Electronic supplementary information for

A *sui generis* electrode-driven spatial confinement effect responsible for strong twisting enhancement of floppy molecules in closely packed self-assembled monolayers

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S1 Notations

Let us first mention that we use throughout the term "unit cell" with reference to the SAM periodicity (which should be more properly termed "SAM supercell") and not to the lattice periodicity of the metal/electrode/substrate; this should not create confusions because the latter does not directly enter the discussion presented in this work.

- acronym "MF-2D-MoFS": periodic metal-free two-dimensional monolayer of BPMT molecules on fictitious substrate, wherein the sulfur atoms are constrained to occupy the positions optimized for the SAMs adsorbed on metal. The fictitious substrate of the MF-2D-MoFS constrains the sulfur BPMT-ends relative to each other exactly as the real metal (substrate) surface does. The MF-2D-MoFS has the same periodicity as the adsorbed SAM and the same unit cell, which contains two translationally nonequivalent BPMT molecules, wherein, rather than being attached to metals ($\mathscr{M}$), sulfur atoms have hydrogen atoms attached, forming S-H bonds instead of S-$\mathscr{M}$ bonds (Fig. 1b).
- acronym "0.02": geometry relaxation until forces on all atoms were smaller than $F_{max} = 0.02\,\text{eV/Å}$ (used in Tables S1, S2, S3, S4, and S5)
- acronym "0.001": geometry relaxation until forces on all atoms were smaller than $F_{max} = 0.001\,\text{eV/Å}$ (used in Tables S1, S2, S3, S4, S5, and Tables 3 and 4 in the main text)
- acronym "vdw": SIESTA DFT calculations using the VDW-DRSLL functional [1] accounting for dispersion corrections (used in Tables S2, S3, S4, and S5)
- L: length of an isolated BPMT molecule
- φ: (twisting/torsional/dihedral) angle formed by the two rings of an isolated BPMT molecule
- $L_{1,2}$: lengths of the two crystallographically nonequivalent BPMT molecules of a unit cell

- $\varphi_{1,2}$: (twisting/torsional/dihedral) angles characterizing the two crystallographically nonequivalent BPMT molecules of a unit cell
- $\theta_{1,2}$: (tilt) angles between the normal to substrate surface and S-C axes of the two crystallographically nonequivalent BPMT molecules
- α: angle between the S-C molecular axes of the two crystallographically nonequivalent BPMT molecules
- β_l: angle between the ("lower", label l) phenyl rings of the two crystallographically nonequivalent BPMT molecules opposite to the thiol groups
- β_u: angle between the ("upper", label u) phenyl rings of the two crystallographically nonequivalent BPMT molecules adjacent to the thiol groups (*cf.* Fig. 1b)
- CC_u: distance between the carbon atoms of the two crystallographically nonequivalent BPMT molecules at the molecular ends opposite to the thiol groups (*cf.* Fig. 1b)
- SS_l: distance between the sulfur atoms of the two crystallographically nonequivalent BPMT molecules (*cf.* Fig. 1b)
- HH_{ll}: distance between the closest hydrogen atoms of the two lower (l) phenyl rings which are closest to the sulfur atoms (*cf.* Fig. 1b)
- HH_{lu}: distance between the closest hydrogen atoms of the two lower (l) phenyl rings which are most distant from the sulfur atoms (*cf.* Fig. 1b)
- HH_{ul}: distance between the closest hydrogen atoms of the two upper (u) phenyl rings which are closest to the sulfur atoms (*cf.* Fig. 1b)
- HH_{uu}: distance between the closest hydrogen atoms of the two upper (u) phenyl rings which are most distant from the sulfur atoms (*cf.* Fig. 1b)

S2 Computational details

Density functional theory (DFT) calculations done in conjunction with the present work are similar to those presented in detail in ref. 2. Therefore, only a brief description will be given below. Spin-unpolarized calculations were performed

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running the SIESTA[3] 4.0 package[4] in parallel[5] using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional[6], which is a parameter free functional belonging to the class of conjugated gradient approximation (GGA) functionals. Basis sets of double zeta quality with polarization (DZP) for nonmetallic atoms and of single zeta quality with polarization (SZP) for metal atoms were utilized, which turned out to be adequate[2].

Tests that confirmed the robustness of the results presented in this work were also similar to those presented in ref. 2. Therefore, only a few examples will be given below to illustrate this robustness.

Ref. 2 showed that, for geometries relaxed until the forces (F) on all atoms were less that $F_{max} < 0.02\,\mathrm{eV/Å}$ (acronym "0.02"), twisting angles φ are accurate within $\sim 1°$. Although this is acceptable in most cases, the condition $F_{max} < 0.02\,\mathrm{eV/Å}$ would have yielded some numerical noise in Fig. 2. To eliminate this numerical noise, unless otherwise specified, we imposed the more severe condition $F_{max} < 0.001\,\mathrm{eV/Å}$ (acronym "0.001").

Dispersion corrections do not significantly alter the twisting angle. Along with the examples presented recently for similar systems[2], this can be seen by comparing the second and the last lines of Tables S2, S3, S4, and S5, which present results obtained without and with dispersion corrections, respectively. Like in ref. 2, dispersion corrections were considered by means of the VDW-DRSLL functional[1] (acronym "vdw" in Tables S2, S3, S4, and S5).

Unlike common quantum chemical packages (like GAUSSIAN[7], also used in this study), the SIESTA code[3] relies upon basis sets constructed from localized numerical atomic orbitals and does not allow DFT calculations based on genuine hybrid exchange-correlation functionals, known to provide in general results of superior quality. To check the correctness of the SIESTA relaxed geometries, we have also conducted DFT calculations based of the B3LYP hybrid exchange-correlation[8–10] functional and/or 6-31g(d,p)[11,12], D95 Dunning/Huzinaga full double zeta[13], TZV and TZVP[14,15] basis sets as implemented in GAUSSIAN 09[7]. Default settings (optimization=tight) were used for geometry optimization with GAUSSIAN.

All results presented in the main text were obtained *via* SIESTA DFT calculations at the GGA-PBE level and DZP (nonmetal atoms) and SZP (metal atoms) basis sets using $F_{max} = 0.001\,\mathrm{eV/Å}$. All numerical results reported here for SAMs adsorbed on metals were obtained from calculations including three metallic layers, wherein the distances $d_{\mathcal{M}-\mathcal{M}}$ between metal ($\mathcal{M}$) atoms were deduced from the experimental lattice constants: $d_{Pt-Pt} = 2.77483\,\mathrm{Å}$, $d_{Au-Au} = 2.88367\,\mathrm{Å}$, $d_{Ag-Ag} = 2.88874\,\mathrm{Å}$, and $d_{Cu-Cu} = 2.55612\,\mathrm{Å}$. In this context, it may be useful to emphasize that, to improve visibility, instead of showing the three metal monolayers used in our DFT-calculations, only the uppermost metal monolayer is depicted in the schematic representation of Fig. 1a.

For SAMs adsorbed on fcc Au (111), ref. 2 reported that including up to six metal layers does not notably change the twisting angles from the values calculated using three layers. We found that this conclusion also holds for the other (Pt, Ag, and Cu) electrodes considered here.

To end, we found that surface reconstruction effects do not alter the strong twisting enhancement ($\varphi \simeq 76°$). This aspect, already discussed earlier[2,16] for SAMs adsorbed on fcc Au (111), is important especially in view of the fact that surface reconstruction effects are known to have a dramatic impact in many other situations.

S3 Additional details on the modeling of a continuous variation of the SAM coverage within the MF-2D-MoFS

As we briefly anticipated elsewhere (see the discussion on page 130 of ref. 16), the usage of a metal-free model (like the present MF-2D-MoFS) can provide important insight into the specific manner of how the twisting angle depends on a continuously varying coverage.

If we appropriately resize the MF-2D-MoFS unit cell (containing by definition two BPMT molecules, *cf.* main text), it is possible to continuously switch between strongly twisted ($\varphi \simeq 76°$) and weakly twisted ($\varphi \simeq 37°$) conformations. Indeed, we showed (*cf.* Table 2 of the main text) that, for a MF-2D-MoFS unit cell having the same size as the unit cell of the real SAM forming herringbone pattern on real metals, the large twisting angles ($\varphi_{1,2} \simeq 76°$) of the two BPMT molecules are correctly recovered. On the other side, if we rescale the MF-2D-MoFS unit cell to sufficiently large sizes, the two BPMT molecules necessarily approach weakly twisted conformations ($\varphi \simeq 37°$); both BPMT molecules (*cf.* Table S1 and sufficiently large s values in eqn. (S5)) and pairs of BPMT molecules (*cf.* Table 4 in the main text and sufficiently large s-values in eqn. (S4)) far away from each other are weakly twisted ($\varphi \simeq 37°$).

Denoting by s the dimensionless scaling factor of the linear in-layer dimensions

$$x \to sx, \; y \to sy \tag{S1}$$

the areas $\mathscr{A}$ and $\mathscr{A}_0$ of the scaled and unscaled unit cells are obviously related to each other by

$$\mathscr{A} = s^2 \mathscr{A}_0 \tag{S2}$$

In terms of the coverage of the unscaled MF-2D-MoFS $\Sigma_0 \equiv$

$2/\mathcal{A}_0$,* the average† coverage $\Sigma \equiv 2/\mathcal{A}$ of the scaled MF-2D-MoFS can be expressed as

$$\Sigma = s^{-2}\Sigma_0 \qquad (S3)$$

In the main text, we indicated two extreme ways of rescaling of the MF-2D-MoFS unit cell; either by freezing the distance between the S atoms of the two BPMT molecules per MF-2D-MoFS unit cell to the values of SS_l corresponding to the real SAM on gold (or other metal) (*cf.* Table 1 and Table 2 in the main text)

$$SS_l \rightarrow SS_l \quad \text{(frozen S-S distance)} \qquad (S4)$$

or by rescaling the S-S distance with the same factor s used to resize the MF-2D-MoFS unit cell (eqn (S1))

$$SS_l \rightarrow s \times SS_l \quad \text{(scaled S-S distance)} \qquad (S5)$$

Eqn (S4) and (S5) correspond to the cases (a) and (b) of Sec. 2.3 in the main text, respectively.

Notice that, for sufficiently large values of s, the case described by eqn (S4) approaches the limit of very distant pairs of BPMT molecules whose mates are closed to each other (*cf.* Table 4 in the main text), while the case described by eqn (S5) approaches the limit of very distant BPMT molecules (*cf.* Table S1).

Unlike in calculations to SAMs adsorbed on electrodes realistically modeled as multi-layer metal slabs — requiring large unit cells with many BPMT molecules and metal atoms (*cf.* Sec. S4)—, simulating a continuously varying average coverage within the MF-2D-MoFS approach poses absolutely no problems. Whether also scaling the distance (SS_l) between the sulfur atoms of the two BPMT molecules within the unit cell according to eqn (S5) or keeping it frozen (*cf.* eqn (S4)) along with the scaling of the MF-2D-MoFS unit cell (*cf.* eqn (S1)), geometry optimization via DFT-calculations can be straightforwardly done. These DFT-calculations refer to a unit cell (having an s-dependent area $\mathcal{A}$,

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* For concreteness, let us note here that $\mathcal{A}_0$ represents the area of the unit cell schematically depicted in red in Fig. 1 of the main text, and the coverage value Σ_0 is indicated in cyan in Fig. 2 of the main text.

† Usually, the term "average" refers to (or implicitly assumes) situations wherein the properties of interest exhibit local variations. The term "*average* coverage" appears significant to us in view of the differences between the two manners of scaling the MF-2D-MoFS unit cell discussed in the main text and described by eqn (S4) and (S5). The local coverage is more inhomogeneous in the case where the S-S distance of the two BPMT molecules of the unit cell is frozen at the value SS_l characterizing the real SAM on gold (or other metal) (*cf.* eqn (S4) and Table 1 and Table 2 in the main text) than in the case where the S-S distance of the these two BPMT molecules is scaled by the same factor s as the the scaling in the x and y directions (*cf.* eqn (S5)). In the former case, it is only the mean inter-cell distance between the BPMT molecules that varies with s; the intra-cell BPMT-BPMT distance does not depend on s (*cf.* eqn (S4)). In the latter case, the spatial disposition of the BPMT molecules is more homogeneous because both the inter-cell and the intra-cell BPMT-BPMT distances vary with s.

cf. eqn (S2)) containing two BPMT molecules. They allow to compute the dependence of the twisting angles $\varphi_{1,2} = \varphi_{1,2}(s)$ of the two BPMT molecules of the MF-2D-MoFS unit cell. In view of eqn. (S3), this dependence can be straightforwardly recast as a dependence of the twisting angles $\varphi_{1,2} = \varphi_{1,2}(\Sigma)$ on a continuously varying coverage. In this way, the dependence of the average twisting angle $\varphi \equiv (\varphi_1 + \varphi_2)/2$ on Σ is deduced. The results shown in Fig. 2 of the main text were obtained as described above.

S4 Why a direct modeling of a variable SAM coverage is difficult?

The fact that the twisting angle ($\varphi \simeq 76°$) at the high SAM coverages corresponding to herringbone arrangements is found to be substantially larger than that at low SAM coverages ($\varphi \simeq 37°$)[2] clearly demonstrates that φ depends on the SAM coverage. So, a correlation between the SAM coverage and φ exists. This raises the natural question of whether the increase of φ with increasing Σ is gradual or abrupt[2,16].

Unfortunately, the inherent discreteness of the metal lattice and of the number of (BPMT) molecules constitute an obvious difficulty to directly answer this interesting question; this discreteness prevents a straightforward modeling of a *continuous* variation of the coverage in real SAMs.

Below we aim at illustrating the difficulty of deducing the dependence of the twisting angle φ on the coverage Σ *via* calculations that realistically model BPMT SAMs adsorbed on metal slabs. For convenience, in this section we will express the coverage in terms of the dimensionless variable $\Theta \equiv \Sigma/\Sigma_0 = \mathcal{A}_0/\mathcal{A}$.

The unit cell of a real SAM with herringbone arrangement has two BPMT per unit cell of area; $\mathcal{A} = \mathcal{A}_0$ and $\Theta = 1$. Adopting an approach based on this real unit cell, one can decrease the coverage (only) by removing one BPMT molecule out of the two BPMT molecules contained in the unit cell; this situation corresponds to a coverage $\Theta = 1/2$. DFT-calculations done for this case ($\Theta = 1/2$) yielded values $\varphi \simeq 40°$ only slightly larger than the value $\varphi \simeq 37°$ corresponding to the isolated BPMT molecule and low coverage SAMs[2]. So, if we were able to (nearly) continuously vary the coverage from $\Theta = 1$ to $\Theta = 1/2$ we would be able to answer the question whether the change of φ between the strongly twisted and weakly twisted limits occurs smoothly or abruptly.

However, within the framework based on this unit cell it is impossible to sample coverage values other than $\Theta = 1$ and $\Theta = 1/2$; the unit cell can contain either two or one BPMT molecule. This translates into the impossibility to straightforwardly access *continuous* changes in φ in the whole range of interest ($40° \lesssim \varphi \lesssim 76°$).

Larger unit cells are needed to sample more Θ val-

ues. One can/should start with a unit cell comprising at least ten unit cells of the SAM with herringbone arrangement; this unit cell contains 20 BPMT molecules. Successively removing BPMT molecules one by one until 10 BPMT molecules remain, it is possible to sample the values $\Theta = 20/20; 19/20; 18/20; \ldots; 12/20; 11/20; 10/20 = 1.00; 0.95; 0.90; \ldots; 0.60; 0.55; 0.50$. This represents a reasonably dense grid of coverage values.

However, the largest of these unit cells (that with 20 BPMT molecules) comprises $440 + 180 = 620$ atoms ($10 \times 2 \times 22 = 440$ atoms, corresponding to 20 BPMT molecules and $10 \times 3 \times 3 \times 2 = 180$ atoms, corresponding to the three metal layers used to model the electrode); the smallest unit cell (that comprising 10 BPMT molecules) contains "only" 400 atoms. Based on own experience with SIESTA geometry relaxation for systems based on floppy molecules, we exclude the practical possibility to determine the optimum value of φ with a reasonable accuracy for such large unit cells.

The idea of modeling the variation of the coverage in real SAMs adsorbed on metal by varying the constant of the metal-free two-dimensional monolayer on fictitious substrate (MF-2D-MoFS) presented in Sec. 2.3 of the main text and further discussed in Sec. S3 is based on the fact that, in the limiting cases $\Theta = 1$ and $\Theta = 1/2$, the φ-values obtained within this model agree well with the φ-values obtained within realistic DFT calculations. Table 2 illustrates this agreement for the case $\Theta = 1$ (two BPMT molecules per unit cell). The other limiting case, $\Theta = 1/2$, corresponding to the value $\Sigma = 2.315$ molec./nm^2 of the abscissa in Fig. 2 in the main text, is located slightly to the left of the range visible there. By inspecting that figure and noting that the DFT-based value at $\Theta = 1/2$ is $\varphi \simeq 40°$ (see above), for this case a good agreement can also be inferred.

S5   Additional bond metric data

Table S1, and Tables 3 and 4 of the main text — which collect bond metric data for an isolated BPMT molecule, for a pair of two BPMT molecules, and for a metal-free two-dimensional monolayer on a fictitious gold substrate, respectively — were obtained *via* various DFT flavors, emphasizing the fact that results based on SIESTA DFT/GGA-PBE calculations and numerical localized basis sets do not significantly differ from those obtained by means of more elaborate hybrid exchange-correlation functionals (like B3LYP) and basis sets (like 6-31g(d,p)) used in standard quantum chemical calculations. This aspect is relevant because the latter are not available in the SIESTA package. The results collected in Tables S2, S3, S4, and S5 demonstrate the robustness of the results obtained for SAMs adsorbed on electrodes modeled as metal slabs containing three metal layers.

Isolated BPMT-molecule	L	φ
PBE/DZP[4] 0.02	8.9871	38.9
PBE/DZP[4] 0.001	8.9904	38.7
PBE/DZ[7] 0.001	9.0476	38.5
PBE/TZV[7] 0.001	8.9928	38.7
PBE/TZVP[7] 0.001	8.9286	37.5
PBE/6-31g(d,p)[7]	8.9447	36.0
B3LYP/D95[7]	9.0211	35.5
B3LYP/6-31g(d,p)[7]	8.9218	37.6

Table S1 Length L in angstroms and twisting angle φ in degrees of an isolated BPMT molecule at optimized geometry obtained *via* DFT calculations. Exchange-correlation functionals (PBE or B3LYP), basis sets, and package (SIESTA[17] or GAUSSIAN[7]) utilized are indicated in the left column. Acronyms "0.02" and "0.001" are defined in Sec. S1

Notes and references

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4 Code available under GPL open-source license at https://departments.icmab.es/leem/siesta/.

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BPMT SAM on Pt	φ_1	φ_2	θ_1	θ_2	L_1	L_2	α
0.02	75.4	75.8	1.3	1.4	8.9862	8.9925	0.2
0.001	73.8	75.5	13.9	14.3	8.8950	8.9462	0.4
vdw	74.8	75.6	1.3	1.2	9.0234	9.0315	0.1

BPMT SAM on Pt	β_u	β_l	CC_u	SS_l	HH_{uu}	HH_{ul}	HH_{lu}	HH_{ll}
0.02	75.2	75.0	4.7840	4.8155	2.8060	2.8122	2.8308	2.8659
0.001	73.9	70.5	4.7831	4.8482	2.8347	2.8866	3.1061	3.1493
vdw	74.7	74.5	4.8061	4.7950	2.8321	2.8345	2.8655	2.8894

Table S2 Properties of the two crystallographically nonequivalent BPMT molecules of the supercell of a SAM with herringbone order (Fig. 1a) on fcc Pt (111) surfaces: angles ($\varphi_{1,2}$, $\theta_{1,2}$, $\beta_{l,u}$, α) in degrees and lengths ($L_{1,2}$, CC_u, SS_l, HH's) in angstroms as defined in Fig. 1b and Sec. S1. Results obtained *via* SIESTA DFT/PBE calculations setting the Pt-Pt distance to the value $d = 2.77483$ Å. Acronyms "0.02", "0.001", and "vdw" are defined in Sec. S1

BPMT SAM on Au	φ_1	φ_2	θ_1	θ_2	L_1	L_2	α
0.02	76.0	75.9	5.7	5.7	8.9714	8.9721	0.1
0.001	74.2	77.4	5.2	5.2	8.9771	8.9783	0.1
vdw	72.9	77.7	5.7	5.7	9.0011	9.0037	0.0

BPMT SAM on Au	β_u	β_l	CC_u	SS_l	HH_{uu}	HH_{ul}	HH_{lu}	HH_{ll}
0.02	75.0	76.4	4.9670	4.9574	2.9802	2.9891	2.9943	2.9951
0.001	75.2	74.2	4.9758	4.9670	2.9701	2.9750	3.0023	3.0112
vdw	74.7	74.1	4.9670	4.9705	2.9770	2.9871	3.0206	3.0301

Table S3 Properties of the two crystallographically nonequivalent BPMT molecules of the supercell of a SAM with herringbone order (Fig. 1a) on fcc Au (111) surfaces: angles ($\varphi_{1,2}$, $\theta_{1,2}$, $\beta_{l,u}$, α) in degrees and lengths ($L_{1,2}$, CC_u, SS_l, HH's) in angstroms as defined in Fig. 1b and Sec. S1. Results obtained *via* SIESTA DFT/PBE calculations setting the Au-Au distance to the value $d = 2.88367$ Å. Acronyms "0.02", "0.001", and "vdw" are defined in Sec. S1

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17 Code available at https://departments.icmab.es/leem/siesta/.

BPMT SAM on Ag	φ_1	φ_2	θ_1	θ_2	L_1	L_2	α
0.02	75.1	75.1	0.3	0.4	8.9895	8.9890	0.1
0.001	74.8	75.0	0.4	0.5	8.9891	8.9896	0.1
vdw	74.2	74.4	0.3	0.4	9.0220	9.0219	0.1

BPMT SAM on Ag	β_u	β_l	CC_u	SS_l	HH_{uu}	HH_{ul}	HH_{lu}	HH_{ll}
0.02	75.0	75.1	5.0030	5.0199	2.9977	3.0106	3.0080	3.0037
0.001	74.8	74.8	5.0021	5.0203	2.9997	3.0136	3.0177	3.0100
vdw	74.2	74.2	5.0007	5.0140	3.0111	3.0242	3.0292	3.0194

Table S4 Properties of the two crystallographically nonequivalent BPMT molecules of the supercell of a SAM with herringbone order (Fig. 1a) on fcc Ag (111) surfaces: angles ($\varphi_{1,2}$, $\theta_{1,2}$, $\beta_{l,u}$, α) in degrees and lengths ($L_{1,2}$, CC_u, SS_l, HH's) in angstroms as defined in Fig. 1b and Sec. S1. Results obtained *via* SIESTA DFT/PBE calculations setting the Ag-Ag distance to the value $d = 2.88874$ Å. Acronyms "0.02", "0.001", and "vdw" are defined in Sec. S1

BPMT SAM on Cu	φ_1	φ_2	θ_1	θ_2	L_1	L_2	α
0.02	75.0	75.2	0.4	0.5	8.9990	9.0193	0.1
0.001	74.9	75.1	0.4	0.5	9.0106	9.0102	0.1
vdw	74.3	74.5	0.4	0.5	9.0367	9.0484	0.1

BPMT SAM on Cu	β_u	β_l	CC_u	SS_l	HH_{uu}	HH_{ul}	HH_{lu}	HH_{ll}
0.02	75.2	75.0	4.4271	4.4414	2.4998	2.5068	2.5104	2.5050
0.001	74.9	75.0	4.4284	4.4480	2.5094	2.5174	2.5195	2.5157
vdw	74.3	74.3	4.4277	4.4454	2.5288	2.5337	2.5321	2.5302

Table S5 Properties of the two crystallographically nonequivalent BPMT molecules of the supercell of a SAM with herringbone order (Fig. 1a) on fcc Cu (111) surfaces: angles ($\varphi_{1,2}$, $\theta_{1,2}$, $\beta_{l,u}$, α) in degrees and lengths ($L_{1,2}$, CC_u, SS_l, HH's) in angstroms as defined in Fig. 1b and Sec. S1. Results obtained *via* SIESTA DFT/PBE calculations setting the Cu-Cu distance to the value $d = 2.55612$ Å. Acronyms "0.02", "0.001", and "vdw" are defined in Sec. S1

Atom	X	Y	Z	Charge
H	7.457849	6.215104	-22.106673	0.974250
C	7.203428	6.177523	-20.029233	4.012368
H	4.633729	9.417982	-19.952307	0.955654
H	9.673478	2.908546	-19.443590	0.944543
C	5.631034	7.961520	-18.835188	3.983759
C	8.433368	4.335534	-18.554544	4.056255
C	5.307019	7.912112	-16.193129	4.074625
C	8.081577	4.275699	-15.916836	4.047156
H	4.021730	9.305011	-15.319640	0.951866
H	9.018767	2.780243	-14.802822	0.962018
C	6.533601	6.075621	-14.684570	3.983261
C	6.038458	5.890330	-11.891703	3.995605
H	3.758733	2.485298	-12.367034	0.955772
H	8.212374	9.194021	-10.671487	0.946077
C	4.497056	3.891523	-11.019013	4.065466
C	6.964330	7.627023	-10.075508	4.023738
C	3.827136	3.680148	-8.470587	4.004818
C	6.320326	7.425868	-7.490820	4.065297
H	7.031731	8.823420	-6.109626	0.910258
H	2.547670	2.149819	-7.858781	0.936684
C	4.726230	5.445023	-6.679238	4.147693
S	3.217256	4.911132	-3.648841	6.056671
H	15.317228	10.708770	-22.029798	0.923316
C	15.028421	10.701291	-19.956584	4.062396
H	17.443714	13.989306	-19.268416	0.932023
H	12.513354	7.418526	-19.983498	0.951367
C	16.207187	12.530851	-18.426519	4.077636
C	13.467324	8.868789	-18.822029	4.002603
C	15.817284	12.530562	-15.792998	3.999344
C	13.120933	8.846454	-16.182564	4.082974
H	16.727817	14.009734	-14.638181	0.953452
H	11.885161	7.390303	-15.337979	0.948341
C	14.295385	10.671476	-14.618806	4.050138
C	13.886700	10.612127	-11.805772	3.979208
H	11.471122	13.964149	-11.710144	0.940944
H	16.274798	7.296473	-11.138344	0.959047
C	12.318414	12.413565	-10.599281	4.028877
C	14.984319	8.702015	-10.285396	4.018154
C	11.740600	12.242460	-8.010332	4.120925
C	14.462003	8.527941	-7.682181	4.050362
H	15.284822	6.985145	-6.536558	0.953923
H	10.417108	13.608368	-7.140270	0.886118
C	12.775458	10.260685	-6.545245	4.095198
S	11.183704	9.435805	-3.642016	6.032352
Pt	0.000000	3.027435	0.000000	9.935544
Pt	5.243671	3.027435	0.000000	9.966324
Pt	10.487342	3.027435	0.000000	10.027759
Pt	2.621835	7.568587	0.000000	10.027017
Pt	7.865506	7.568587	0.000000	9.952131
Pt	13.109177	7.568587	0.000000	9.963673
Pt	0.000000	0.000000	4.281441	10.017082
Pt	5.243671	0.000000	4.281441	9.962264
Pt	10.487342	0.000000	4.281441	9.882051
Pt	2.621835	4.541152	4.281441	9.881859
Pt	7.865506	4.541152	4.281441	10.017519
Pt	13.109177	4.541152	4.281441	9.962251
Pt	2.621835	1.513717	8.562880	10.083715
Pt	7.865506	1.513717	8.562880	9.952932
Pt	13.109177	1.513717	8.562880	10.030330
Pt	5.243671	6.054870	8.562880	10.030048
Pt	10.487342	6.054870	8.562880	10.083269
Pt	15.731012	6.054870	8.562880	9.952460

Table S6 Atomic Cartesian coordinates and valence Bader charges for BPMT SAM on fcc Pt (111). All quantities are in atomic units.

Atom	X	Y	Z	Charge
H	11.082915	8.331212	-23.016233	0.900989
H	2.920398	3.607492	-23.019762	0.905053
C	11.050255	8.240886	-20.925264	4.073048
C	2.919900	3.517376	-20.928520	4.085068
H	8.504149	4.977322	-20.775502	0.938632
H	5.468008	0.256812	-20.736861	0.953263
H	13.590932	11.473001	-20.418677	0.941646
H	0.365886	6.745011	-20.463950	0.936689
C	9.615587	6.371233	-19.682762	3.962690
C	4.336828	1.649602	-19.663107	3.935346
C	12.446691	9.992750	-19.484559	4.144030
C	1.496882	5.266703	-19.510786	3.964819
C	9.594684	6.244450	-17.022342	4.111265
C	4.314974	1.523880	-17.002743	4.132126
C	12.399888	9.876461	-16.823792	3.977969
C	1.499077	5.150329	-16.849589	4.113021
H	8.474884	4.750703	-16.081173	0.957312
H	5.420156	0.031315	-16.042770	0.941390
H	13.511586	11.265452	-15.728984	0.946163
H	0.362893	6.534889	-15.774056	0.941162
C	10.983375	7.997471	-15.551557	3.978726
C	2.900213	3.274909	-15.554741	4.024883
H	0.277777	-0.190418	-12.771887	0.959315
C	11.004559	7.787172	-12.718483	3.993743
H	13.565248	4.537868	-12.714004	0.956351
C	2.832519	3.061492	-12.722566	4.017171
H	8.480356	10.991855	-11.997151	0.952152
H	5.346657	6.262481	-11.950181	0.946093
C	1.382798	1.123135	-11.580584	4.061350
C	12.434467	5.851426	-11.546938	4.048314
C	9.605388	9.446144	-11.148324	4.016259
C	4.204197	4.716849	-11.124470	3.996807
C	1.311535	0.817227	-8.946251	4.022437
C	12.454039	5.547921	-8.911333	4.049707
C	9.578092	9.151068	-8.501478	4.072326
C	4.180261	4.418567	-8.477733	4.062258
H	0.171553	-0.718507	-8.101270	0.931379
H	13.574942	4.011961	-8.041687	0.905642
C	10.991054	7.177260	-7.366962	4.165199
C	2.742599	2.446012	-7.371826	4.143301
H	8.446043	10.443946	-7.307337	0.919436
H	5.288618	5.710086	-7.260095	0.938262
S	10.877562	6.524394	-4.048846	6.130232
S	2.764561	1.803944	-4.049462	6.131648
Au	0.000000	3.146184	0.000000	10.999283
Au	5.449349	3.146184	0.000000	10.952206
Au	10.898697	3.146184	0.000000	10.892162
Au	2.724674	7.865457	0.000000	10.892383
Au	8.174023	7.865457	0.000000	10.951873
Au	13.623372	7.865457	0.000000	10.999486
Au	0.000000	0.000000	4.449375	10.958487
Au	5.449349	0.000000	4.449375	11.003732
Au	10.898697	0.000000	4.449375	10.914381
Au	2.724674	4.719274	4.449375	10.914523
Au	8.174023	4.719274	4.449375	10.957317
Au	13.623372	4.719274	4.449375	11.004909
Au	2.724674	1.573092	8.898748	10.955340
Au	8.174023	1.573092	8.898748	11.011393
Au	13.623372	1.573092	8.898748	11.063972
Au	5.449349	6.292365	8.898748	11.011712
Au	10.898697	6.292365	8.898748	10.955384
Au	16.348046	6.292365	8.898748	11.064252

Table S7 Atomic Cartesian coordinates and valence Bader charges for BPMT SAM on fcc Au (111). All quantities are in atomic units.

Atom	X	Y	Z	Charge
H	2.830951	4.822588	-22.881145	1.012199
C	2.825237	4.819090	-20.787978	3.979255
H	0.293929	8.081838	-20.462613	0.962774
H	5.353499	1.554088	-20.459294	0.966835
C	1.412720	6.636469	-19.446529	4.037820
C	4.229806	2.996736	-19.444777	4.036180
C	1.417099	6.636686	-16.783001	4.011176
C	4.208688	2.986135	-16.781374	4.014224
H	0.301604	8.081248	-15.763492	0.959338
H	5.314544	1.535263	-15.760232	0.957551
C	2.808567	4.808777	-15.410788	4.004419
C	2.791315	4.795373	-12.570896	4.009020
H	0.281667	1.519194	-12.250383	0.955990
H	5.296707	8.067271	-12.164738	0.919370
C	1.385603	2.963485	-11.217093	4.048092
C	4.174993	6.609134	-11.170163	3.985801
C	1.338836	2.941998	-8.558852	4.021535
C	4.175550	6.595790	-8.510420	4.083427
H	5.281188	8.022977	-7.454283	0.936044
H	0.213401	1.503019	-7.540996	0.925848
C	2.745288	4.760106	-7.187177	4.236719
S	2.714195	4.725395	-3.800681	6.216947
H	11.019059	9.550413	-22.878494	1.012609
C	11.010086	9.547565	-20.785338	3.980206
H	13.538513	12.810864	-20.443008	0.959616
H	8.480011	6.282513	-20.473429	0.965328
C	12.412635	11.365709	-19.434461	4.030371
C	9.596229	7.725656	-19.451429	4.039500
C	12.388861	11.367284	-16.771020	4.018892
C	9.598093	7.716256	-16.787942	4.022699
H	13.495455	12.813365	-15.744013	0.957134
H	8.484233	6.266506	-15.774007	0.946527
C	10.988115	9.539497	-15.407994	4.006013
C	10.980206	9.528874	-12.568103	4.028383
H	8.473702	12.802806	-12.192945	0.936702
H	13.489847	6.254636	-12.216411	0.949937
C	9.581721	11.344084	-11.184245	3.997131
C	12.371652	7.698472	-11.197562	4.001288
C	9.548832	11.331360	-8.525021	4.054163
C	12.385720	7.677408	-8.538780	4.018015
H	13.498124	6.238575	-7.506372	0.963985
H	8.431037	12.759106	-7.482661	0.897929
C	10.961203	9.494440	-7.184694	4.274713
S	10.938802	9.453798	-3.798716	6.219821
Ag	0.000000	3.151715	0.000000	10.859786
Ag	5.458930	3.151715	0.000000	10.894407
Ag	10.917859	3.151715	0.000000	10.929131
Ag	2.729465	7.879286	0.000000	10.929641
Ag	8.188394	7.879286	0.000000	10.861456
Ag	13.647324	7.879286	0.000000	10.893514
Ag	0.000000	0.000000	4.457197	10.976570
Ag	5.458930	0.000000	4.457197	11.014092
Ag	10.917859	0.000000	4.457197	10.935938
Ag	2.729465	4.727571	4.457197	10.935919
Ag	8.188394	4.727571	4.457197	11.014128
Ag	13.647324	4.727571	4.457197	10.976551
Ag	2.729465	1.575856	8.914393	11.042032
Ag	8.188394	1.575856	8.914393	10.954093
Ag	13.647324	1.575856	8.914393	10.995459
Ag	5.458930	6.303430	8.914393	10.953987
Ag	10.917859	6.303430	8.914393	11.041943
Ag	16.376789	6.303430	8.914393	10.995409

Table S8 Atomic Cartesian coordinates and valence Bader charges for BPMT SAM on fcc Ag (111). All quantities are in atomic units.

Atom	X	Y	Z	Charge
H	2.528194	4.271107	-22.551146	0.993718
C	2.519884	4.269831	-20.457525	4.001246
H	0.009186	7.515849	-20.109834	0.911091
H	5.026688	1.022582	-20.093395	0.913721
C	1.119974	6.070281	-19.106982	3.989748
C	3.908430	2.467554	-19.097890	3.976459
C	1.119721	6.071595	-16.448541	4.110509
C	3.885426	2.463013	-16.439725	4.149514
H	0.006606	7.523229	-15.459573	0.967322
H	4.985349	1.008067	-15.440825	0.931357
C	2.497335	4.266780	-15.055951	4.077614
C	2.480789	4.254815	-12.215428	4.004237
H	-0.011899	0.991706	-11.855822	0.971521
H	4.969578	7.510762	-11.771178	0.935603
C	1.087899	2.441296	-10.847195	4.014043
C	3.854280	6.047334	-10.799762	4.014114
C	1.044789	2.416236	-8.194500	4.001618
C	3.855785	6.037688	-8.144777	4.093774
H	4.945261	7.468440	-7.094124	0.879002
H	-0.066269	0.975356	-7.182701	0.910181
C	2.438362	4.217436	-6.818076	4.227035
S	2.395796	4.176617	-3.431501	6.255169
H	9.778098	8.458312	-22.551263	0.994569
C	9.766154	8.455825	-20.457659	4.001068
H	12.273132	11.701701	-20.083376	0.913924
H	7.256368	5.207702	-20.119432	0.919851
C	11.152606	10.255420	-19.092430	3.967788
C	8.364666	6.652452	-19.112604	3.988540
C	11.126161	10.255369	-16.434195	4.170096
C	8.361237	6.646313	-16.454218	4.106652
H	12.226594	11.708053	-15.432840	0.929910
H	7.249642	5.191675	-15.467807	0.966309
C	9.735464	8.449465	-15.056051	4.063177
C	9.722333	8.439069	-12.215486	4.009328
H	7.233434	11.699103	-11.802237	0.940346
H	12.212721	5.177422	-11.823578	0.928933
C	8.334417	10.234007	-10.817211	3.999189
C	11.099564	6.627007	-10.829375	4.061763
C	8.300222	10.224373	-8.162650	4.068137
C	11.110537	6.602508	-8.176007	4.028320
H	12.207398	5.161329	-7.149079	0.911157
H	7.196710	11.655326	-7.127243	0.872398
C	9.699657	8.403988	-6.817505	4.234525
S	9.686354	8.359997	-3.430568	6.253646
Cu	0.000000	2.788815	0.000000	10.902828
Cu	4.830369	2.788815	0.000000	10.864476
Cu	9.660737	2.788815	0.000000	10.896467
Cu	2.415184	6.972036	0.000000	10.897389
Cu	7.245553	6.972036	0.000000	10.908676
Cu	12.075922	6.972036	0.000000	10.860475
Cu	0.000000	0.000000	3.943979	10.988274
Cu	4.830369	0.000000	3.943979	10.984607
Cu	9.660737	0.000000	3.943979	10.936476
Cu	2.415184	4.183222	3.943979	10.936642
Cu	7.245553	4.183222	3.943979	10.987801
Cu	12.075922	4.183222	3.943979	10.984673
Cu	2.415184	1.394407	7.887958	11.026128
Cu	7.245553	1.394407	7.887958	11.022454
Cu	12.075922	1.394407	7.887958	10.969162
Cu	4.830369	5.577629	7.887958	10.969114
Cu	9.660737	5.577629	7.887958	11.026407
Cu	14.491106	5.577629	7.887958	11.022548

Table S9 Atomic Cartesian coordinates and valence Bader charges for BPMT SAM on fcc Cu (111). All quantities are in atomic units.

Atom	X	Y	Z	Charge
H	11.004446	8.377510	-23.045709	0.922917
H	2.883955	3.657759	-23.032166	1.010208
C	10.998952	8.255540	-20.955516	4.062865
C	2.873889	3.534426	-20.943097	3.928400
H	8.457189	4.988366	-20.822951	0.980267
H	5.422013	0.272623	-20.789098	0.953614
H	13.546103	11.477123	-20.432891	0.956618
H	0.316244	6.752162	-20.440638	0.973873
C	9.579164	6.367904	-19.723179	3.980351
C	4.286661	1.649153	-19.698942	4.008738
C	12.412749	9.985389	-19.505275	3.945208
C	1.444850	5.261275	-19.504477	3.946309
C	9.581534	6.208017	-17.064651	4.062228
C	4.261165	1.487972	-17.039760	4.090089
C	12.392124	9.833156	-16.845712	4.118486
C	1.442464	5.107344	-16.844433	4.115372
H	8.466418	4.703528	-16.134940	0.954196
H	5.370086	-0.015515	-16.100189	0.967744
H	13.516363	11.208994	-15.747679	0.952855
H	0.304854	6.480325	-15.755102	0.941633
C	10.980623	7.942958	-15.582780	4.024062
C	2.846424	3.219806	-15.568831	4.010557
H	0.252320	-0.252683	-12.706684	0.972622
C	10.984636	7.722425	-12.748289	3.994601
H	13.534452	4.467000	-12.680968	0.972110
C	2.809757	2.996386	-12.735614	4.002445
H	8.465839	10.936857	-12.050658	0.988846
H	5.334230	6.197518	-12.001895	0.971053
C	1.384990	1.067605	-11.550601	4.032374
C	12.386512	5.789659	-11.542063	4.019305
C	9.575463	9.384131	-11.195189	3.985853
C	4.203957	4.651244	-11.162920	3.981800
C	1.359486	0.772905	-8.910246	4.061540
C	12.371793	5.495615	-8.901028	3.990957
C	9.513883	9.094650	-8.549486	4.019132
C	4.223109	4.363228	-8.516178	4.054224
H	0.218472	-0.759880	-8.056483	0.921789
H	13.493799	3.958482	-8.030306	0.973731
C	10.898773	7.128389	-7.377521	4.165164
C	2.812520	2.402429	-7.364965	4.130680
H	8.361915	10.412572	-7.402236	0.969666
H	5.358451	5.679494	-7.349562	0.963226
S	10.870233	6.530212	-4.049752	5.124521
S	2.775194	1.814991	-4.034247	5.108449
H	9.306378	8.516324	-3.418137	1.713511
H	4.362611	3.776508	-3.384377	1.731072

Table S10 Atomic Cartesian coordinates and valence Bader charges for BPMT MF-2D-MoFS . All quantities are in atomic units.

Atom	X	Y	Z	Charge
H	11.269975	10.536908	-22.698959	0.971403
H	3.044949	3.649622	-23.020906	0.977747
C	11.232871	10.119115	-20.649786	4.015006
C	3.032038	3.463808	-20.937514	3.995493
H	10.555870	6.073002	-21.164330	0.928579
H	1.510392	-0.377823	-20.976901	0.963655
H	11.896272	14.038760	-19.522376	0.915394
H	4.559311	7.247979	-20.270623	0.921243
C	10.846885	7.625507	-19.792187	3.992318
C	2.163626	1.218617	-19.792359	3.988055
C	11.573962	12.076381	-18.872396	4.027079
C	3.882478	5.468945	-19.401557	3.989828
C	10.802101	7.094244	-17.185366	4.011724
C	2.145208	0.983426	-17.143018	4.011356
C	11.531403	11.544367	-16.266419	4.023860
C	3.856788	5.234703	-16.751080	4.093242
H	10.433870	5.136670	-16.545163	0.947639
H	1.514332	-0.811784	-16.273177	0.956266
H	11.858187	13.089103	-14.893482	0.969683
H	4.481494	6.846684	-15.572503	0.962694
C	11.143893	9.043741	-15.374320	3.989224
C	2.986117	2.988506	-15.569018	3.939234
H	-0.559995	0.566084	-12.616084	0.957347
C	11.086692	8.482619	-12.612294	3.967531
H	13.090638	4.876849	-12.917895	0.968666
C	2.958799	2.737216	-12.762637	3.986515
H	9.067806	11.939636	-11.572228	0.938579
H	6.467532	4.857211	-12.145762	0.966003
C	1.008159	1.392450	-11.504517	4.064108
C	12.146689	6.224740	-11.626002	4.019544
C	9.959185	10.181729	-10.870021	4.020276
C	4.884194	3.826020	-11.245623	3.988162
C	0.979855	1.134168	-8.862275	3.977996
C	12.081901	5.680072	-9.027621	3.978607
C	9.874959	9.655979	-8.267557	4.060557
C	4.878462	3.580144	-8.601789	4.009244
H	-0.577988	0.085951	-7.937827	0.937778
H	12.941132	3.908756	-8.317539	0.959232
C	10.935803	7.390953	-7.315034	4.131358
C	2.923605	2.223791	-7.375901	4.193237
H	8.946902	11.011354	-6.970905	0.936107
H	6.425309	4.438362	-7.483625	0.956732
S	10.870233	6.530212	-4.049752	5.063239
S	2.775194	1.814991	-4.034247	5.091655
H	9.726591	8.706470	-3.200413	1.748200
H	4.991364	3.077572	-3.504386	1.701825

Table S11 Atomic Cartesian coordinates and valence Bader charges for 2×BPMT. All quantities are in atomic units.