectra we want to calculate) with one where a half core electron has been removed. This is based on the transition-potential approach of DFT [M. Cavalleri, M. Odelius, A. Nilsson and L. G. M. Pettersson, J. Chem. Phys. **121**, 10065 (2004) and the references therein]. We note that since the eigenvalue of the N1s state of the complex has been approximated with that of a N atom, the absolute values of the peak positions are unphysical, whereas the energy level hierarchy and the relative positions should be compared with the experimental data.

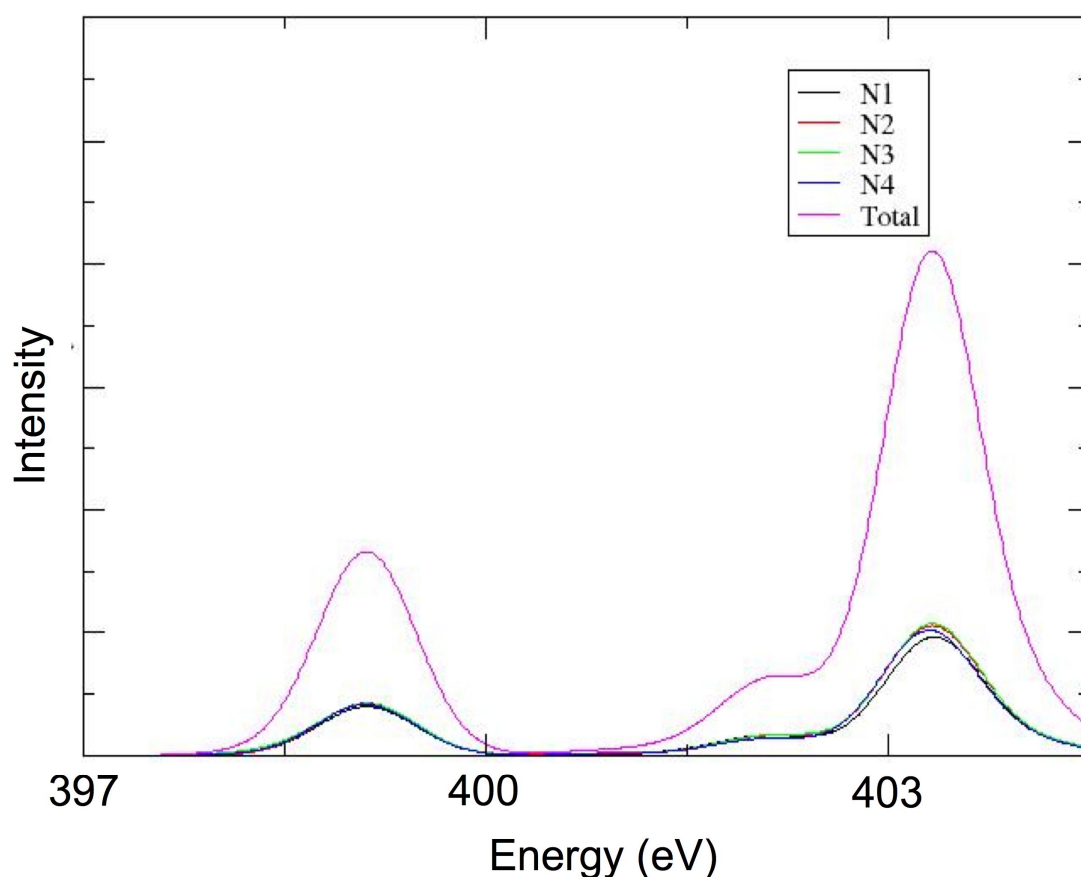


Fig. S.2.1: Theoretically calculated N1s NEXAFS for ZnTPP-C₇₀ complex. The black, red, green and blue curves show contributions from each of the N atoms present in the ZnTPP macrocycle. The magenta curve shows the sum of all the contributions. The calculated spectra have been shifted in the right energy range to be compared with the experiments.

Fig. S.2.1 shows the theoretically obtained N1s NEXAFS spectra for ZnTPP+C₇₀ complex which is in reasonably good agreement with the experimentally obtained spectra. The contributions from each of the N atoms present in the porphyrin macrocycle are also shown. In absence of C₇₀, the contributions from each of the N atoms would have been exactly same. The presence of fullerene in the complex results in slight variations of the contributions from each atom. However, the slight variations in the contribution to the NEXAFS exhibited by each N atom suggest very weak interaction between C₇₀ and ZnTPP. The first peak (π_1^*) is due to transition from N1s to LUMO+4 of the complex (this is the LUMO corresponding to ZnTPP only).

The second and the third peak (π_2^* and π_3^*) correspond to several transitions to higher energy levels. However, for the second peak there are two strong transitions, and for the third peak there is only one strong transition. For each peak, we plot the wave functions of the final state which has the largest contribution (Figs. S.2.2, S.2.3 and S.2.4). It is interesting to note that in all the cases the wave functions are localized on porphyrin, further strengthening the fact that there is little change in the local electronic structures of the individual components, after they form the complex, which in turn implies a small interaction between ZnTPP and C₇₀ (pictures are drawn for a single N atom colored in grey in the figures. Equivalent results are found for the other N atoms).

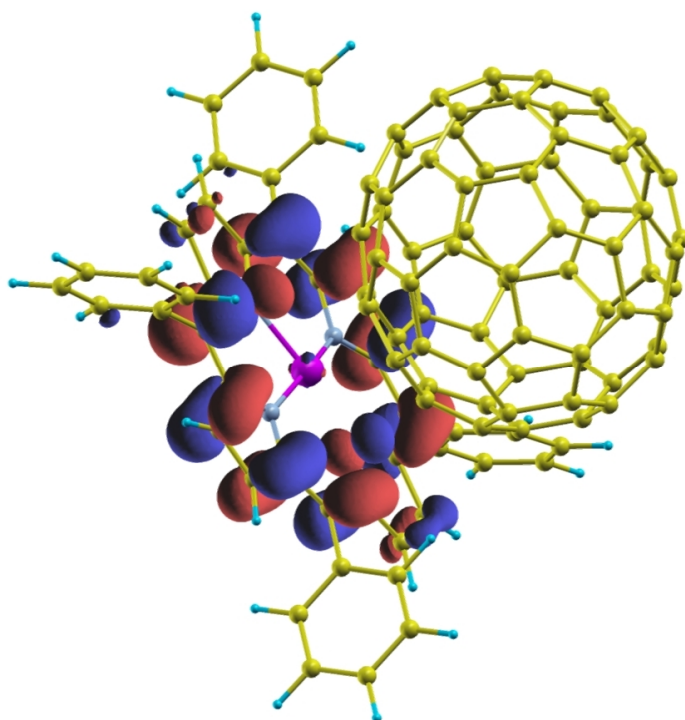


Fig. S.2.2: The LUMO+4 KS state of the ZnTPP+C₇₀ complex which is the final state for the transition corresponding to the π_1^* peak.

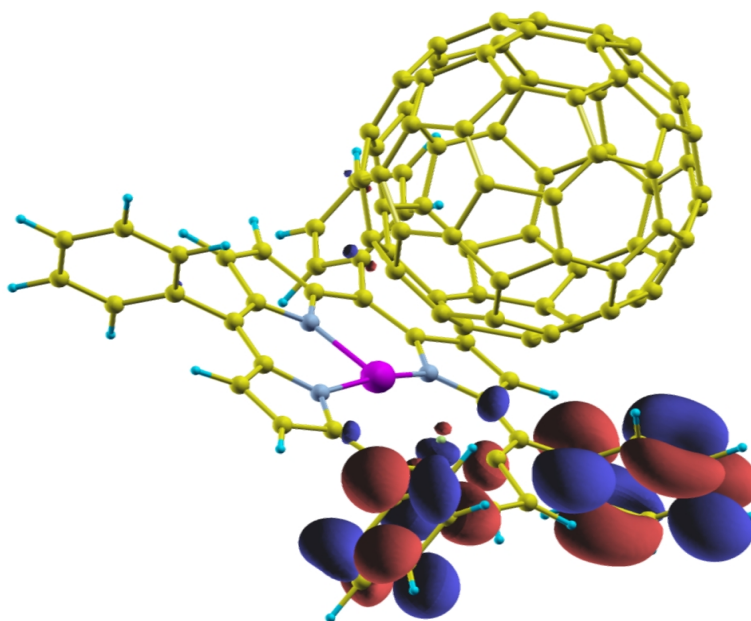


Fig. S.2.3: The KS state which has maximum contribution to the transition corresponding to π_2^* peak

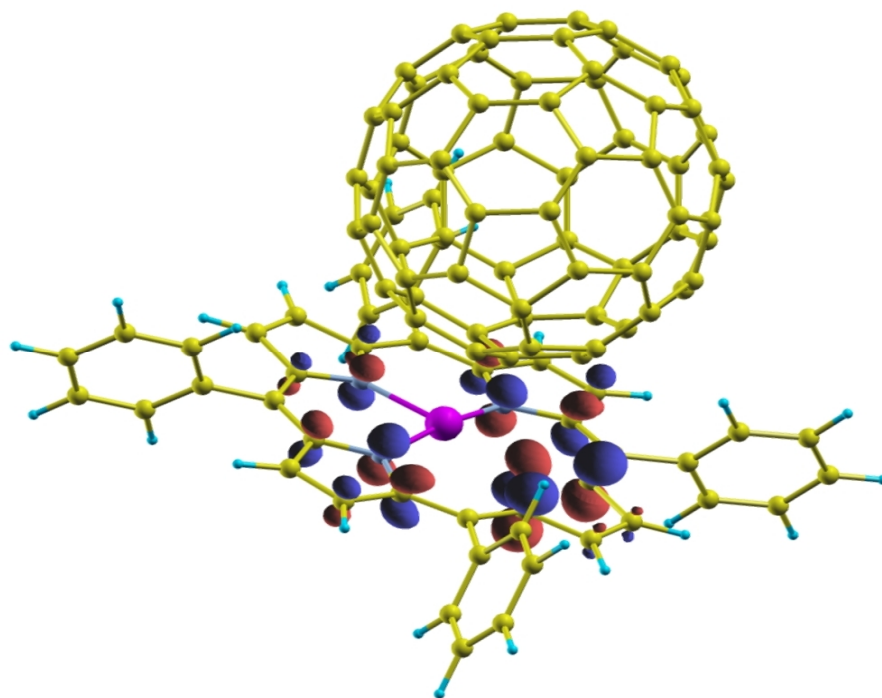


Fig. S.2.4: The KS state which has maximum contribution to the transition corresponding to the π_3^* peak

S.3 C1s NEXAFS spectrum

In Fig. 4a the pristine porphyrin spectrum has been shifted by 0.5 eV to higher photon energy, while the remaining spectra are in the original positions. With this method it is easy to locate the various excitations on the single molecular species that contribute to the co-deposited spectrum. In particular, the first excitation at ~ 284.2 eV is located at the macrocycle and comes from the porphyrin ring alone [13]. The first strong peak at ~ 284.5 eV, instead, belongs almost completely to C₇₀ [17, 18]. Finally, all the other peaks are a combination of porphyrin and C₇₀ features: the double peak at 285.4 eV is the superposition of the phenyl groups of the porphyrin and the equatorial belt of C₇₀, the structure at 286.6 eV belongs mainly to C₇₀ [18] and the other excitations are common to the two molecular species since they belong to π^* excitations typical for aromatic carbon bonding. Finally, the region above 291 eV is characterized by the σ^* states.

The reason why the Aloisa spectrum is more surface sensitive, is that the incidence of the light is very grazing and below the critical angle [12] (while at SuperESCA it was at normal incidence). The way the spectra are collected (Auger vs. Partial Yield) does not influence too much the probing depth because in one case we collect the Auger and in the other case we collect the Auger+all the electrons having a kinetic energy higher than the Auger (i.e. from 250 eV up to a maximum energy of 315 eV).

S.4 The Auger spectrum

In correspondence of the ionization threshold a strong Auger emission is detected in the valence band range. The Auger contribution has almost a constant shape but its intensity follows the profile of the C1s NEXAFS spectrum and, therefore, has to be removed for an appropriate data analysis of the resonant photoemission spectra.

In order to subtract the Auger contribution from the ResPES spectra we measured the KVV Auger spectrum at photon energy of 389.07 eV, far above the ionization edge in order to avoid resonance effects and leave out other emission contributions. We fitted the spectrum with a polynomial background and a minimum number of Gaussian functions. In Fig. S.3.1 are plotted the experimental data, the background and the curve fitting. This Auger contribution has been used to analyse the ResPES data.

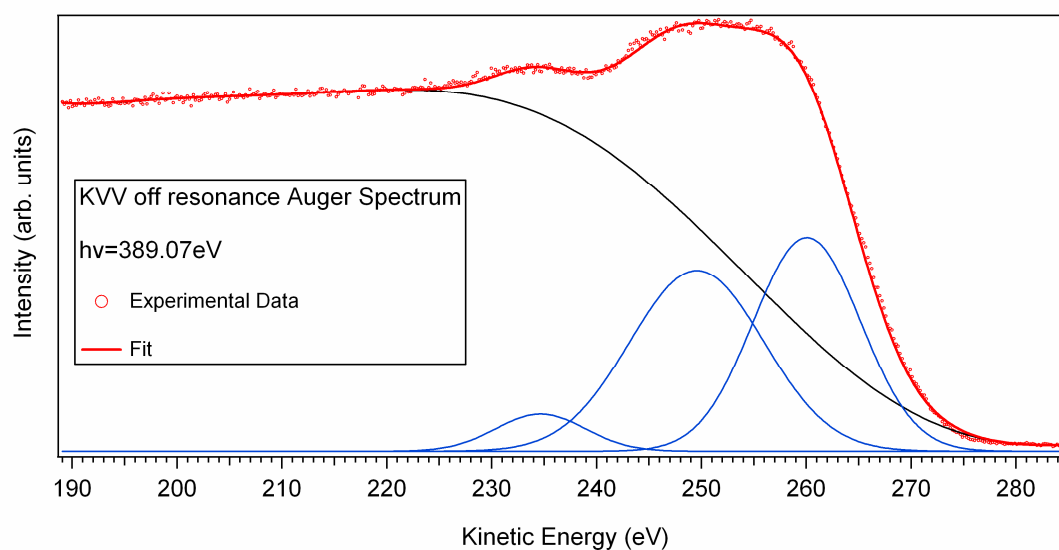


Fig. S.3.1: KVV Auger spectrum of the co-deposited system measured at $h\nu=389.07$ eV and the relative fit.