# Supporting Information for Molecular Identification, Bond Order Discrimination and Apparent Intermolecular Features in Atomic Force Microscopy Studied with a Charge Density Based Method

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## S1 Computational details

### S1.1 First principles calculations

All the DFT calculations were carried out with the projector augmented-wave (PAW) method as implemented in VASP<sup>1</sup> with a 600 eV plane-wave cutoff, a  $10^{-6}$  eV accuracy for the electronic self-consistency loop and the PBE exchange and correlation (XC) functional<sup>2</sup> supplemented by vdW DFT-D3.<sup>3</sup> A  $3 \times 3 \times 1$  Monkhorst-Pack grid was used for the Brillouin zone integration. The dipole correction was applied to the z-direction in order to eliminate ES spurious interactions among the repeated unit cells. This is especially important when calculating the electrostatic potential of the sample.

Before calculating DFT tip-sample interaction curves, the geometrical positions of the molecules were obtained through DFT ionic relaxation using the conjugate gradient algorithm and a  $F_{\rm min} = 0.01 \text{ eV/Å}$  cutoff for the residual forces. The BreitfussinA molecule examined in the main text was relaxed on a 4-layer Cu(111) slab on a (14.51, 12.62, 18)Å<sup>3</sup> cell. The rest of the molecules were relaxed without a substrate.

For the tip-sample interaction calculations the substrate was eliminated and the molecules were frozen to their relaxed positions (on top of the substrate). In HR-AFM imaging with CO tips, the substrate usually only adds a small vdW background that does not change the overall contrast.<sup>4,5</sup> Notice that, in the presence of an important substrate-molecule charge transfer, this simplification could fail.

In order to reduce the spurious effects coming from interaction with image cells, a large vacuum is used on all the calculations. The N heteroatom six-membered rings were placed on a (13.06, 11.31, 18)Å<sup>3</sup> cell, the C60 molecule was placed on a (10.57, 11.57, 25)Å<sup>3</sup> cell, while the 8-hq dimer was placed on a (19.43, 16.82, 18)Å<sup>3</sup> cell.

#### S1.2 AFM simulations with the model

The charge density and the electrostatic potential of the tip and the sample were extracted on a uniform 3D mesh of  $\lambda \approx 0.075$  Å spacing from separate VASP<sup>1</sup> calculations. The force vs. distance as well as the images simulated with the method used the same cell size and probe (isolated CO molecule) as the DFT calculations (see section S1.1). For the simulation of maps with CO tilt, the probe position was relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm until the generalized gradients were less than  $5 \times 10^{-3}$  eV/Å.

In contrast with our previous model,<sup>5</sup> where the ES interaction was calculated from the overlap of the charge density of the tip and the ES potential of the sample and the SR from a sum of pairwise species-dependent Morse potentials, our current approach takes into account explicitly the details of the charge distribution of tip and sample in the calculation of ES and SR. This is important to describe accurately the strong cancellation between ES and SR revealed by the DFT calculations of the tip-sample interaction in molecular systems.<sup>5</sup> Although our previous method was already a significant improvement from pure pair–wise models based on parametrized Lennard–Jones potentials,<sup>6</sup> it still fails to address in a realistic way charge density effects such as bond–order discrimination,<sup>7</sup> needs system specific parameters that are species dependent and even the inclusion of ghost species<sup>5</sup> in order to reach DFT accuracy. The approach proposed here fixes these problems with just two SR parameters that, for a CO tip, show a very small variation for the different samples. Thus, with very little loss of accuracy, universal SR parameters can be used in the model eliminating the need of a system specific fit.



Figure S1: z-component of the electric field,  $E_z$ , at 3 Å from the molecule plane of the N atom 6-membered heterocyclic compounds and the benzene molecule. From left to right: benzene, pyridine, pyrazine, pyrimidine, 1,2,4-triazine and an s-triazine. Color code: red, negative values or repulsion to electrons; blue, positive values or electron attraction.



Figure S2: Force curves of the N atom 6-membered heterocyclic compounds. The sites are labelled in the corresponding molecular structures. CTR corresponds to the center of the hexagonal ring.



Figure S3: (Left panel) z-component of the electric field,  $E_z$ , at 3.2 Å from the top of the molecule of the C60 (red: negative values, corresponding to repulsion to electrons; blue: positive values or electron attraction). Force maps of the C60 relaxing the system with the total PES (central panel, labelled TOT) and with a PES that does not include the ES contribution (only the SR + vdW, right panel). These force maps confirm the crucial role of the SR interaction, that clearly discriminates the bond order (right panel). The ES contribution, in particular, the electrostatic lateral forces, shift the saddle lines of the SR+vdW-PES outward from the center, enhancing the difference in the apparent distances associated with single and double bonds. The probe relaxation in these images has been performed by minimizing the xy position of the probe in the static 2D PES including a lateral spring from the tip position.



Figure S4: Intra- and intermolecular sites used for the fitting of the two SR parameters in the study of the 8-hq tetramer (left) and dimer (right).



Figure S5: Force curves on a selection of the sites used for the fitting of the two SR parameters in the study of the 8-hq tetramer (left) and dimer (right). (see Fig. S4).



Figure S6: Simulated images of an 8-hq tetramer. (a) Force gradient map at a height of z = 3.04 Å in the area covered by the square in the inset of (d). The positions of the atoms involved in the hydrogen bonds are marked with empty circles: nitrogen (blue), oxygen (red), carbon (grey), hydrogen (black). Profiles in the intermolecular region -along the dashed line shown in the inset of (d), and calculated at a height z = 3.04 Å- for the tetramer and the four isolated molecules: (b) Charge density profiles. (c) Energy profiles for four isolated molecules (dashed orange line) and the tetramer (solid blue line) calculated with the model, and the one obtained for the tetramer from DFT calculations (dotted green line). (d) Force gradient profiles for four isolated molecules (dashed orange line) and the tetramer from DFT calculations (dotted green line). (d) Force gradient profiles for four isolated molecules (dashed orange line) and the tetramer (solid blue line) calculated with the model.



Figure S7: Differential charge density for an 8–hq tetramer. Induced charge redistribution by the H-bond formation calculated as the difference between the charge density of the 8–hq tetramer minus the sum of the charge densities of the four isolated molecules. The red color indicates positive differences, i.e. an increase of the electronic charge; blue color is associated with negative difference or electronic charge depletion.



Figure S8: Comparison of simulations performed with system-specific (SSP) and general (universal) parameters (GP) for the intermolecular region of the 8-hq dimer. Left: Energy profile in the intermolecular region along a line that transverse the two H-bonds (see balland-stick model) for three tip-sample distances Right: Force gradient images (proportional to  $\Delta f$ ) at z=2.97 Å. While the SSP parameters are important to describe accurately the subtle variation of the tip-sample interaction in the intermolecular region, AFM images with the GP parameters cannot be distinguished from the ones calculated with SSP parameters



Figure S9: Comparison of simulations performed with system-specific (SSP) and universal (general) parameters for the N atom 6-membered heterocyclic compounds. The force maps are calculated at z=3.1Å. For the six-membered rings with N heteroatoms, the results are quantitatively similar: the average RMSE increases only from 7.3 pN to 12.0 pN.

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