Supporting Information

Computational Study of Amino Mediated Molecular Interaction evidenced in N1s NEXAFS: 1,4-Diaminobenzene on Au (111).

Gabriele Balducci,^a Michele Romeo, ^a Mauro Stener, ^a Giovanna Fronzoni, ^a Dean Cvetko,^{b,c} Albano Cossaro, ^b Martina Dell'Angela,^b Gregor Kladnik, ^{b,c,d} Latha Venkataraman,^e Alberto Morgante, ^{b,d}

a Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L. Giorgieri 1, I-34127 – Trieste, Italy.

b CNR-IOM Laboratorio Nazionale TASC, Basovizza SS-14, km 163.5, I-34012 Trieste, Italy

c Department of Physics, Faculty of Mathematics and Physics, University of Ljubljana, SI-1000, Ljubljana,

Slovenia

d Department of Physics, University of Trieste, Trieste, Italy

e Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY

Theoretical methods

A. Geometry optimization at periodic level

Periodic first principle calculations were performed in the frame of density functional theory with the Kohn-Sham orbitals expanded in plane waves and the effects of atomic core regions accounted for by pseudopotentials. The Ouantum-Espresso suite of codes [1] was used as the practical implementation of this methodology. The adsorption of diaminobenzene on the (111) surface of gold was modeled with the slab method. A gold crystal slab with the open surface parallel to the (111) family of planes was set up by periodic repetition of a supercell consisting of 6 layers of Au atoms. The supercell was built with a conventional lattice parameter of 4.237Å obtained from a preliminar relaxation of bulk gold and in good agreement with the value obtained in a previous study under comparable conditions [2]. A vacuum region of 10 Å was added along the z axis (normal to the surface) in order to minimize spurious interactions between the upper and lower faces of successive images. After relaxation of the clean slab, one or two BDA molecules were placed on the exposed surface of the supercell, according to the adsorption configurations considered in this paper (see fig. S1). Ultrasoft pseudopotentials [3] were used throughout the calculations. The exchange-correlation part of the energy functional was modeled with the (spin-unpolarized) generalized gradient approximation (GGA), in the PBE parameterization [4]. Van der Waals interactions were accounted for by use of the vdW-DF functional, available in the Quantum-Espresso suite. The plane wave expansion of the crystalline orbitals was truncated at a cutoff energy of 25Ry and a corresponding cutoff of 250Ry was used for the expansion of the augmentation charge needed by the ultrasoft pseudopotential method. The first Brillouin zone was sampled at a regular $(4 \times 4 \times 2)$ grid of k points, built according to the Monkhorst and Pack recipe[5]. During structural relaxations, all coordinates were allowed to be refined. Convergence thresholds for geometry optimization were 1×10^{-4} Ry for total energy and 1×10^{-4} Ry for total energy ener 10-3 Ry/Å for the maximum force component acting on atoms.

B. Simulation of the NEXAFS spectra

The electronic structure of the finite clusters have been obtained by scalar relativistic (SR) selfconsistent field (SCF) Kohn-Sham (KS) calculations employing the gradient corrected Perdew- Wang exchange functional [6] and the Perdew correlation functional [7] using the Amsterdam Density Functional (ADF) program [8],[9]. Relativistic effects have been included at the SR level within the SR zero-order regular approximation (ZORA) formalism [10]. Different basis sets consisting of Slater-Type Orbital (STO) functions have been selected to calculate the N K-edge spectra of the adsorbed BDA, taken from the ADF database. The BDA molecule considered for the spectra calculation ("central BDA") has been described employing a QZ3P-3DIF basis set for the excited N atom and a TZP basis set for all the other atoms. The core orbital (N1s) of the second N atom has been treated by the Frozen Core (FC) technique (TZP.1s basis set). The use of diffuse functions on the excited atom allows for an improved representation of relaxation effects of the inner orbitals as well as for the description of the higher energy excitations contributing to the near-edge structures. The FC procedure ensures the localization of the core hole on the excited N atomic site. This basis set has been used also for the calculation of the free BDA NEXAFS spectrum. The N and C atoms of the side adsorbed BDA molecules have been described with a DZ - FC(1s) basis set, while the H atoms with a SZ basis set. The Au atoms of the cluster which directly interact with the N atoms of the BDA molecules selected for the spectra calculations have been described with a ZORA Triple Zeta Polarized basis set (TZ2P), with a FC up to 4f (TZ2P.4f); a ZORA TZP.4f set has been instead employed for the Au atoms interacting with the surrounding BDA molecules and a ZORA DZ.4f basis set for all the remaining Au atoms of the cluster. This choice results from several tests with different basis sets and allows to reduce the computational effort without losing accuracy. The DFT transition potential (TP) method [11] has been employed for the calculations of the N1s core excitation spectra. In the TP computational technique half an electron is removed from the 1s orbital of the excited N atom, relaxing all the orbitals until self-consistency is obtained. This scheme includes most of the relaxation effects following the core hole formation and provides a single set of orthogonal orbitals useful for the calculation of the transition moments. The oscillator strengths are calculated from the so-obtained TP relaxed orbitals via dipole transition moments: oscillator strengths for fixed in space molecule are calculated with the following expression:

$$f_{i \to f} = 2\omega_{if} n_i \left| \vec{\varepsilon} \cdot \left\langle \varphi_f^{TP} \right| \vec{r} \left| \varphi_i^{TP} \right\rangle \right|^2 \tag{1}$$

where n_i is the ground state occupation number of the initial core orbital, $\vec{\varepsilon}$ is the light polarization vector and φ^{TP} corresponds to TP orbitals. ω_{if} corresponds to the excitation energies which are obtained as the differences between the eigenvalue of the virtual orbital and that of the 1s orbital calculated with TP configuration. For randomly oriented molecules in gas phase the oscillator strength corresponds to the rotational average of expression (1):

$$f_{i \to f} = \frac{2\omega_{if} n_i}{3} \left| \left\langle \varphi_f^{TP} \middle| \vec{r} \middle| \varphi_i^{TP} \right\rangle \right|^2 \tag{2}$$

In the TP approach the energy of ionization threshold is obtained from the eigenvalue

$$E_{ion} = - \varepsilon_i^{TP} \quad (3)$$

The TP approach leads to a less attractive potential and the absolute transition energies are generally too large. In order to correct the NEXAFS energies, ΔKS (Δ SCF Kohn-Sham) calculations of the relaxed

ionization energies have been performed, allowing a full relaxation of the ionized core hole. The energy of the 1s⁻¹ ionic state is obtained from a *KS* unrestricted calculation. The TP excitation energies are then shifted with respect to the Δ IP value corresponding to [$\varepsilon_{1s}^{TP} - \Delta KS$].

The excitation spectrum at each non-equivalent N site of the adsorbed BDA is obtained as a single calculation, while the total N1s NEXAFS spectrum is obtained by summing up the different contributions. All the calculated spectral profiles have been convoluted by Gaussian functions of appropriate Full Width at Half Maximum (FWHM) value, which has been chosen referring to the N1s figures of the experimental spectra. The use of Gaussians functions to smooth calculated discrete lines allows to include on average and statistically all effects which can cause line broadening and facilitates the comparison with the experiments (see the corresponding figure captions for further details).



Figure S1 Perspective view of the supercells used for the periodic model of the tilted binding mode.

(A) simple *tilted* configuration; (B) *tilted-facing* configuration: to make the connection with the cluster used in the NEXAFS calculations clearer, the N1R and N1L nitrogen atoms have been indicated.

The flat phase

To simulate the molecules condition in the flat phase we setup a $\begin{vmatrix} 3 & 0 \\ 2 & 4 \end{vmatrix}$ surface unit cell containing a single BDA molecule. Coverage definition is not straightforward in this case: considering every Au atom as a possible adsorption site is not meaningful due to steric constraints. If we consider an adsorption site to be an Au atom with its hexagonal shell of nearest neighbors, then the coverage for this configuration is 1/4. We have considered two variants of this binding mode: the *on-top* variant, in which the two N atoms bind on top of two corresponding Au atoms of the surface, and the *hollow* variant, in which the two N atoms are positioned over two corresponding tetrahedral sites of the FCC structure. For the *on-top* configuration (see panels A, D of Fig. S2), we find equal Au–N distances of 3.07 Å, larger than the Au–N distance found for the tilted phase (2.92 Å). This can be explained with an unfavorable interaction of the phenyl ring with the surface, suggested by its slight outwards displacement , which gives the adsorbed molecule a small convexity (distance from the center of the phenyl ring to the Au surface: 3.47 Å). In the *hollow* variant (see panels B, E of Fig. S2), the BDA is even more weakly bound to the surface, with a distance of the N atoms from the center of the three Au atoms defining the hollow position of 3.34Å and 3.35Å; the distance from the center of the phenyl ring to the Au surface is equal to that of the on-top variant.



Figure S2

Perspective and top view of the supercells used for the periodic model of the flat binding mode. (A)(D): *on-top* configuration; (B)(E) *hollow* configuration; (C)(F) *H-bond on-top* configuration: to make the connection with the cluster used in the NEXAFS calculations clearer, the N1R and N1L nitrogen atoms have been indicated.

Similar to the tilted binding mode, we have probed any possible effect of H-bond formation also in this case. For this purpose, two BDA molecules have been arranged in the *flat ontop* configuration in a $\begin{vmatrix} 6 & 0 \\ 2 & 4 \end{vmatrix}$ surface unit cell, at a distance such that an H-bond could be established (see panels C, F of Fig. S2). After relaxation, the two N atoms not directly involved in the H-bond are found at equal distances of 3.02 Å from the corresponding Au atoms of the surface; the remaining two N atoms (the ones connected by the H-bond) are slightly moved away from the surface [Au – N distances: 3.14Å (N1L) and 3.09Å (N1R)]; an H-bond weaker than that found in the case of the "tilted-facing" configuration is indicated by a N – H distance of 2.84Å. For both the flat and the tilted phase we calculated the spectra for two different

polarizations of the electric field of the photon beam with respect to the surface, s and p, in order to have a direct comparison with the experimental spectra and investigate the origin of the observed dichroism.



Figure S3 View of the cluster models of p-diaminobenzene on Au(111)) employed for the N1s NEXAFS spectra calculations. Panel a): *on top flat* with one BDA on Au55 surface cluster; panel b): *H-bond on top flat* with two BDA on

Au66 surface cluster; panel c) *tilted* with seven BDA on Au52 surface cluster; panel d): *facing tilted* with eight BDA on Au48 surface cluster.

In the *on-top* configuration the N atoms of the BDA bind on top of two corresponding Au atoms of the surface; the quite long calculated distance between the N atoms and the surface (3.07 Å) describes a weak interaction, far from a bonding interaction. The cut cluster (panel a of Fig. S3) is large enough to accommodate only one BDA molecule, considering negligible the interaction with neighbour molecules in a lower coverage simulation. The calculated polarized spectra (reported in Fig. S4¹, together with the experimental data [12]) accordingly show very low intensity in the lower energy region (around 399 eV), where excitations to final orbitals largely localized on the surface are present with negligible contribution from N2p atomic functions. The intensity starts to increase beyond 401 eV where the final orbitals have predominant π^* (C=C) character; the N2p contributions mapped by the intensity are involved in antibonding interactions of the nitrogen lone pair with the π^* (C=C) ring orbitals and in the σ^* (N-H) orbitals. The intensity reaches a maximum in the p-pol spectrum around 402 eV due to a single transition towards a final MO with a main σ^* (N-H) character. This virtual MO has a large diffuse nature with a significant extension along the z direction which is probed by the p-polarization. The s-pol spectrum in this energy region acquires intensity from the rather large components of the σ^* (NH) orbitals in the xy plane. The excited states in the 403-405 eV energy range have a mixed Rydberg and σ^* (N-H) valence character; the final MOs mainly extend in the xy plane and are actually enhanced in the s-polarization with respect to the p polarization. The match with the experimental spectra is only partial for two main discrepancies: the double-peak shape of the main p-pol experimental structure which is represented as a

¹ All the theoretical spectra have been shifted in energy by -1.4 eV (-0.8 eV) for isolated (H-coupled) case to match the experimental data.

single peak by the theory and the more pronounced dichroic effects provided by the calculations with respect to the experiment. This behavior suggests that this on-top flat configuration is not effective to simulate the disposition of the molecules on the surface in the experimental low coverage conditions, some level of disorder is missing in the model and/or possible inter-molecular interactions. For the hollow variant of the flat configuration (Fig. S2) we cut a cluster analogous to that used for the *on-top flat* mode of adsorption; the calculated N1s spectra do not provide significant variations with respect to the *on-top* model, therefore we do not report the relative results. The effect of intermolecular interactions on the N1s spectra has been explored by means of the *H*-bond on-top model where pairs of BDA molecules can interact through two amino groups. The relative cut cluster is shown in Fig. S1 (panel b) and the calculated polarized spectra are compared with the experimental ones in Fig. S5. In this configuration there are four non-equivalent N atoms: in the sketch of the cluster reported in Fig. S5, the N1L and N1R labels indicate the nitrogen atoms of the two interacting amino groups while N2L and N2R labels refer to the two free amino groups. The match with the experiment is improved with respect to the simpler *on-top* model, in particular as concerns the appearance of a lower energy shoulder of the main peak in the p-pol spectrum, around 401.7 eV. This feature is present also in the s-pol spectrum and mainly derives from N1L and N1R transitions with σ^* (N-H) character. These final states are strongly localized on the hydrogen atoms of the two amino groups and extend in all the three directions giving rise to structures both in the p- and s-polarized spectra. The most evident dichroic effect in the theoretical spectra is associated to the strong peak located around 402.7 eV which dominate the p-pol spectrum; a correspondent intensity drop is present in the s-pol spectrum. All the N sites contribute to the p-pol peak; the transitions are due to final MOs where the N2p contributions participate to antibonding interactions with the π^* (C=C) ring orbitals as well as to the σ^* (N-H) antibonding interactions. The major extension of these final states along the z direction accounts for the enhanced intensity in the polarization normal to the surface. At higher energy a reverse of the intensity trend is observed with an increase in the s-pol spectrum and a decrease in the ppol one. The trend follows the nature of the transitions with mostly σ^* (N-H) character; the final MOs appear very diffuse and localized on the hydrogen atoms of the amino groups with major extension in the

xy plane. These results seem to indicate that in the experimental conditions of low coverage the molecules can accommodate almost parallel to the surface but a certain extent of disorder with possible intermolecular interactions have to be considered in the design of the adsorption geometry.



Figure S4. Calculated N-K edge polarized spectra of p-diaminobenzene in the *on-top flat* adsorption mode. Calculated lines are convoluted with Gaussian functions of FWHM= 0.8 eV. For each polarized spectrum the corresponding experimental profile is superimposed with appropriate energy shift to facilitate the comparison. The experimental spectra are reported on top of the figure together with the sketch of the cluster model employed for the spectra calculations.

Vertical dashed lines : Δ KS N1s ionization thresholds (eV) : 404.3 eV



Figure S5. Calculated N-K edge polarized spectra of p-diaminobenzene in the *on-top H-bond flat* adsorption mode. Black lines: total N1s spectrum; the calculated lines are convoluted with Gaussian functions of FWHM= 0.3 eV. Coloured lines representing the convolution of the four N non-equivalent sites are show in the insert; the spectral profiles have been convoluted with Gaussian functions of FWHM= 0.5 eV. For each calculated polarized spectrum the experimental profile is superimposed with appropriate energy shift to facilitate the comparison. The experimental spectra are reported on top of the figure together with the sketch of the cluster model employed for the spectra calculations.

Vertical dashed lines : ∆KS N1s ionization thresholds (eV) (N1L: 405 eV; N2L: 404.85 eV; N1R: 405.05 eV; N2R: 404.8 eV).

Coverage determination

The BDA coverage in molecular monolayers on Au(111) has been determined by the photoemission spectroscopy (XPS) intensities as reported in fig. S6. We have monitored both, the attenuation of the Au 4f XPS signal when the BDA overlayers are formed as well as the intensity of the C1s and N1s XPS signals belonging to the grown molecular film. We have estimated the electron inelastic mean free path [13] in the BDA layer as λ =13.5 Å, 8 Å and 5 Å for electron kinetic energy of 410 eV (Au 4f), 210 eV (C1s) and 95 eV (N1s), respectively. We therefore consistently determine the thickness of the flat BDA (tilted BDA) phase as 0.55 Å ± 0.05 Å (1.6 Å ± 0.05 Å).



Figure S6. N1s (left panel), C1s (middle panel) and Au4f (right panel) XPS for flat (grey curve) and tilted (blue curve) BDA phases. The spectra are taken with photon energy of 500 eV.

Molecular adsorption geometry from NEXAFS

Molecular adsorption geometry has been determined by polarization dependent NEXAFS measurements. We have performed C K-edge NEXAFS in two complementary experimental configuration in which the electric field vector of the incoming photons lies along the surface normal (p-pol) and in the surface plane (s-pol) and measured the NEXAFS signal intensity (I_p and I_s). According to NEXAFS selection rules the intensity of the C1s π^* transition is polarized with maximum intensity for electric field normal to the molecular aromatic ring and vanishes for electric field vector lying parallel to the ring. The opposite holds for C1s $\rightarrow \sigma^*$ transition, where the intensity vanishes for electric field normal to the aromatic ring. The average molecular angle θ relative to the surface is hence obtained from the ratio of the C1s $\rightarrow \pi^*$ intensity measured with two complementary polarizations as $\theta = \tan^{-1}\left(\sqrt{\frac{2I_s}{I_p}}\right)$ [14]. Fig. S7 Shows a set of Carbon K-edge NEXAFS for "gas phase", "multilayer phase", "tilted monolayer" and "flat monolayer" phase (top to bottom panels) Light and dark shaded signals denote NEXAFS measured in s-pol and p-pol configurations respectively. We measure $\theta = 48^\circ \pm 5$ for the tilted and $\theta < 5^\circ$ for the flat monolayer phase.



Figure S7. Carbon K-edge NEXAFS for gas, multilayer, tilted Ml and flat ML phases (top to bottom). Light and dark shaded signals denote NEXAFS measured in s-pol and p-pol configurations respectively. Schematical models of the BDA molecule, multilayer arrangement and molecular adsorption geometry are shown aside.

P-toluidine / Au(111) - a case of a monoamine molecule adsorbed on Au(111)



Figure S8 Carbon 1s (left panel) and Nitrogen 1s (middle panel) XPS of p-toluidine in gas phase (brown color), tilted monolayer (blue color) and flat monolayer on Au(111) (green color). Spectral decomposition of the C1s peak in the gas phase shows two main components at 285 eV and 286.1 eV with the latter assigned to the C next to amine end [15]. Spectra of the monolayer films evidence an overall ~0.5 eV (~1.0 eV) shift to lower binding energies for the tilted (flat) phase, relative to the multilayer phase, due to screening effects in the proximity of the Au substrate [16]. N1s XPS peak for the tilted (blue color) and flat phase (green color) displays identical shift to lower binding energies (0.6 eV) relative to the gas phase (brown color), evidencing that N in both monolayer phases is similarly coupled to the Au(111). Inset: sketch of p-toluidine molecule (C7H9N).

Right panel: Carbon K-edge NEXAFS of p-toluidine for gas (brown curve), tilted monolayer (blue color) and flat monolayer (green color) on Au(111). P-pol and s-pol refer to experimental geometries with photon electric field perpendicular and parallel to the substrate, respectively. From the intensity ratios $I_s/I_p = \frac{1}{2} tg^2(\theta)$ we obtain average molecular orientation [14] from the surface $\theta = 57^{\circ} \pm 2^{\circ} (20^{\circ} \pm 5^{\circ})$ for the tilted (flat) phase.

References.

[1] Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli D.; Chiarotti,

G.L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: a Modular and Open-Source Software

Project for Quantum Simulations of Materials. J.Phys.Condens. Matter 2009, 21, 395502-1 – 395502-19.

URL http://www.quantum-espresso.org.

[2] Le D., Aminpour M., Kiejna A., Rahman T. S. The role of Van der Waals interaction in the tilted binding of amine molecules to the Au (111) surface. J.Phys.Condens. Matter **2012**, 24(22).

[3] Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism., *Phys.Rev. B* **1990**, 41, 7892-7895.

[4] Perdew J. P., Burke K., Ernzerhof M. Generalized gradient approximation made simple. *Phys.Rev.Lett.*, 1996, 77(18):3865–3868,

[5] Pack, J.P. Special Points for Brillouin-Zone Integrations. *Phys.Rev. B* **1976**, 13, 5188-5192.

[6] Perdew, J.P. Density-Functional Approximation for the Correlation Energy of the InhomogeneousElectron Gas *Phys. Rev. B* 1986, 33, 8822-8824.

[7] Perdew, J. P. Erratum: Density-Functional Approximation for the Correlation Energy of the

Inhomogeneous Electron Gas Phys. Rev. B 1986, 34, 7406-7406.

[8] Baerends, E.J.; Ellis, D.E.; Roos, P. Self-Consistent Molecular Hartree—Fock—Slater Calculations I. The Computational Procedure. *Chem. Phys.* **1973**, 2, 41-51.

[9] Fonseca Guerra, C.; Snijders, J.G. ; te Velde, G.; Baerends, E.J. Towards an Order-N DFT Method. *Theor. Chem. Acc.* **1998**, 99, 391-403.

[10] van Lenthe, E.; Baerends, E. J.; Snijders, J. G. J. Chem. Phys. 1993, 99, 4597-4610.

[11] Triguero, L.; Pettersson, L.G.M.; Ågren, H. Calculations of Near-Edge X-Ray-Absorption Spectra of Gas Phaseand Chemisorbed Molecules by Means of Density-Functional and Transition-Potential Theory. *Phys. Rev. B*, **1998**,58, 8097-8110.

[12] Kladnik, G.; Cvetko, D.; Batra, A.; Dell'Angela, M.; Cossaro, A.; Kamenetska, M.; Venkataraman L.;
Morgante, A., Ultrafast Charge Transfer through Noncovalent Au–N Interactions in Molecular Systems, *The Journal of Physical Chemistry C*, **2013**, *117* (32), 16477-16482

[13] Cumpson, P.; Seah, M. Elastic Scattering corrections in AES, XPS. II Estimating attenuation lengthts and conditions required for their valid use in Overlayer/Substrate experiments, *Surface and Interface Analysis* **1997**, 25, 430-446.

[14] J.Stohr, NEXAFS spectroscopy, Springer Series in Surface Science, 1992, Vol.25, Springer Science & Business Media, 1992.

[15] Solomon J.L.; Madix R.J.; Stohr J. Orientation and absolute coverage of benzene, aniline, and phenol on Ag(110) determined by NEXAFS and XPS. *Surface Science*, **1991**, 255, 12-30

[16] Smith, N. V.; Chen, C. T.; Weinert, M. Phys. Rev. B 1989,40(11), 7565–7573