Electronic Supplementary Material (ESI) for Nanoscale.

Adsorption of Alkylamines on Cu Surfaces: Identifying Ideal Capping Molecules Using First-Principles Calculations

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Supplementary Text and Equations

Details of DFT Calculations

Alkylamines are adsorbed on one side of a six-layer Cu slab with a vacuum space of about 37 Å in the direction perpendicular to the slab (**Figure S1**). A dipole correction was applied along the surface normal direction. The bottom three layers of the slab were fixed at the bulk positions during optimization, with the experimental lattice constant of 3.615 Å[1], while all other atoms were fully relaxed in all directions. With the same unit cells applied here, tests of convergence for *k* points, vacuum spacing, and cutoff energy can be found in ref. 2.

We applied the DFT-D2 method, in which the vdW interaction is given by a sum of pair-wise interactions between species.[3] Two parameters are involved: $C_{6,AB}$ represents the dispersion coefficient between two elements A and B while $R_{0,A}$ defines the vdW radius for element A. In this study, the C_6 and R_0 parameters for Cu were taken from the study by Ruiz *et al.* to account for screening effects in the bulk metal and default values were used for all other species.[4] The cutoff radius for DFT-D2 method was set to 40.0 Å. By applying DFT-D2 method with the parameters for Cu by Ruiz et al., we limit the over-estimation of the vdW interactions for Cu.

The intra- and inter-molecular interaction $E_{\mathrm{Ads-Ads}}$ is given by

$$E_{\mathrm{Ads-Ads}} = (N_{\mathrm{Ads}} E_{\mathrm{Ads}} - E_{\mathrm{Ads,o}})/N_{\mathrm{Ads}}\,. \quad \text{(S1)}$$

Here, $E_{\mathrm{Ads,o}}$ is the energy of an isolated adlayer of molecules with a fixed configuration that is exactly the same as in the optimized adsorption system, but without the Cu slab. $E_{\mathrm{Ads-Ads}}$ quantifies the interactions between and within the adlayer of capping molecules. $E_{\mathrm{Cu-Ads}}$ is the interaction between one adsorbed alkylamine and the Cu slab and is given by

$$E_{\mathrm{Cu-Ads}} = (E_{\mathrm{Ads,o}} + E_{\mathrm{Cu,o}} - E_{\mathrm{Cu-Nads}})/N_{\mathrm{Ads}}. \quad \text{(S2)}$$

Here, $E_{\mathrm{Cu,o}}$ is the energy of a Cu slab with the same configuration as in the optimized adsorption system, but without the adsorbed layer. The remaining term in Equation (2), ΔE_{Cu}, represents the energy change in the Cu slab after binding. ΔE_{Cu} is obtained from the difference between E_{bind} and the sum of $E_{\mathrm{Ads-Ads}}$ and $E_{\mathrm{Cu-Ads}}$.

We evaluated the bond distance $d_{\mathrm{Cu-N}}$ from an N atom to the nearest Cu atom in the surface for the alkylamine series and the orientation/tilt angles for the linear alkylamines. The tilt angle α is defined as the angle between the backbone connecting two N atoms in linear alkylamines and the Cu surface (the *x*-*y* plane), while the orientation angle γ is the angle between the surface projection of the backbone on the *x*-*y* plane and the *x*-axis, as shown in **Figure S1**.

Supplementary Tables

Table S1. Coverages studied on Cu(100) and Cu(111) with corresponding unit cells.

	Cu(100)						
θ_{Ads} (ML)	0.25*	0.17	0.13*	0.11	0.10	0.08	0.06
Unit Cell	(2×2)	(3×2)	(4×2)	(3×3)	(5×2)	(4×3)	(4×4)
	Cu(111)						
θ_{Ads} (ML)	0.25*	0.17	0.13*	0.11	0.10	0.08	0.06
Unit Cell	(2×2)	(3×2)	(4×2)	(3×3)	(5×2)	(4×3)	(4×4)

* Zigzag patterns at the same coverage use unit cells with doubled sizes

Table S2. Key energies of TrMDA and PMDA adsorption configurations with the highest total binding energy on Cu(100) and Cu(111) at different coverages. Configurations with the highest binding energy on each surface are shaded.

Candidate	θ_{Ads} (ML)	E_{bind} (eV)	$E_{\mathrm{Ads-Cu}}^{\mathrm{short}}$ (eV)	$E_{\mathrm{Ads-Cu}}^{\mathrm{vdW}}$ (eV)	$E_{\mathrm{Ads-Ads}}^{\mathrm{short}}$ (eV)	$E_{\mathrm{Ads-Ads}}^{\mathrm{vdW}}$ (eV)
TrMDA	{100}-0.17	1.25	0.59	0.59	-0.00	0.13
	{100}-0.13	1.11	0.52	0.59	-0.06	0.11
	{100}-0.11	1.26	0.67	0.60	-0.01	0.07
	{100}-0.08	1.35	0.91	0.71	-0.16	0.01
	{111}-0.17	1.12	0.44	0.63	-0.10	0.23
	{111}-0.13	1.05	0.44	0.60	-0.06	0.13
	{111}-0.11	1.21	0.58	0.64	-0.01	0.08
	{111}-0.08	1.06	0.53	0.61	-0.02	0.01
PMDA	{100}-0.17	1.29	0.53	0.61	-0.20	0.38
	{100}-0.13	1.52	0.65	0.78	-0.01	0.16
	{100}-0.11	1.43	0.56	0.80	0.04	0.09
	{100}-0.10	1.31	0.57	0.74	-0.03	0.09
	{100}-0.08	1.64	0.93	0.93	-0.16	0.03
	{111}-0.17	0.85	0.36	0.58	-0.61	0.57
	{111}-0.13	1.47	0.49	0.82	-0.05	0.29
	{111}-0.11	0.81	-0.11	0.73	0.01	0.19
	{111}-0.10	1.26	0.42	0.80	-0.09	0.20
	{111}-0.08	1.32	0.53	0.79	-0.01	0.08

Table S3. Energies and structural characteristics of optimal TrMDA and PMDA configurations on Cu surfaces.

Molecule	Surface	θ_{Ads} (ML)	E_{bind} (eV)	d^1_{N-Cu} (Å)	d^2_{N-Cu} (Å)	α (°)	γ (°)
TrMDA	{100}	0.08	1.35	2.14	2.14	0.01	1.01
	{111}	0.11	1.21	2.10	3.10	11.40	61.97
PMDA	{100}	0.08	1.64	2.12	2.12	0.00	44.89
	{111}	0.13	1.47	2.12	3.28	7.22	60.82

Table S4. Key energies of TeMDA and HMDA adsorption configurations with the highest total binding energy on Cu(100) and Cu(111) at different coverages. Configurations with the highest binding energy on each surface are shaded.

Candidate	θ_{Ads} (ML)	E_{bind} (eV)	$E_{\mathrm{Ads-Cu}}^{\mathrm{short}}$ (eV)	$E_{\mathrm{Ads-Cu}}^{\mathrm{vdW}}$ (eV)	$E_{\mathrm{Ads-Ads}}^{\mathrm{short}}$ (eV)	$E_{\mathrm{Ads-Ads}}^{\mathrm{vdW}}$ (eV)
TeMDA	{100}-0.17	1.36	0.52	0.70	-0.06	0.27
	{100}-0.13	1.22	0.49	0.73	-0.05	0.11
	{100}-0.11	1.18	0.54	0.69	-0.04	0.05
	{100}-0.08	1.30	0.78	0.86	-0.19	0.02
	{111}-0.17	1.16	0.51	0.64	-0.29	0.39
	{111}-0.13	1.20	0.44	0.72	-0.08	0.19
	{111}-0.11	1.25	0.53	0.72	-0.04	0.12
	{111}-0.08	1.24	0.55	0.74	-0.01	0.04
HMDA	{100}-0.13	1.76	0.64	0.91	-0.02	0.31
	{100}-0.11	1.41	0.65	0.81	-0.24	0.24
	{100}-0.08	1.53	0.67	0.91	-0.13	0.13
	{100}-0.06	1.72	0.98	1.04	-0.18	0.02
	{111}-0.13	1.41	0.54	0.71	-0.19	0.42
	{111}-0.11	1.17	0.48	0.65	-0.16	0.26
	{111}-0.08	1.53	0.55	0.93	0.04	0.09
	{111}-0.06	1.31	0.46	0.94	-0.05	0.02

Table S5. Energies and structural characteristics of optimal TeMDA and HMDA configurations on Cu surfaces.

Molecule	Surface	θ_{Ads} (ML)	E_{bind} (eV)	d^1_{N-Cu} (Å)	d^2_{N-Cu} (Å)	α (°)	γ (°)
TeMDA	{100}	0.17	1.36	2.12	3.33	8.72	1.01
	{111}	0.11	1.25	2.14	3.26	7.96	38.10
HMDA	{100}	0.13	1.76	2.10	3.19	5.82	34.13
	{111}	0.08	1.53	2.11	3.44	5.54	54.76

Table S6. Key energies of PTA and TZ adsorption configurations with the highest total binding energy on Cu(100) and Cu(111) at different coverages. Configurations with the highest binding energy on each surface are shaded.

Candidate	θ_{Ads} (ML)	E_{bind} (eV)	$E_{\mathrm{Ads-Cu}}^{\mathrm{short}}$ (eV)	$E_{\mathrm{Ads-Cu}}^{\mathrm{vdW}}$ (eV)	$E_{\mathrm{Ads-Ads}}^{\mathrm{short}}$ (eV)	$E_{\mathrm{Ads-Ads}}^{\mathrm{vdW}}$ (eV)
PTA	{100}-0.13	1.75	0.63	0.93	0.04	0.24
	{100}-0.10	1.86	0.93	1.08	-0.21	0.18
	{100}-0.08	2.09	1.31	1.10	-0.31	0.06
	{100}-0.06	2.24	1.46	1.10	-0.27	0.04
	{111}-0.13	1.58	0.34	0.91	0.01	0.45
	{111}-0.10	1.88	0.65	1.04	0.14	0.26
	{111}-0.08	1.68	0.78	1.19	-0.31	0.14
	{111}-0.06	1.72	0.85	1.15	-0.31	0.17
TZ	{100}-0.25	1.38	0.37	0.58	0.04	0.43
	{100}-0.17	1.45	0.44	0.59	0.22	0.21
	{100}-0.11	1.60	0.91	0.83	-0.09	0.02
	{100}-0.11*	1.23	0.83	0.73	-0.28	0.00
	{111}-0.13	1.44	0.63	0.88	-0.13	0.10
	{111}-0.11	1.63	0.84	0.91	-0.10	0.03
	{111}-0.11*	1.05	0.62	0.79	-0.30	0.01

*Boat conformation

Supplementary Figures

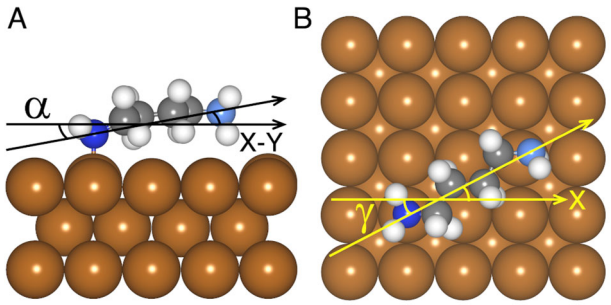

Figure S1. Side view (A) and top-down view (B) of the linear alkylamine adsorption model. The angles α and γ are explained on p. S3. (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

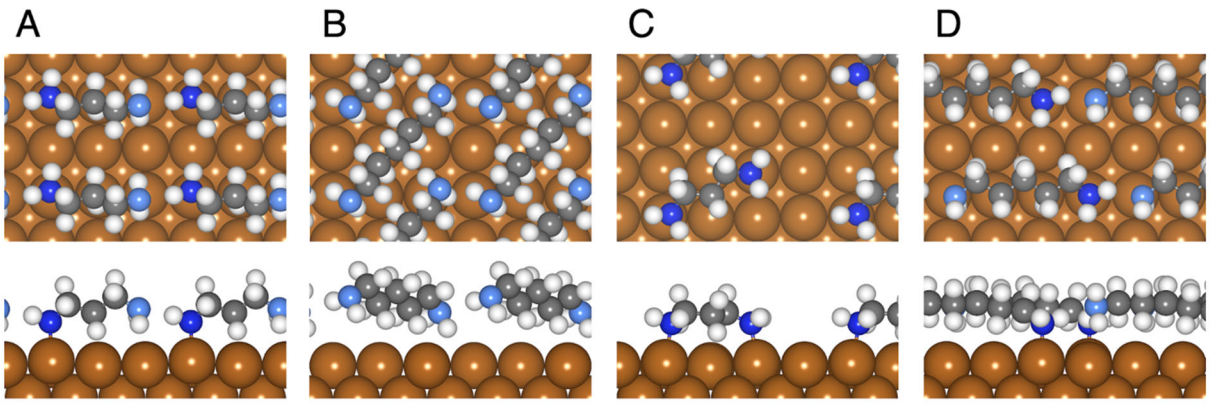

Figure S2. Top-down (upper) and side (lower) views for optimized binding conformations of (**A**) TrMDA on Cu(100), (**B**) PMDA on Cu(100), (**C**) TrMDA on Cu(100), and (**D**) PMDA on Cu(100) (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

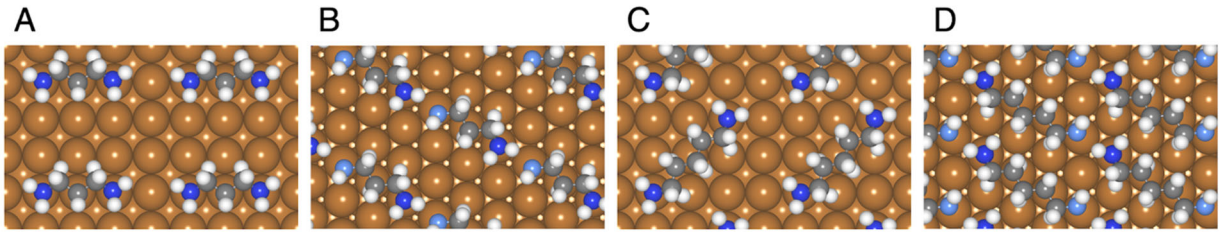

Figure S3. Top-down views of binding configurations with the highest binding energies for (**A**) 0.08 ML TrMDA on Cu(100), (**B**) 0.11 ML TrMDA on Cu(111), (**C**) 0.08 ML PMDA on Cu(100), and (**D**) 0.13 ML PMDA on Cu(111) (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

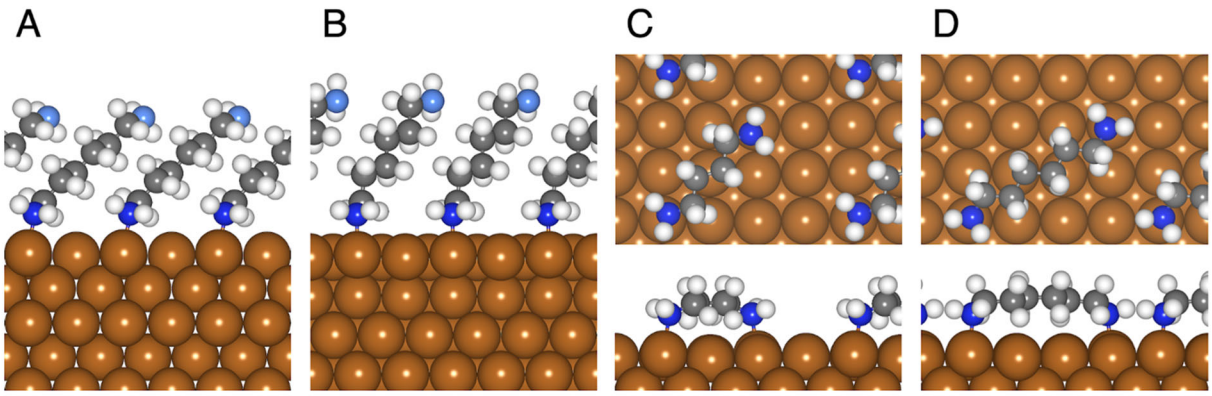

Figure S4. Side view for optimized binding conformations of (**A**) standing HMDA on Cu(100) and (**B**) Cu(111), top-down (upper) and side (lower) views for optimized binding conformations of (**C**) TeMDA on Cu(100) with two Cu-N bonds and (**D**) HMDA on Cu(100) with two Cu-N bonds (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

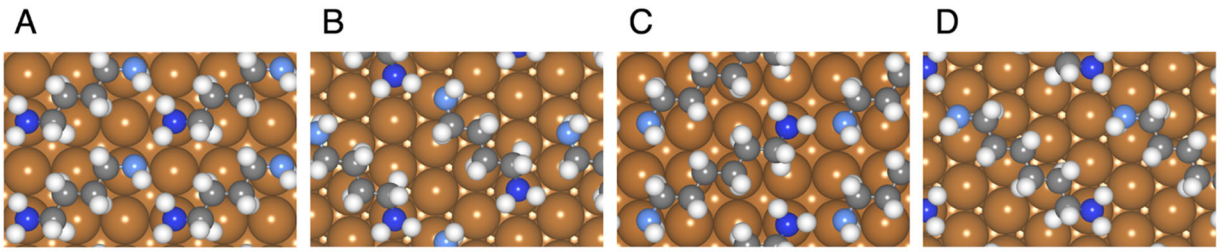

Figure S5. Top-down views of binding configurations with the highest binding energies of (**A**) 0.17 ML TeMDA on Cu(100), (**B**) 0.11 ML TeMDA on Cu(111), (**C**) 0.13 ML HMDA on Cu(100), and (**D**) 0.08 ML HMDA on Cu(111) (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

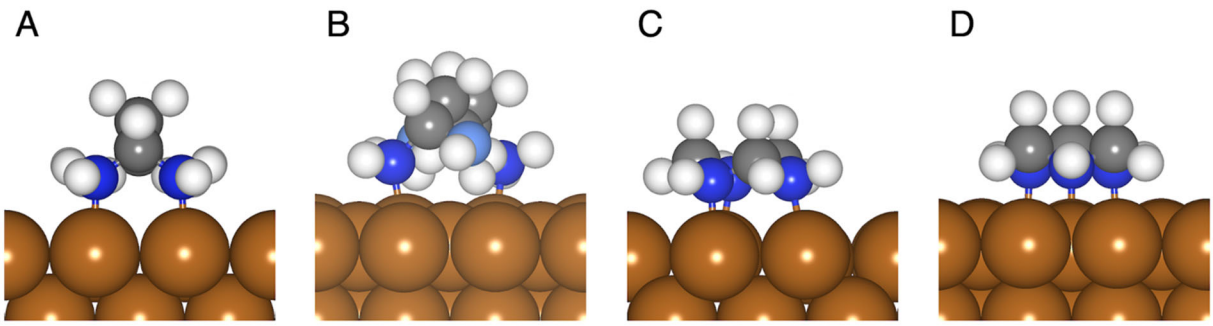

Figure S6. Side views for optimal binding conformations with highest binding energy of (**A**) 0.06 ML PTA on Cu(100), (**B**) 0.10 ML PTA on Cu(111), (**C**) 0.11 ML TZ on Cu(100), and (**D**) 0.11 ML TZ on Cu(111) (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

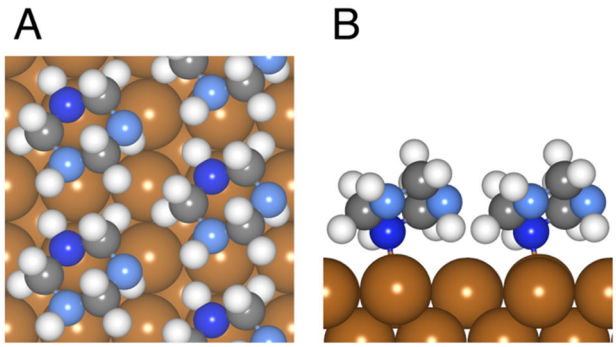

Figure S7. Top-down (**A**) and side (**B**) views for the optimized zigzag pattern of TZ on Cu(100) (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

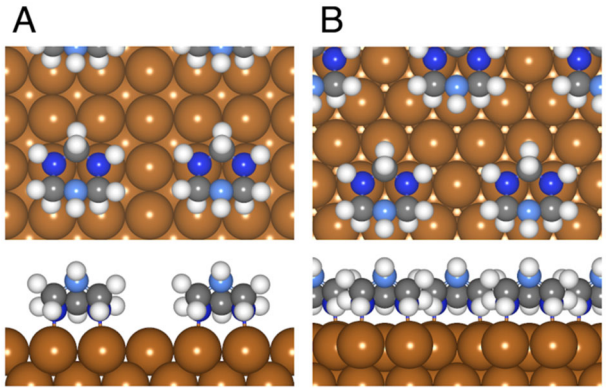

Figure S8. Top-down (upper) and side (lower) views for optimized binding conformations of boat TZ on (**A**) Cu(100) and (**B**) Cu(111) (Brown: Cu, Dark Blue: bound N, Light Blue: unbound N, Gray: C, and White: H).

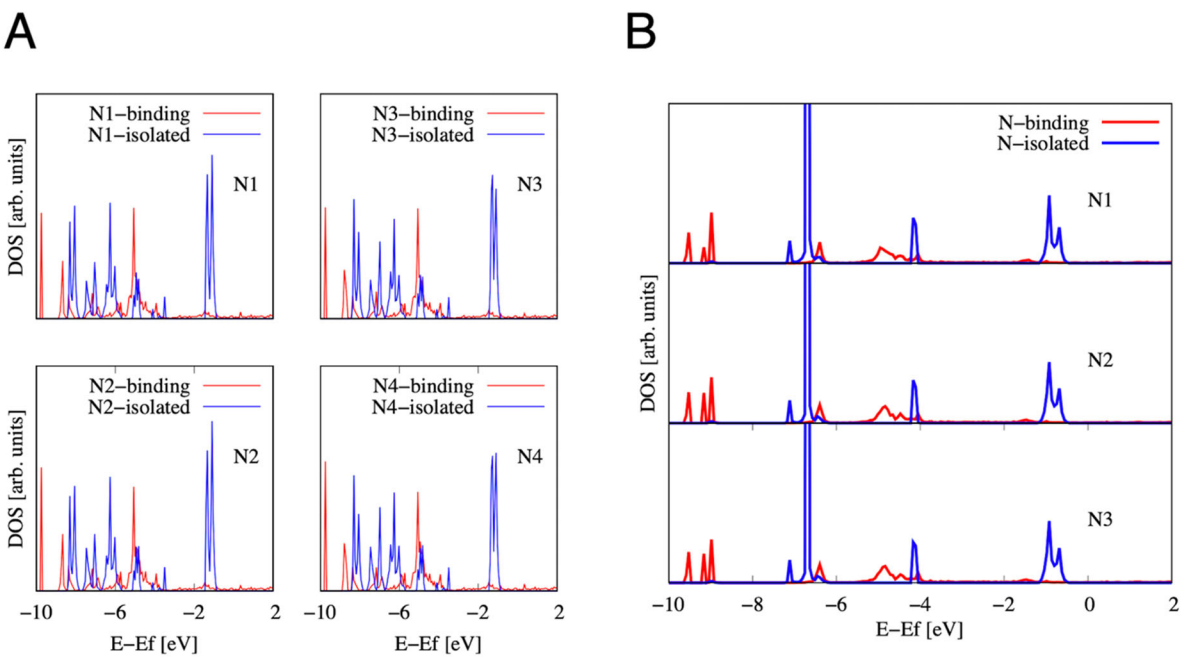

Figure S9. PDOS analysis of (**A**) PTA on Cu(100) and (**B**) TZ on Cu(111).

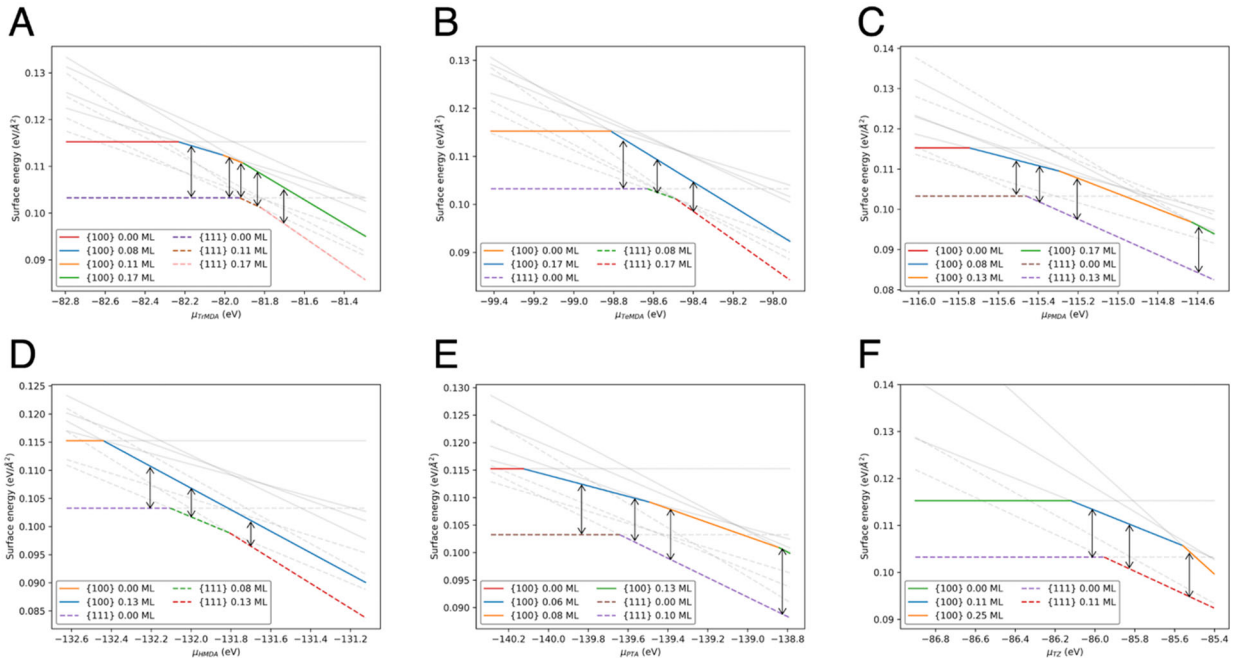

Figure S10. Surface energies as a function of SDA chemical potential for (**A**) TrMDA, (**B**) TeMDA, (**C**) PMDA, (**D**) HMDA, (**E**) PTA, and (**F**) TZ. The vertical double arrows delineate all unique pairs of Cu(100)/Cu(111) surface coverages. Along the whole range of capping-molecule chemical potential, the line for the surface structure with the lowest surface energy is colored. Gray lines indicate less energy-favored structures.

Supplementary References

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4 V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler and A. Tkatchenko, *Phys. Rev. Lett.*, 2012, **108**, 146103.