Supporting Information: On the decoupling of molecules at metal surfaces

Xiaosheng Yang,[†,‡] Ina Krieger,[¶] Daniel Lüftner,[§] Simon Weiß,[†,‡] Timo Heepenstrick,[¶] Michael Hollerer,[§] Philipp Hurdax,[§] Georg Koller,[§] Moritz Sokolowski,[¶] Peter Puschnig,[§] Michael G. Ramsey,[§] F. Stefan Tautz,[†,‡] and Serguei Soubatch[*,†,‡]

†*Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany*
‡*Jülich Aachen Research Alliance (JARA)–Fundamentals of Future Information Technology, 52425 Jülich, Germany*
¶*Institut für Physikalische und Theoretische Chemie, Universität Bonn, 53115 Bonn, Germany*
§*Institute of Physics, University of Graz, NAWI Graz, 8010 Graz, Austria*

E-mail: s.subach@fz-juelich.de

Sample Preparation

A bilayer of MgO(100) was grown on Ag(100) following the recipe from Pal *et al.*[S1] (*cf.* Ref. S2 for details). A $(\sqrt{2}\times 2\sqrt{2})$R45°-2O Cu(100) missing-row reconstruction was prepared by exposing the Cu(100) surface to 750 L of O_2 at the temperature of 500 K[S3–S5] and confirmed by the appearance of $\frac{1}{4}$ superstructure reflexes in the low-energy electron diffraction (LEED) pattern. Subsequently, a submonolayer of PTCDA was deposited from a pre-calibrated evaporator in ultra-high vacuum conditions onto the two surfaces mentioned above which were kept at room temperature.

Photoemission Experiments

The photoemission experiments were carried out using a toroidal electron analyzer[S6] (photon energy $h\nu = 21$ eV, angle of incidence $\alpha = 40°$) at the BESSY II storage ring, Helmholtz-Zentrum Berlin (HZB), Germany. This type of electron analyzer detects photoemission at polar angles between −85° and 85° simultaneously in the plane of incidence. The energy distribution curves were generated from measured $E(k_{||})$ band maps along chosen azimuths where maxima or minima of molecular orbitals are expected by integrating the photoemission intensity in a $k_{||}$ range from 1.1 Å^{-1} to 1.8 Å^{-1} as shown in Fig. 1c,e in the main text.

Normal Incidence X-ray Standing Wave Experiments

The NIXSW experiments were performed at the beamline I09 of the Diamond Light Source, Didcot, UK. Photoelectron yield data were fitted with the program Torricelli.[S7] The yield signal was integrated over the acceptance angle of analyzer. Angle-dependent non-dipolar correction parameters[S8–S10] were calculated for a weighted average of the detection angles (74.8°). The energy of the (200) Bragg reflection in the experimental geometry with a 3.5° tilt angle against normal incidence was 3436 eV. Coherent positions P_c carries information about the height of the corresponding atoms above the crystal Bragg planes, while coherent fractions F_c specifies their vertical scatter. Coher-

Table S1: Coherent positions P_c and coherent fractions F_c from the NIXSW analysis and adsorption heights d of different chemical species with respect to the topmost copper layer. The adsorption height d with respect to the Bragg plane is given by $(n + P_c)d_{200}$ where $n = 0$ for O_{surf}, $n = 1$ for O_{an}, C_1, and C_{234}, $n = 2$ for O_{carb}.

	P_c	F_c	d(Å)
	O/Cu(100)		
O_{surf}	0.180(4)	1.16(7)	0.19(1)
	PTCDA/O/Cu(100)		
O_{surf}	0.18(1)	1.13(3)	0.18(1)
O_{carb}	0.01(1)	0.41(1)	3.49(2)
O_{an}	0.96(1)	0.52(2)	3.41(2)
C_1	0.92(2)	0.73(8)	3.33(2)
C_{234}	0.927(3)	0.79(1)	3.342(5)

ent positions and coherent fractions, averaged over three data sets, are given in Table S1.

Density Functional Theory Calculations

Two types of calculations within the framework of DFT were performed: (1) for the gas-phase PTCDA molecule the ABINIT code[S11] was used. The simulated momentum maps of the gas-phase molecule were obtained as the Fourier transforms of the respective Kohn–Sham orbitals.[S12] (2) for PTCDA monolayers adsorbed on the oxygen-reconstructed Cu(100) as well as on the bare Cu(100) surface, the VASP code[S13,S14] was used.

A repeated slab calculation was performed, where the metallic substrate was modeled by five metallic layers and a vacuum layer of ∼15 Å was added between the slabs. To avoid spurious electrical fields, a dipole layer was inserted in the vacuum region.[S15] In both cases the exchange-correlation effects have been calculated with the generalized gradient approximation (GGA).[S16] We used a Monkhorst–Pack $3 \times 3 \times 1$ grid of k-points[S17] and the projector augmented wave approach,[S18] allowing a relatively low kinetic-energy cutoff of ∼500 eV.

The super cell geometry has been constructed according to the experimental LEED structure of the PTCDA/Cu(100) interface.[S19] On both surfaces, the adsorption height has been fixed to the experimentally obtained value of PTCDA on the oxygen-reconstructed Cu(100) surface (3.34 Å). The vdW-surf method according to Tkatchenko *et al.*[S20,S21] was applied to account for van der Waals interactions.

References

(S1) Pal, J.; Smerieri, M.; Celasco, E.; Savio, L.; Vattuone, L.; Rocca, M. *Phys. Rev. Lett.* **2014**, *112*, 126102.

(S2) Hollerer, M.; Lüftner, D.; Hurdax, P.; Ules, T.; Soubatch, S.; Tautz, F. S.; Koller, G.; Puschnig, P.; Sterrer, M.; Ramsey, M. G. *ACS Nano* **2017**, *11*, 6252–6260.

(S3) Zeng, H.; McFarlane, R.; Mitchell, K. *Surf. Sci.* **1989**, *208*, L7–L14.

(S4) Wuttig, M.; Franchy, R.; Ibach, H. *Surf. Sci.* **1989**, *213*, 103–136.

(S5) Kittel, M.; Polcik, M.; Terborg, R.; Hoeft, J.-T.; Baumgärtel, P.; Bradshaw, A.; Toomes, R.; Kang, J.-H.; Woodruff, D.; Pascal, M.; Lamont, C.; Rotenberg, E. *Surf. Sci.* **2001**, *470*, 311–324.

(S6) Broekman, L.; Tadich, A.; Huwald, E.; Riley, J.; Leckey, R.; Seyller, T.; Emtsev, K.; Ley, L. *J. Electron Spectrosc. Relat. Phenom.* **2005**, *144-147*, 1001–1004.

(S7) Bocquet, F.; Mercurio, G.; Franke, M.; van Straaten, G.; Weiß, S.; Soubatch, S.; Kumpf, C.; Tautz, F. *Comput. Phys. Commun.* **2018**, in press.

(S8) Fisher, C. J.; Ithin, R.; Jones, R. G.; Jackson, G. J.; Woodruff, D. P.; Cowie, B. C. C. *J. Phys.: Condens. Matter* **1998**, *10*, L623.

(S9) van Straaten, G.; Franke, M.; Bocquet, F. C.; Tautz, F. S.; Kumpf, C. *J. Electron Spectrosc. Relat. Phenom.* **2018**, *222*, 106–116.

(S10) Weiß, S.; Krieger, I.; Heepenstrick, T.; Soubatch, S.; Sokolowski, M.; Tautz, F. S. *Phys. Rev. B* **2017**, *96*, 075414.

(S11) Gonze, X.; Amadon, B.; Anglade, P.-M.; Beuken, J.-M.; Bottin, F.; Boulanger, P.; Bruneval, F.; Caliste, D.; Caracas, R.; Côté, M.; Deutsch, T.; Genovese, L.; Ghosez, P.; Giantomassi, M.; Goedecker, S.; Hamann, D.; Hermet, P.; Jollet, F.; Jomard, G.; Leroux, S.; Mancini, M.; Mazevet, S.; Oliveira, M.; Onida, G.; Pouillon, Y.; Rangel, T.; Rignanese, G.-M.; Sangalli, D.; Shaltaf, R.; Torrent, M.; Verstraete, M.; Zerah, G.; Zwanziger, J. *Comput. Phys. Commun.* **2009**, *180*, 2582 – 2615.

(S12) Puschnig, P.; Berkebile, S.; Fleming, A. J.; Koller, G.; Emtsev, K.; Seyller, T.; Riley, J. D.; Ambrosch-Draxl, C.; Netzer, F. P.; Ramsey, M. G. *Science* **2009**, *326*, 702–706.

(S13) Kresse, G.; Hafner, J. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *47*, 558–561.

(S14) Kresse, G.; Joubert, D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(S15) Neugebauer, J.; Scheffler, M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 16067–16080.

(S16) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(S17) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1976**, *13*, 5188–5192.

(S18) Blöchl, P. E. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953–17979.

(S19) Gärtner, S.; Fiedler, B.; Bauer, O.; Marele, A.; Sokolowski, M. M. *Beilstein J. Org. Chem.* **2014**, *10*, 2055–2064.

(S20) Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.

(S21) Ruiz, V. G.; Liu, W.; Zojer, E.; Scheffler, M.; Tkatchenko, A. *Phys. Rev. Lett.* **2012**, *108*, 146103.