

Charged and Metallic Molecular Monolayers through Surface-Induced Aromatic Stabilization

G. Heime^{*1}, S. Duhm^{§,2}, I. Salzmann¹, A. Gerlach³, A. Strozecka⁴, J. Niederhausen¹, C. Bürker³, T. Hosokai^{3,5}, I. Fernandez-Torrente⁴, G. Schulze⁴, S. Winkler^{1,6}, A. Wilke¹, R. Schlesinger¹, J. Frisch¹, B. Bröker¹, A. Vollmer⁶, B. Detlefs⁷, J. Pflaum⁸, S. Kera⁹, K. J. Franke⁴, N. Ueno⁹, J. I. Pascual^{4,†}, F. Schreiber³, and N. Koch^{1,6}

¹ *Institut für Physik, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 6, D-12489 Berlin, Germany;*

² *Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, P.R. China;*

³ *Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, D-72076, Tübingen, Germany;*

⁴ *Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany;*

⁵ *Department of Materials Science and Technology, Iwate University, 4-3-5 Ueda, Morioka, Iwate 0208551, Japan;*

⁶ *Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany;*

⁷ *European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, BP 220, 38043 Grenoble Cedex 9, France;*

⁸ *Experimental Physics VI, University of Würzburg and ZAE Bayern, 97074 Würzburg, Germany;*

⁹ *Graduate School of Advanced Integration Science, Chiba University, Chiba 263-8522, Japan.*

^{*} Email: georg.heimel@physik.hu-berlin.de

[§] Email: duhm@suda.edu.cn

[†] Present address: *CIC nanoGUNE, 20018 Donostia-San Sebastian and Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain.*

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A. Low-temperature scanning-tunnelling microscopy

The lateral adsorption structure of P2O and P4O on Au(111) and Cu(111) was determined by scanning-tunnelling microscopy (STM). The Au(111) and Cu(111) single-crystal surfaces were cleaned and prepared under ultra-high vacuum (UHV) conditions by repetitive cycles of sputtering and annealing, resulting in atomically flat surfaces. Submonolayer coverages of the respective molecules were then deposited onto these substrates in the same UHV experimental setup at room temperature using a custom-made Knudsen cell. The pre-covered surfaces were then cooled down and inserted into the cold (4.5 K) STM for the microscopy studies. The scanning conditions used to obtain the images shown in Fig. S1 were $I = 1$ nA, $U = 1.3$ V for P2O/Au(111); $I = 0.1$ nA, $U = 1$ V for P2O/Cu(111); $I = 0.3$ nA, $U = 0.8$ V for P4O/Au(111); and $I = 1.2$ nA, $U = 1$ V for P4O/Cu(111) with U denoting the sample bias. The molecules are identified by their elongated shape in the empty-state images shown in Figure S1. The large-scale $23 \times \sqrt{3}$ herringbone reconstruction^{S1-4} of the underlying Au(111) substrate (not shown) permits to unambiguously determine their orientational alignment. The derived structural models are shown next to the STM images in Fig. S1 and the unit-cell parameters are listed in Table S1.

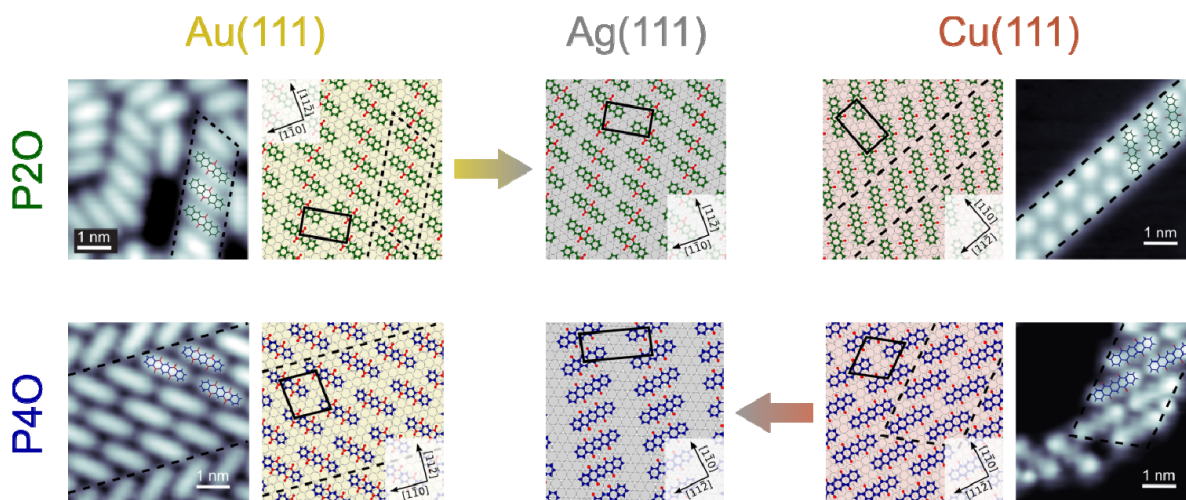


Figure S1 | Experimental STM images and deduced structural models used in periodic DFT calculations. The STM images for P2O and P4O on Au(111) and Cu(111) yield the respective structural models (unit cells indicated as black rhomboids). Equivalent areas in the STM images and the models are outlined by black dashed lines. For P2O, the structural model on Ag(111) was chosen to yield the same inter-molecular packing as on Au(111), where P2O also interacts only weakly with the surface. For P4O, the structural model on Ag(111) was chosen to allow the same registry of the oxygen atoms interacting with the surface as on Cu(111), without introducing improbably small inter-molecular distances.

Table S1 | Unit-cell parameters deduced from the STM images and used in periodic DFT calculations. Lengths and angles are derived from the periodicity of the structural models in Fig. S1 and literature values for the lattice constants of gold (4.08 Å), silver (4.09 Å), and copper (3.61 Å).

	Au(111)	Ag(111)^a	Cu(111)
	<u>p(3×3√3)</u>	<u>p(3×3√3)</u>	<u>p(2√3×6)R30°</u>
P2O	<i>a</i> = 8.7 Å	<i>a</i> = 8.7 Å	<i>a</i> = 8.8 Å
	<i>b</i> = 15.0 Å	<i>b</i> = 15.0 Å	<i>b</i> = 15.3 Å
	<i>γ</i> = 90.0°	<i>γ</i> = 90.0°	<i>γ</i> = 90.0°
	<u>p(4×√19)</u>	<u>p(√7×√43)R40.9°</u>	<u>p(√19×√19)R36.6°</u>
P4O	<i>a</i> = 11.5 Å	<i>a</i> = 7.7 Å	<i>a</i> = 11.1 Å
	<i>b</i> = 12.6 Å	<i>b</i> = 19.0 Å	<i>b</i> = 11.1 Å
	<i>γ</i> = 96.6°	<i>γ</i> = 86.7°	<i>γ</i> = 106.8°

^a Unit cells chosen to yield similar packing as P2O on gold and similar registry as P4O on copper.

Bending of the molecular carbon backbones on the surface

Our van der Waals corrected^{S5} DFT calculations yield essentially flat molecular carbon backbones in all cases with the exception of P2O on Cu(111). Even there, as shown in Figure S2, the bending is minimal. This is in contrast to previous reports^{S6} for P2O and P4O on Cu(111), where significantly distorted backbones have been reported. We attribute this discrepancy to the fact that metal-molecule van der Waals interaction has not been taken into account in the DFT calculations performed there. As the experimental STM results reported in Ref. [S6] are in good agreement with our own findings (Fig. S1), we suggest that the observed intra-molecular contrast is predominantly of electronic nature in the case of P4O on Cu(111) and, at least in part, also for P2O.



Figure S2 | Molecular structures on Cu(111) optimized with van der Waals corrected DFT. **a**, Side view of DFT optimized P2O on Cu(111) including metal-molecule van der Waals interaction^{S5}. **b**, Same for P4O on Cu(111).

B. Normal incidence X-ray standing waves experiments

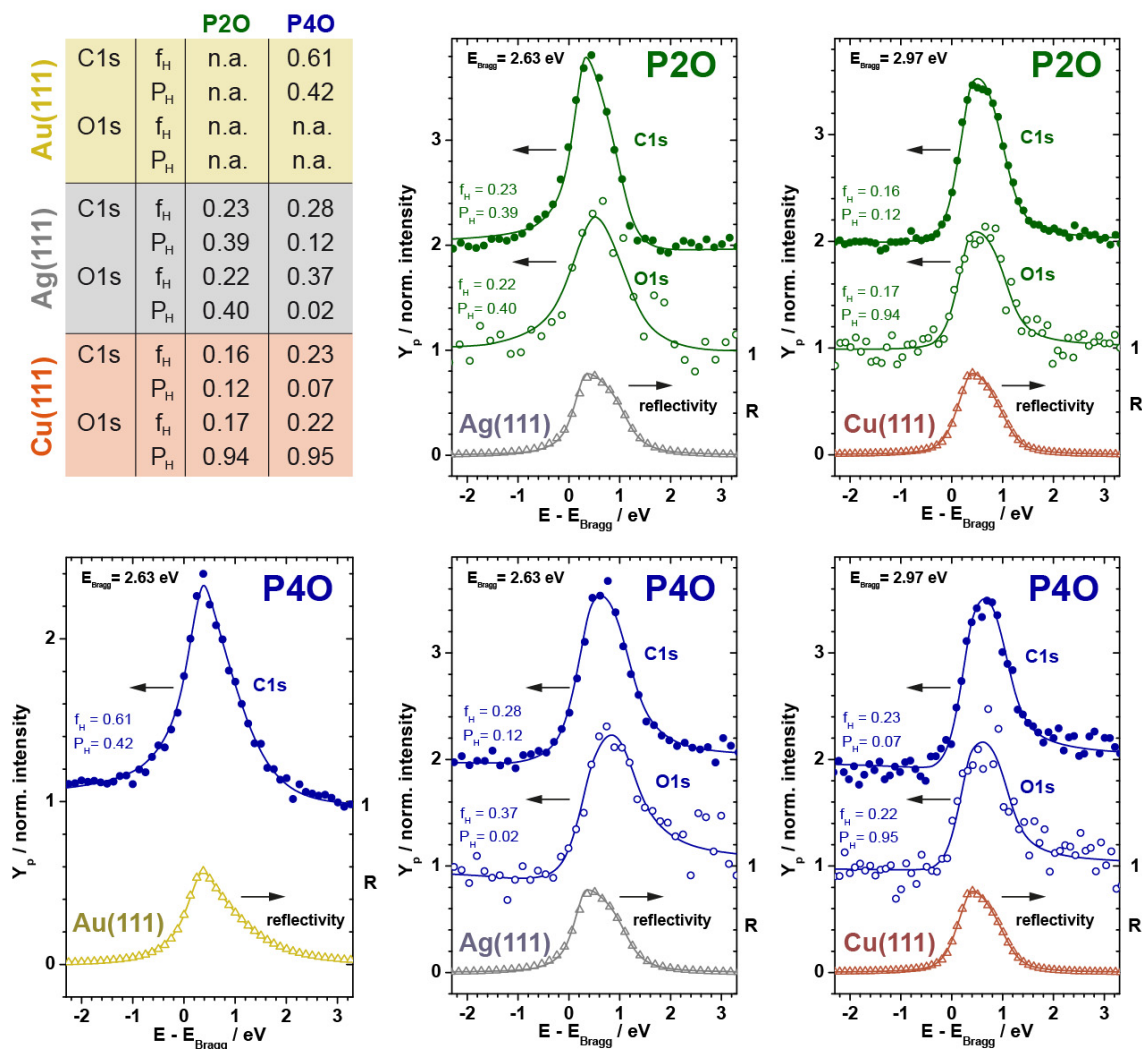


Figure S3 | NIXSW data, fits, and fitting results obtained on the first-order Bragg reflection of the substrates. Photoelectron yield (Y_p) and reflectivity (R) as a function of the relative photon energy ($E - E_{\text{Bragg}}$) for P2O and P4O on all three coinage-metal surfaces. Symbols correspond to the experimental data and lines to the least mean square fits. Curves are vertically shifted for the sake of clarity. The table summarizes the coherent fractions (f_H) and the coherent positions (P_H) for the carbon and oxygen signals, respectively.

C. Surface-induced aromatic stabilisation as general feature across molecular architectures

In this section we discuss the applicability of the mechanism of surface-induced aromatic stabilisation, established for P2O and P4O in the main manuscript, on other systems, where a (partial) filling of the LUMO on certain metal substrates has been reported in literature. Prior to delving into conceptually different molecular architectures, we note that a structurally very similar molecule, octafluoro-anthraquinone (FAQ) indeed appears to exhibit a (partially) filled LUMO on Ag(111) surfaces as well, possibly already on Au(111)^{S7}.

C.1 PTCDA and NTCDA

The certainly most studied molecule in the present context is 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA)^{S8-15}, shown in Figure S4a. On Au(111), where an adsorption height typical for weak physisorption is found^{S8-10}, no LUMO filling occurs. In contrast, on Ag(111) and Cu(111), a bent adsorption geometry and a considerably reduced adsorption height accompany a marked reduction of the molecular gap compared to the bulk material^{S13} and a substantial filling of the (former) LUMO in the monolayer^{S8-12}. As this is complemented by differential mono- to multilayer shifts of the carbon and oxygen core levels^{S9,14,15}, all signs of surface-induced aromatic stabilisation as found and discussed for P2O and P4O in the main text appear to be present for PTCDA as well as for its smaller analogue 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA)^{S15-20}. Based on essentially the same rationale as we followed in the main text (Fig. 4), it has been argued that these molecules re-hybridise on the surface, tending towards a quinoidal form (red in Fig. S4a) upon LUMO filling on the surface^{S10,11,21}.

However, neither has this been related to an *increase* in the extent of the conjugated π -electron system, nor has this been strictly correlated with the observed *decrease* of the (former) molecular gap upon LUMO filling on the surface. Rather than in the fully quinoidal configuration, the former becomes more apparent when considering a 1:1 superposition of the free-molecule and the fully quinoidal mesomeric forms (Fig. S4a), which reveals that, on the surface, π -conjugation now extends from the perylene (naphthalene) core over the carboxy groups into the metal. The resulting increase in the extent of the π -electron system becomes even more apparent in the dianionic resonance structure, which can be thought of exhibiting zwitterionic character on the carboxylic anhydrides (Fig. S4a). As also the resonance structures responsible for the bent adsorption geometries can be drawn in analogy to P2O and P4O, the very same mechanism of surface-induced aromatic stabilisation might indeed be operative for PTCDA on Ag(111) and Cu(111), for NTCDA, and, potentially, also for the related 3,4,9,10-perylene-tetracarboxylic-diimide (PTCDI) and NTCDI.

We note here that a more physical model for some aspects of the observed mono- to multilayer changes in the XPS spectra of PTCDA and PTCDI has very recently been proposed^{S15}, which does not, however, take into account possible changes to their structure and chemical nature upon (partial) LUMO filling. It is interesting to see that two more molecules, 3,3',4,4'-benzene-tetracarboxylic-dianhydride (BTCDA) and BTCDI, which have carefully been investigated in that study on Ag(111), are also potentially susceptible to surface-induced aromatic stabilisation (Fig. S4b). Whether this is, in fact, the case or not will be easier to judge once more experimental data is available, ideally also on Cu(111).

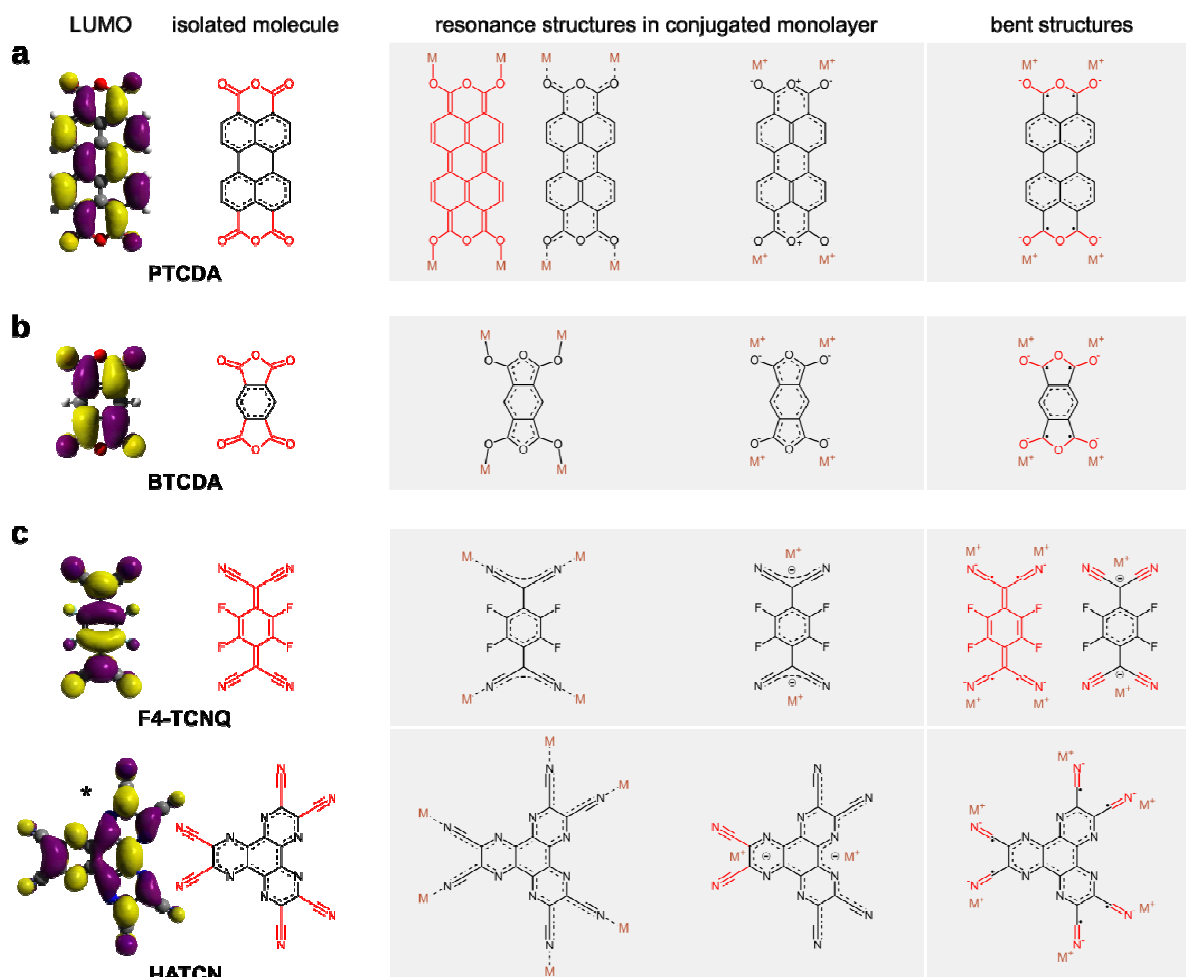


Figure S4 | Surface-induced aromatic stabilisation in metallic molecular monolayers reported in literature. a, Calculated LUMO wave functions as well as PTCDA resonance structures that are dominant in the free molecule and on those metal surfaces where LUMO filling occurs. **b,** Calculated LUMO wave functions as well as BTCDA resonance structures that are dominant in the free molecule and if LUMO filling were to occur on certain metal surfaces. **c,** Calculated LUMO wave functions as well as F4-TCNQ and HATCN resonance structures that are dominant in the free molecules and on those metal surfaces where LUMO filling occurs, respectively. As the LUMO of HATCN (*) is twofold degenerate, the (unique) HOMO of the anion is shown instead. Compare to Fig. 4 in the main manuscript and see accompanying text in the Supplementary Information for details.

C.2 F4-TCNQ and HATCN

Both 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ)^{S22-24} and its non-fluorinated analogue TCNQ^{S25} have been seen to adsorb in a bent geometry on several metal surfaces, where an appreciable filling of the LUMO and telltale differential shifts in the XPS spectra^{S22} are apparent. That these molecules tend towards an aromatic structure on the surface and that their (di)anionic resonance structures (Fig. S4c, far right) are responsible for the bent adsorption geometry has been reported by several authors in the past^{S23-25}.

What has not been considered so far, however, is that this re-hybridisation of the molecule leads to a significant increase in the overall degree of π -conjugation and to a lowering of the molecular gap as well as the LUMO, which allows overcoming Fermi-level pinning also for this class of acceptors. Note that, in contrast to P4O, only two metal-molecule single bonds (or four half, *i.e.*, dashed bonds)

lead to a meaningful aromatic and π -conjugated resonance structure for the covalently bonded mesomeric form (Fig. S4c, center). The very same mechanism of surface-induced aromatic stabilisation is likely to be operative also for 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ)^{S26} and, as shown at the bottom of Fig. S4c, also for hexaazatriphenylene-hexacarbonitrile (HATCN)^{S27,28}, for which LUMO filling on silver has been reported and calculations indicate a slightly bent adsorption geometry (at least in the flat-lying monolayer phase)^{S27}. The asterisk (*) in Fig. S4c denotes that the LUMO of HATCN is twofold degenerate and, therefore, no unique wave function can be plotted for the neutral molecule. To single out a unique linear combination of the two degenerate LUMOs, we therefore chose to plot the HOMO of the HATCN anion instead.

C.3 Estimating the effect of surface-induced aromatic stabilisation in electron acceptors

To estimate an upper limit for the effect of surface-induced aromatic stabilisation on the fundamental gap and the LUMO energies of the molecules where it appears applicable, we followed the procedure outlined in Fig. S5. Starting from the optimised geometries of the free molecules (A), hydrogen atoms were attached to the keto oxygens, carboxylic oxygens, or to the cyano nitrogens, and the geometry was re-optimised, leading to a molecular structure that reflects the surface-induced re-hybridisation upon LUMO filling. Subsequently, the hydrogen atoms were again removed and the resulting electronic structure (B) was compared to that of the free molecule in its equilibrium geometry (A).

The numerical results of this procedure are reported in Table S2 for the molecules discussed in the main text and in Fig. S4 above. The molecular gap is significantly reduced (by up to ~3 eV) due to surface-induced aromatic stabilisation. Even more striking is the finding that the reduction of the gap is not symmetric but that the LUMO is brought down more in energy than the HOMO is pushed up, lending further support to the notion that the re-hybridisation of the molecules upon LUMO filling indeed provides the mechanism needed to overcome Fermi-level pinning.

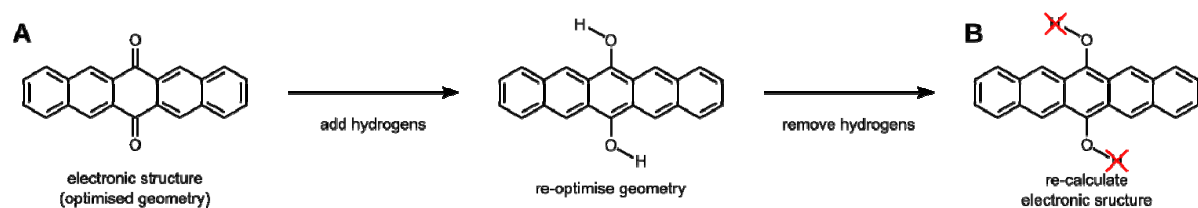


Figure S5 | Schematic of the computational procedure employed to estimate an upper limit of the impact of the geometry changes resulting from surface-induced aromatic stabilisation on molecular energy levels. Step **A** is simply calculating the vertical ionisation energies and electron affinities of the free molecules in the fully relaxed structure of the neutral species (left). To emulate bonding to the surface, LUMO filling, and the resulting re-hybridisation, hydrogen atoms are attached onto those groups that are responsible for molecule-metal bonding, the keto oxygens in the case of P2O (center). The geometries of these modified (charge neutral) molecules are then fully relaxed. Finally, step **B** is to remove the extra hydrogen atoms again and to re-calculate ionisation energies and electron affinities on that structure (right). Unless otherwise noted, all molecules were treated in that way to produce the numbers reported in Table S2.

Table S2 | Theoretical estimates for the upper limits of LUMO lowering and band-gap narrowing upon surface-induced aromatic stabilisation. DFT-calculated gas-phase ionisation energies (IE) and electron affinities (EA, typeset in *italics*) of the molecules discussed in the main text and in the Supplementary Information above (Fig. S4) in their two configurations A and B as described in Fig. S5. Their fundamental gaps, *i.e.*, the differences IE - EA, are denoted as E_g and E_{RH-FL} , respectively, and the differences in IE and EA between the two configurations as ΔIE and ΔEA . In all cases, the gaps in configuration B are considerably smaller, largely due to an increase in EA.

molecule	configuration A		configuration B		$\Delta EA / \Delta IE$	$E_{RH-FL} - E_g$
	<i>EA / IE</i>	E_g	<i>EA / IE</i>	E_{RH-FL}		
P2O	<i>1.54</i>	6.35	<i>2.34</i>	5.53	<i>0.80</i>	-0.82
	7.89		7.87		-0.02	
P4O	<i>2.47</i>	6.56	<i>3.38</i>	5.58	<i>0.91</i>	-0.98
	9.03		8.96		-0.07	
FAQ	<i>2.36</i>	7.38	<i>3.32</i>	6.25	<i>0.96</i>	-1.13
	9.75		9.58		-0.17	
COHON	<i>3.46</i>	5.69	<i>4.60</i>	4.78	<i>1.14</i>	-0.91
	9.15		9.38		0.23	
PTCDA	<i>3.05</i>	5.09	<i>4.18</i>	3.98	<i>1.16</i>	-1.11
	8.14		8.16		0.02	
NTCDA	<i>2.83</i>	6.86	<i>4.21</i>	5.36	<i>1.38</i>	-1.50
	9.69		9.57		-0.12	
BTCDA	<i>2.57</i>	8.21	<i>4.16</i>	6.55	<i>1.59</i>	-1.66
	10.78		10.70		-0.08	
BTCDI	<i>2.02</i>	7.88	<i>3.53</i>	6.51	<i>1.51</i>	-1.38
	9.91		10.04		0.13	
PTCDI	<i>2.74</i>	5.04	<i>3.41</i>	4.53	<i>0.67</i>	-0.51
	7.78		7.94		0.16	
NTCDI	<i>2.45</i>	6.74	<i>3.77</i>	5.28	<i>1.32</i>	-1.46
	9.19		9.05		-0.14	
F4-TCNQ ^a	<i>4.13</i>	5.43	<i>4.88</i>	4.23	<i>0.75</i>	-1.20
	9.56		9.11		-0.45	
TCAQ ^a	<i>3.21</i>	5.56	<i>4.64</i>	2.57	<i>1.43</i>	-2.99
	8.77		7.21		-1.56	
HATCN	<i>3.68</i>	6.80	<i>3.97</i>	6.05	<i>0.29</i>	-0.75
	10.48		10.02		-0.46	

^a Only two of the four cyano groups were (symmetrically) hydrated; see text for details.

C.4 The case of electron-donor molecules

While not as widely studied, owing to the lack of environmentally stable representatives, also strong electron-donor molecules appear susceptible to the mechanism of surface-induced aromatic stabilisation. In particular, a (partial) emptying of the HOMO on high work-function metals, such as gold, has been reported for tetrathiafulvalene (TTF)^{S29,30} and 1,1'-dimethyl-4,4'-bipyridinylidene, commonly termed methyl-viologen (MVO)^{S30,31}. As shown in Fig. S6 (left), the quinoidal form of the isolated molecules is stabilised by the electrons in their respective HOMOs, *i.e.*, electrons occupying the wave functions' anti-nodes strengthen the respective double bonds. Upon initial HOMO emptying, this quinoidal character is successively reduced on the surface, as the contribution from a covalently bound and fully π -conjugated mesomeric structure increases, where the hetero-atoms (sulphur and nitrogen, respectively) can be thought of as directionally interacting with the underlying

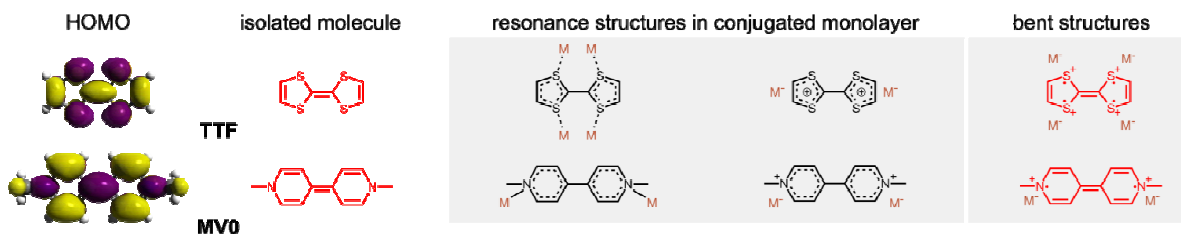


Figure S6 | Surface-induced aromatic stabilisation of electron-donor molecules. From left to right: Calculated LUMO wave functions, chemical structures of isolated TTF and MV0 molecules, resonance structures gain in importance on high work-function metals, where (partial) HOMO emptying occurs, and potential bent resonance structures. In the case of TTF, the dashed bonds between sulphur and metal atoms in the center panel represent the resonant superposition of mesomeric structures with one sulphur-metal bond per ring.

metal through their lone pairs (Fig. S6, center)^{S29}. Even more weight must be attributed to the dicationic resonance structures of the donors, which equally exhibit extended π -conjugation. The expected changes in bond-length alternation have indeed been observed in DFT-calculations and aromatic stabilisation has been invoked as their cause.^{S30} What our study adds to these observations is that the re-hybridisation of the donor molecules on the surface leads to a marked upward shift of the HOMO in energy and that this upward shift is, in fact, required to overcome Fermi-level pinning and, thus, to significantly empty the HOMO in the first place: Comparing the neutral molecule at its equilibrium structure and in the equilibrium structure of the dication, we calculated the ionisation energy in the latter case to be reduced by an appreciable ~ 0.7 eV. Lastly we note that, while bent mesomeric structures can formally be drawn in analogy to the acceptors (Fig. 4 in the main text and Fig. S4 above), both TTF and MV0 are non-planar already as isolated species in gas phase.

C.5 Limitations of the model

Several metal-phthalocyanines (MPc) have also been reported to exhibit substantial LUMO filling on certain metal surfaces^{S16,32-37}. However, the high symmetry of these molecules renders the identification of a few insightful resonance structures impossible. We note here that the molecular ring structure, exhibiting $4n$ π -electrons, is generally said *not* to be aromatic. Only upon assigning a formal charge of +2 to the central metal atom and -2 to the organic ligand, does one arrive at an aromatic structure (according to Hückel's rule) with $4n+2$ electrons. Keeping in mind that a formal charge does not necessarily reflect the actual charge distribution within an MPc molecule, one could equally assume that full aromaticity and, therefore, stabilization of the LUMO and reduction of the fundamental gap, is achieved upon uptake of two electrons from the metal. However, our current understanding does not allow to unambiguously identify the mechanism of LUMO filling in MPc as surface-induced aromatic stabilisation (in the sense introduced in the main text), not the least because the occupation and splitting of the metal centre's d -orbitals as well as the degeneracy of the ligand LUMO must be expected to play a non-negligible role as well.

Furthermore, it is to be noted that strong mixing between metal (surface) states and the π -systems of organic semiconductors that do *not* exhibit acceptor groups on the periphery has been reported on crystal facets of copper that are known to be significantly more reactive than the close-packed (111) surface considered in the present work. This seems to be the case, *e.g.*, for *para*-sexiphenyl on Cu(110)^{S38,39} and for PEN on Cu(110)^{S40} or Cu(100)^{S41}. There, the observed interfacial electronic structure can no longer be straightforwardly correlated with free-molecule orbitals and metal-to-molecule electron transfer, if present at all, can no longer be understood in terms of

“LUMO-filling” only. While certainly intriguing, it remains to be seen whether a chemically intuitive picture will eventually emerge also for these cases, where conceptually separating metal and molecule seems even harder than in the systems investigated for the present work.

Lastly, also C_{60} is known to exhibit a partially filled LUMO on certain metal surfaces^{S28,42-44}. As with MPC, the high symmetry of this molecule together with ambiguities in the definition of aromaticity of a spherical (as opposed to planar) species^{S45} leave the applicability of the proposed mechanism for surface-induced aromatic stabilisation an open question for future investigations.

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