High resolution NEXAFS of perylene and PTCDI: a surface science approach to molecular orbital analysis†

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1 SUPPLEMENTARY INFORMATION

1.1 Splitting of the PTCDI LUMO resonance

A discrepancy between the gas and condensed phase spectra is the 0.25 eV splitting of the first resonance state, which is effectively observed in the multilayer, whereas an unresolved single state is observed in the gas phase spectrum albeit its asymmetric shape suggests a multicomponent structure underneath. Like for perylene, we will show in the next paragraphs that this splitting is expected to stem from simple initial-state effects, i.e. to reflect the core level shifts of the different carbon atoms of the perylene core, without contributions from the imide carbon atom C7. Previously reported high resolution NEXAFS spectra taken on DiMe-PTCDA [1] and EP-PTCDI [2] consistently display a splitting of the first NEXAFS resonance. PTCDA (whose core level shifts for the perylene core have been shown to be the same of PTCDI, cfr. Table 1 in the main text) also displays a resolved multicomponent fine structure of the first resonance state. [1,3] From the comparison with perylene, PTCDI derivatives and PTCDA, we can conclude that the smearing of the splitting observed in the gas phase is associated with the presence of molecular fragments, likely due to minor impurities (precursors) in the PTCDI powder, which do not affect the condensed phase spectra because of a negligible sticking on TiO_2.

1.2 Wavefunctions of unoccupied molecular orbitals

Molecular orbitals (MO) computed at the PBE level are shown in Fig. 1 for perylene and in Fig. 2 for PTCDI. We report the orbitals for the neutral molecule and those in presence of half core hole at the various carbon atoms. The energy of the orbitals reported therein is shifted to match the experimental most prominent peak of molecular multilayers, as in the main text. Percentages show the weight of the unoccupied MOs on the $2p_z$ (orthogonal to the molecular plane) wavefunction of the carbon atom with the core hole.

1.3 Atom-by-atom simulated NEXAFS spectra

Atom-by-atom simulated spectra, resolved for the photon electric field parallel to the short (X) and long (Y) molecular axes and orthogonal to the molecular plane (Z) are shown in Fig. 3 for perylene and in Fig. 4 for PTCDI. Thick lines are the result of NEXAFS simulation by the xspectra code, while thin lines show the density of unoccupied molecular states DOS projected on the pz orbital of the carbon atom with the core hole. The DOS is truncated at high energies, where eigenvalues have not been computed; such truncation does not influence the NEXAFS calculation. Energies are referred to the average photoemission threshold, whose absolute value is not determined in our pseudopotential-based method.

1.4 Final state effects on PTCDI NEXAFS

Final state effects are predicted to strongly affect the main resonance (at 285.6 eV in the solid state), which is participated from both LUMO+1 resonances and higher energy unoccupied MOs of several carbon atoms. We remark that PBE calculations for the neutral molecules indicate that the LUMO+1 and LUMO+3 of perylene and PTCDI display an inversion of their energy hierarchy, namely the PTCDI LUMO+1 π^* orbital corresponds to the perylene LUMO+3. Inversely, the perylene LUMO+1 corresponds to the PTCDI LUMO+3 π^* orbital. The latter, although largely distorted in its spatial distribution, preserves its two nodal planes parallel to Y axis wherever the core hole is located, and no contributions from C3, C4 and C7 atoms are predicted (see Fig. 8 in the main text). In the case of perylene, PBE calculations do not predict

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variations of neither the double nodal plane in LUMO+1 nor the single one in LUMO+3.

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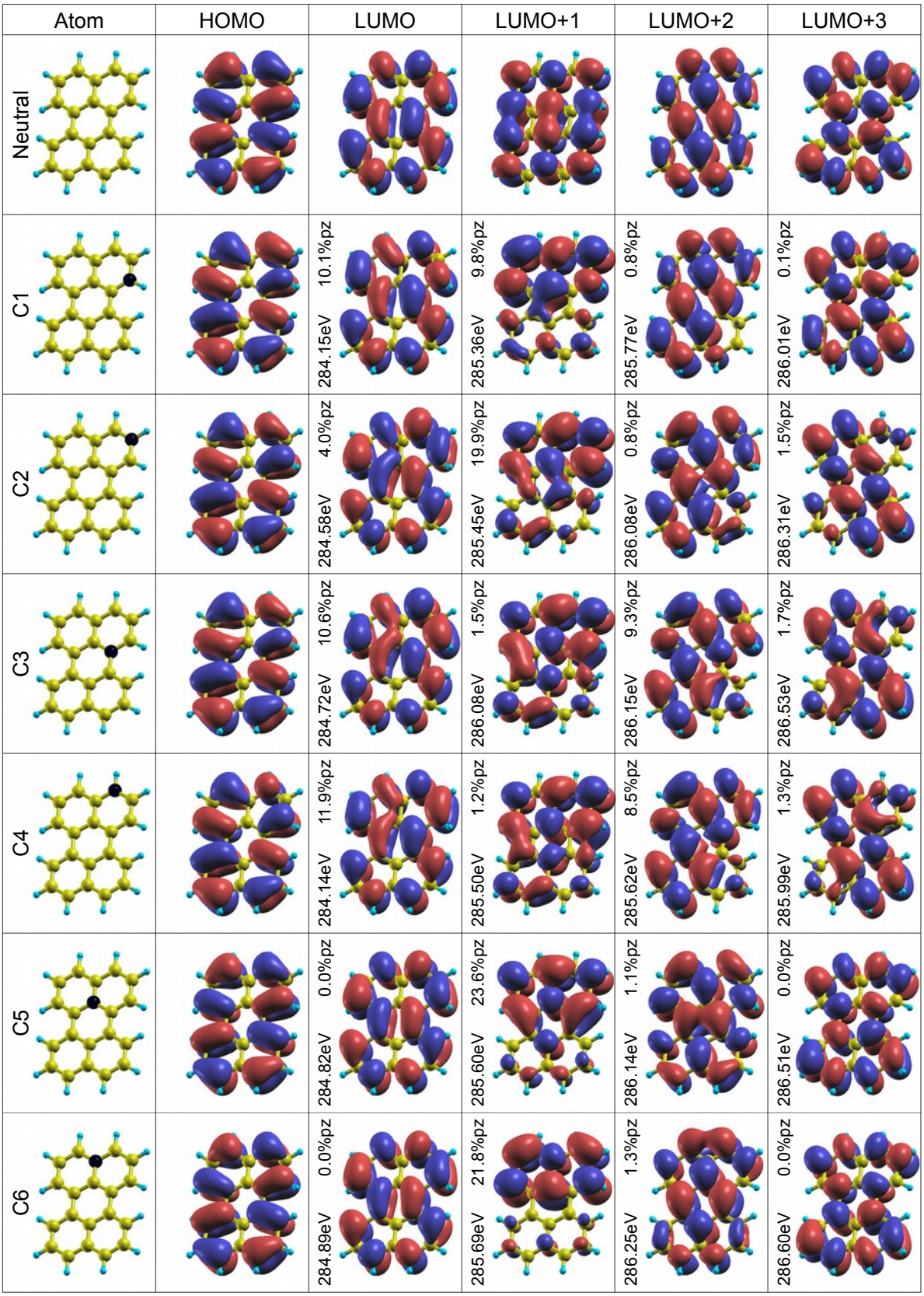
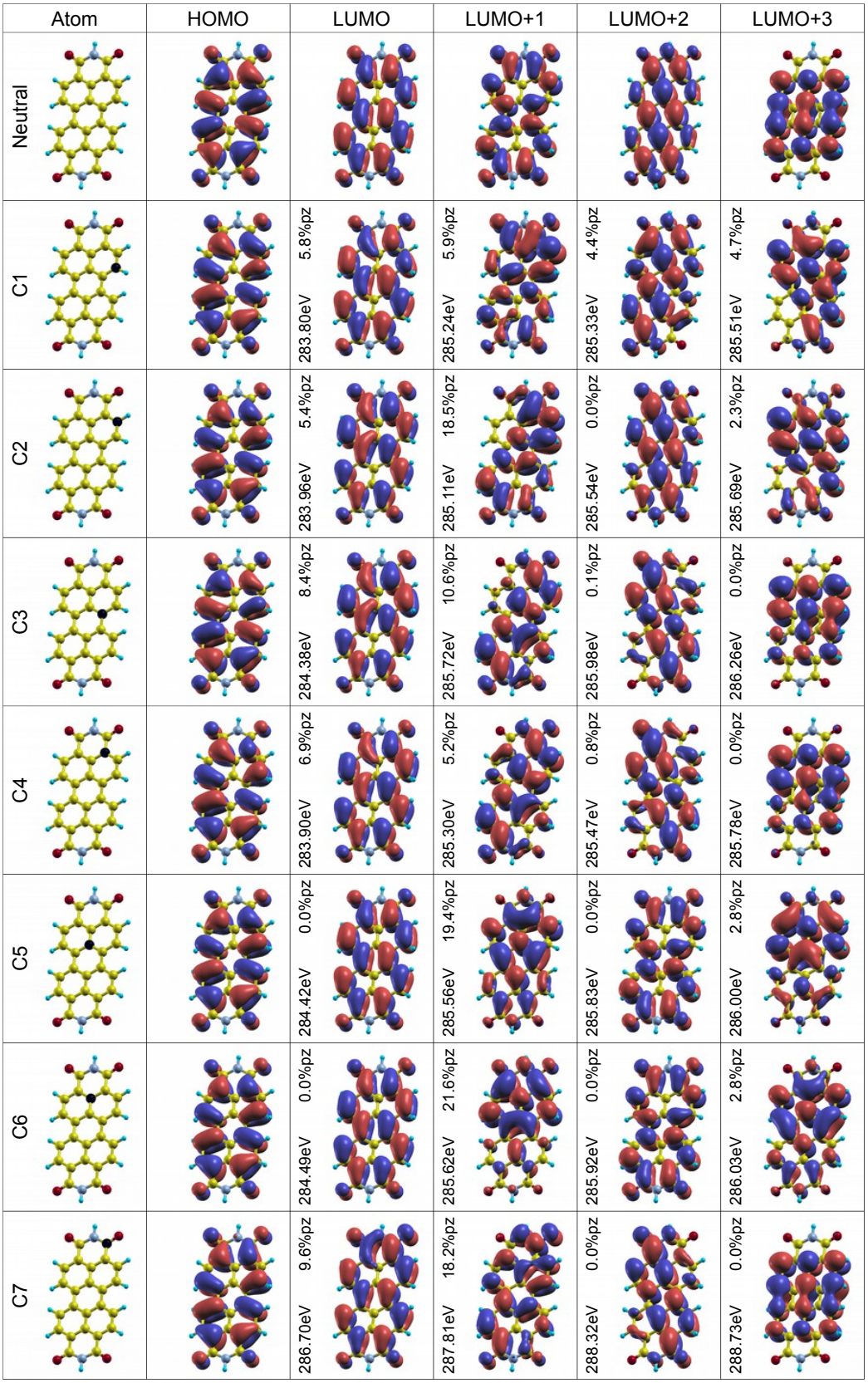
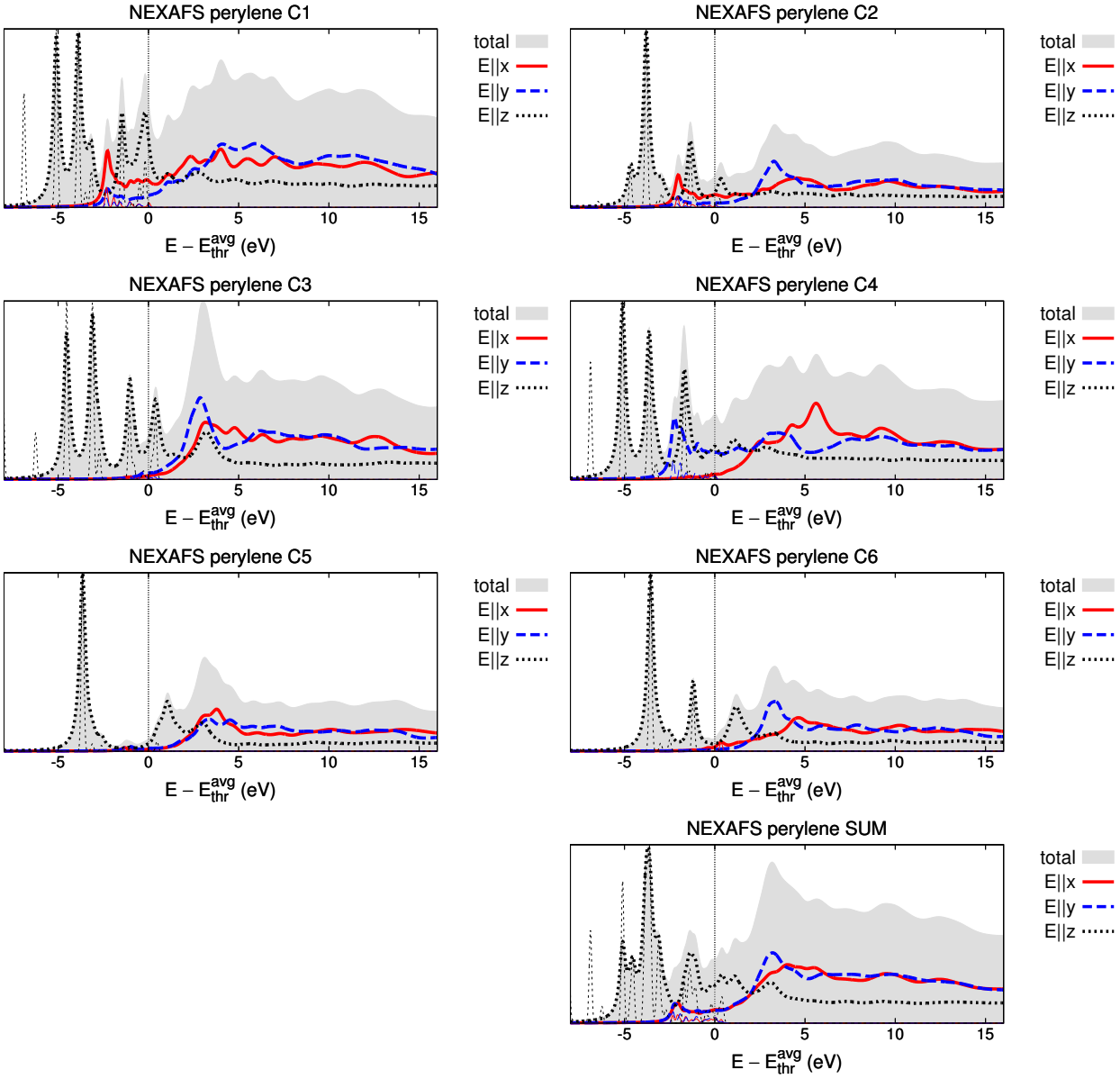

Atom
HOMO
LUMO
LUMO+1
LUMO+2
LUMO+3
Neutral
C1
284.15eV 10.1%pz
285.36eV 9.8%pz
285.77eV 0.8%pz
286.01eV 0.1%pz
C2
284.58eV 4.0%pz
285.45eV 19.9%pz
286.08eV 0.8%pz
286.31eV 1.5%pz
C3
284.72eV 10.6%pz
286.08eV 1.5%pz
286.15eV 9.3%pz
286.53eV 1.7%pz
C4
284.14eV 11.9%pz
285.50eV 1.2%pz
285.62eV 8.5%pz
285.99eV 1.3%pz
C5
284.82eV 0.0%pz
285.60eV 23.6%pz
286.14eV 1.1%pz
286.51eV 0.0%pz
C6
284.89eV 0.0%pz
285.69eV 21.8%pz
286.25eV 1.3%pz
286.60eV 0.0%pz




NEXAFS perylene C1
NEXAFS perylene C2
NEXAFS perylene C3
NEXAFS perylene C4
NEXAFS perylene C5
NEXAFS perylene C6
NEXAFS perylene SUM
total
E||x
E||y
E||z
-5
0
5
10
15
E – E$_{thr}^{avg}$ (eV)