Supporting information

Figure S1:

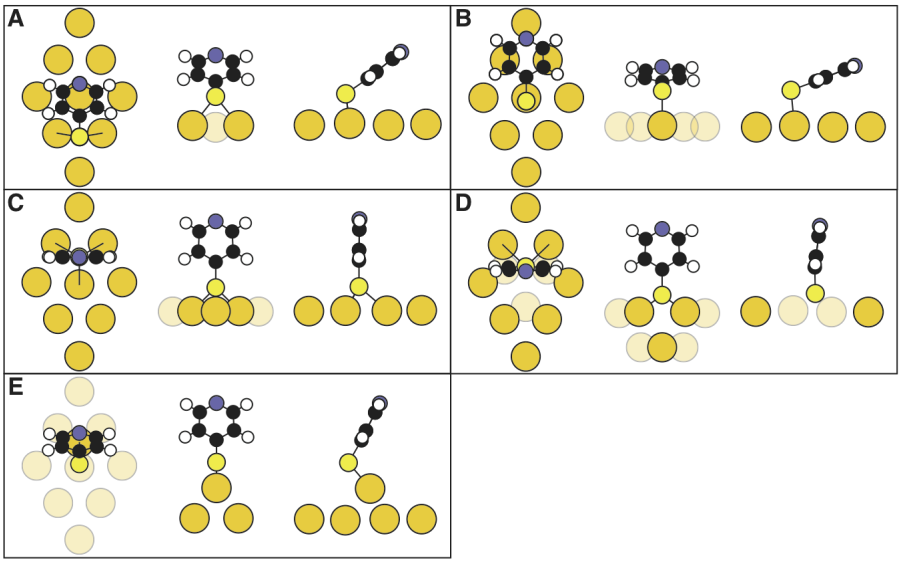


Figure S1. Adsorption geometries of the molecule at different adsorption sites: (**A**) b-hcp site, (**B**) t-fcc site, (**C**) fcc site, (**D**) defect site, (**E**) adatom site.

Table S2:

Mode number	Mode assignment	ω_{harm} (b-hcp)	$\nu_{fVCIPSI}$ (b-hcp)	ω_{harm} (t-fcc)	$\nu_{fVCIPSI}$ (t-fcc)	ω_{harm} (hollow)	$\nu_{fVCIPSI}$ (hollow)
1	frustrated rotation	2.2	2.0	2.0	4.8	-	-
2	frustrated rotation	3.0	8.3	2.7	4.7	-	-
3	frustrated rotation	4.1	3.5	4.2	8.2	-	-
4	frustrated translation	6.4	(18.5)	5.2	6.2	-	-
…							
14	AuSC bend	37.7	36.2	33.5	32.9	34.6	34.5
15	CC bend (oop)	44.3	43.5	43.9	41.4	44.5	43.0
16	CS stretch	49.0	46.9	49.5	48.1	50.6	48.5
17	ring buckling	60.0	63.2	60.8	60.9	56.7	59.5
18	CC bend	80.8	80.6	80.7	(81.1)	80.1	80.0
19	CC bend	84.2	82.3	85.2	84.6	83.7	80.8
20	ring buckling	89.3	88.6	89.5	88.8	87.5	87.4
21	CH bend (oop) sym.	97.3	97.3	98.2	85.5	97.0	91.4
22	CH bend (oop)	103.5	102.8	104.4	102.9	102.7	97.7
23	CH bend (oop)	116.7	117.5	116.8	107.6	116.9	109.5
24	CH bend (oop)	118.9	118.4	118.9	116.5	119.0	112.7
25	CNC trig.breathing	120.5	120.6	120.5	120.1	119.8	119.9
26	CCC trig. breathing	131.1	130.3	131.1	129.9	128.9	128.0
27	CH rock	132.9	134.3	131.9	130.9	132.8	131.9
28	CS stretch	132.9	130.3	133.2	132.9	131.5	130.4
29	CH bend asym.	149.6	147.9	149.4	146.4	149.5	146.3
30	CC/CN stretch sym.	157.8	156.7	157.2	148.7	157.7	158.9
31	CH bend sym.	161.4	161.7	160.9	159.3	161.1	159.8
32	CH bend asym.	171.8	168.5	171.6	168.5	171.2	169.0
33	CH bend sym.	179.7	177.8	179.4	175.4	178.8	175.3
34	CC/CN stretch asym.	189.9	190.4	188.8	176.7	189.6	191.2
35	CC stretch	191.4	190.9	191.1	190.8	189.3	188.0

Table S2. Vibrational energies (in meV) and mode assignment of 4MPy in the b-hcp, t-fcc and hollow site (oop indicates out-of-plane modes). Modes 5-13 are omitted since they contain significant components involving the surface atoms and thus are strongly dependent on the details of the partial Hessian calculation.

Sample preparation

Gold films on Cr seeded glass were flame annealed in a butane flame to expose preferentially the (111) face. After introduction into the ultra-high vacuum system, the films were annealed at up to 700 °C to remove contaminants. The Au films were checked for cleanliness and crystalline quality by low-temperature STM and XPS. The STM tip was annealed to up to 2300 K and conditioned by field emission and field desorption against an epitaxial Nb(110) film. To ensure that the tip behaves well with respect to scanning tunnelling spectroscopy, cycles of field emission and spectroscopic measurements (*I*-*V* curves, *z*-*V* curves and barrier measurements) were performed on Au(111) and Nb(110) until the tip showed the expected behaviour. Molecules were evaporated from a crucible (~58° C) onto the Au(111) film (well below room temperature) at a rate of 5-10 pm/s.

Figure S3:

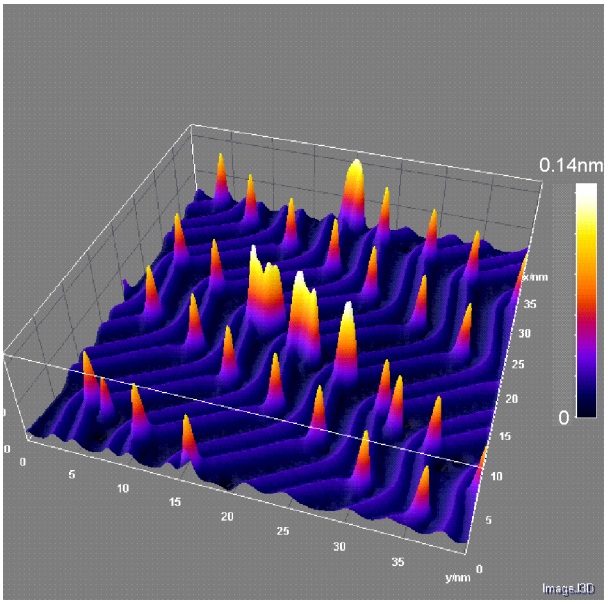


Figure S3: Topography (40×40×0.14 nm^3) of 0.01 monolayers of 4MPy on Au(111) in quasi-3D representation. Single 4MPy adsorb preferentially in elbow sites of the Au(111) (22×√3) reconstructed surface. Few isolated 4MPy are found in fcc regions (lower left corner of the image), and some form short 1-D lines originating in elbow sites (centre of the image).

Table S4: Experimental IETS signatures and mode assignment - Elbow site

Center	**Height**	**Area**	**FWHM**	**Assignment**	**SERS**
eV	fA	fA×eV	eV	Theory mode	meV
0.0409	0.96	0.0025	0.0024	14	40.0
0.0459	2.5777	0.0159	0.0058	15	48.2
0.0546	1.0709	0.0055	0.0048	16	52.7
0.0643	2.4539	0.0181	0.0069	17	60.6
0.0760	2.5975	0.0131	0.0047	-	-
0.0849	3.4739	0.0279	0.0076	18, 19, 20	82.0, 88.3, (89.6)
0.0964	2.0983	0.0093	0.0042	21	96.3
0.1016	2.5637	0.0131	0.0048	22	100.3
0.1116	2.0127	0.0181	0.0085	23, 24	(106.5), 114.1
0.1208	1.3150	0.0035	0.0025	25	124.6
0.1267	3.0980	0.0257	0.0078	26, 28	127.5, 131.5
0.1387	3.8307	0.0209	0.0051	27	136.3, 140.2
0.1467	3.4373	0.0141	0.0039	29	148.9
0.1577	2.3568	0.0182	0.0072	30	158.6
0.1630	2.3076	0.0088	0.0036	31	-
0.1702	2.3205	0.0090	0.0036	32	-, (174.6)
0.1811	1.5018	0.0120	0.0075	33	178.5, 182.9
0.1870	1.8777	0.0082	0.0041	-	-
0.1976	3.0766	0.0156	0.0047	34	196.0
0.2033	4.3111	0.0244	0.0053	35	199.9
	Average:	0.0120	0.0044		

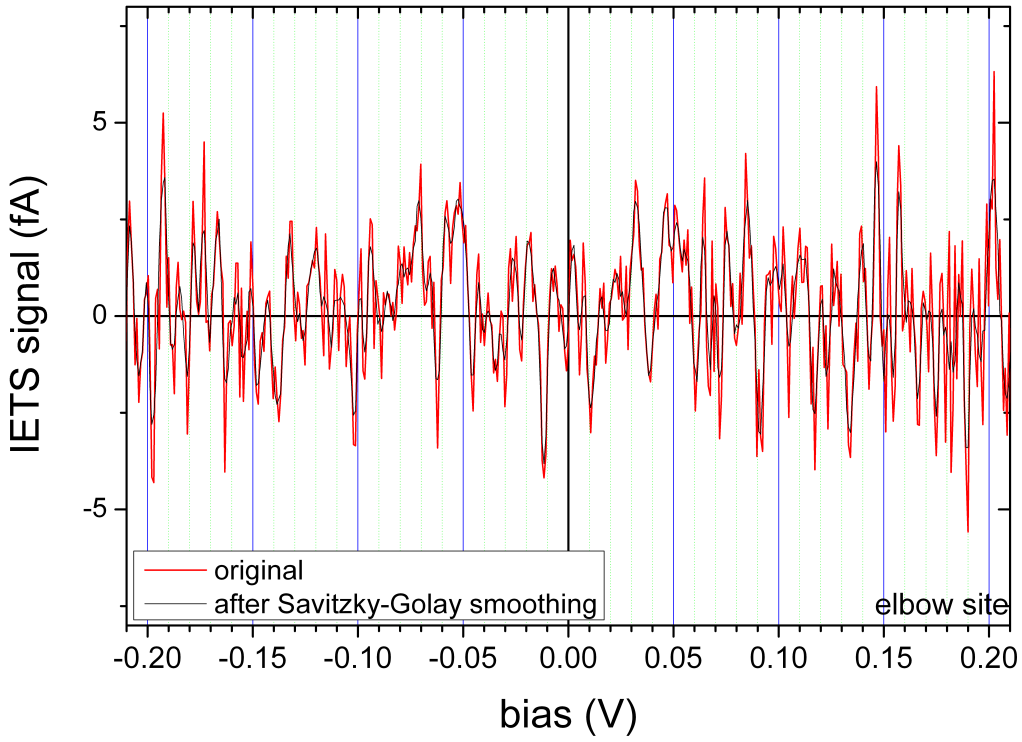
Table S4: Parameters of Gaussian functions fit to the experimental data after SG filtering (7 points corresponding to ΔE = 3.5 meV, 2nd order) and after subtracting a base line from experimental data such that all data shift to positive values. The average FWHM considers the sum of 18 peaks assigned to 22 modes. SERS data have been taken from Ref. 14. Grey numbers indicate unassigned signatures; numbers in parenthesis indicate SERS modes which are close to that IETS transition but deviate by more than the experimental resolution.

Table S5: Experimental IETS signatures and mode assignment - fcc region

Center	**Height**	**Area**	**FWHM**	**Assignment**	**SERS**
eV	fA	fA×eV	eV	Theory mode	meV
0.0369	2.24	0.0171	0.0072	14	40.0
0.0479	4.6892	0.0235	0.0047	15	48.2
0.0554	3.1639	0.0187	0.0056	16	52.7
0.0655	3.4926	0.0188	0.0051	17	60.6
0.0748	2.8859	0.0281	0.0091	-	-
0.0836	2.3099	0.0068	0.0028	18, 19	82.0
0.0885	3.3926	0.0146	0.0041	20	88.3, 89.6
0.0989	2.8971	0.0198	0.0064	21	96.3
0.1053	3.4644	0.0154	0.0042	22	100.3
0.1122	4.7435	0.0416	0.0082	23, 24	106.5, 114.1
0.1249	2.8642	0.0120	0.0040	25	124.6
0.1306	5.6691	0.0265	0.0044	26, 28	127.5, 131.5
0.1361	3.4369	0.0150	0.0041	27	136.3
0.1427	5.4424	0.0375	0.0065	29	140.2, (148.9)
0.1526	1.8770	0.0056	0.0028	-	-
0.1567	2.3954	0.0072	0.0028	30	158.6
0.1631	2.3764	0.0113	0.0045	31	-
0.1692	2.4219	0.0156	0.0060	32	174.6
0.1747	4.6992	0.0137	0.0028	-	-
0.1808	3.0861	0.0102	0.0031	33	178.5, 182.9
0.1880	3.5236	0.0374	0.0100	-	-
0.1982	4.3771	0.0218	0.0047	34, 35	196.0, 199.9
	Average:	0.0135	0.0040		

Table S5: Parameters of Gaussian functions fit to the experimental data after SG filtering (7 points corresponding to ΔE = 3.5 meV, 2nd order) and after subtracting a base line from experimental data such that all data shift to positive values. The average FWHM considers the sum of 18 peaks assigned to 22 modes. SERS data have been taken from Ref. 14. Grey numbers indicate unassigned signatures; numbers in parenthesis indicate SERS modes which are close to that IETS transition but deviate by more than the experimental resolution.

Figure S6:


IETS signal (fA)
5
0
-5
original
after Savitzky-Golay smoothing
elbow site
-0.20
-0.15
-0.10
-0.05
0.00
0.05
0.10
0.15
0.20
bias (V)

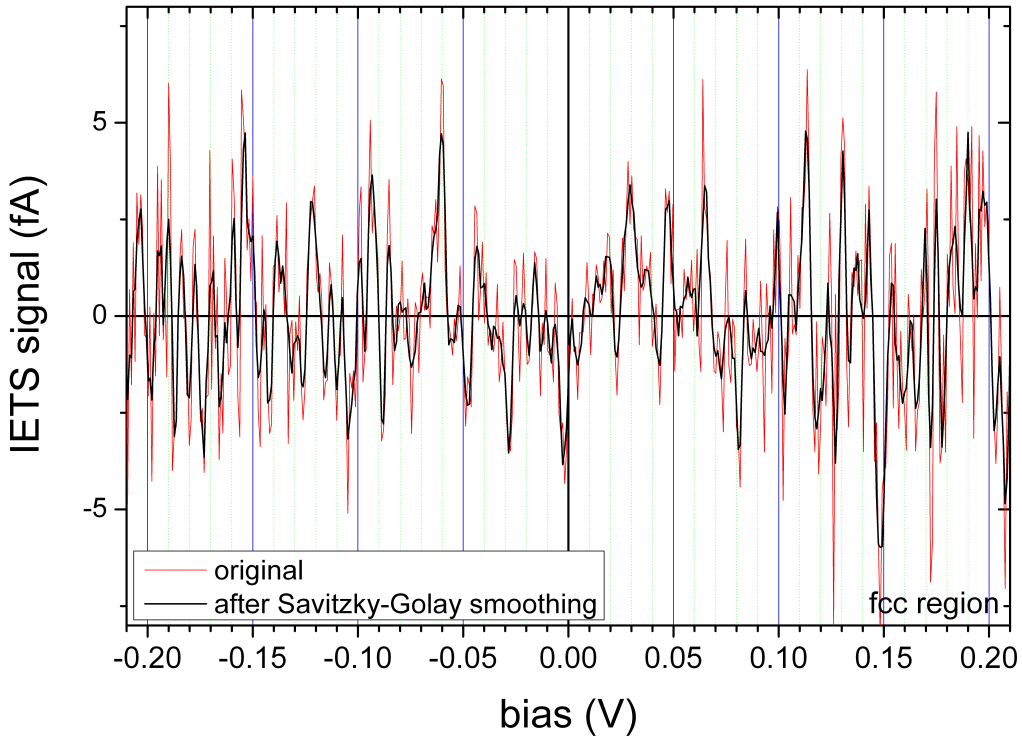

IETS signal (fA)
5
0
-5
original
after Savitzky-Golay smoothing
fcc region
-0.20
-0.15
-0.10
-0.05
0.00
0.05
0.10
0.15
0.20
bias (V)

Figure S6: Original IETS spectra, as measured, with their even and odd components and for positive and negative branches. Upper panel: elbow site, lower panel: fcc region.