Supporting information

Investigation of ultra-thin layers of bis(phthalocyaninato)lutetium(III) on graphite

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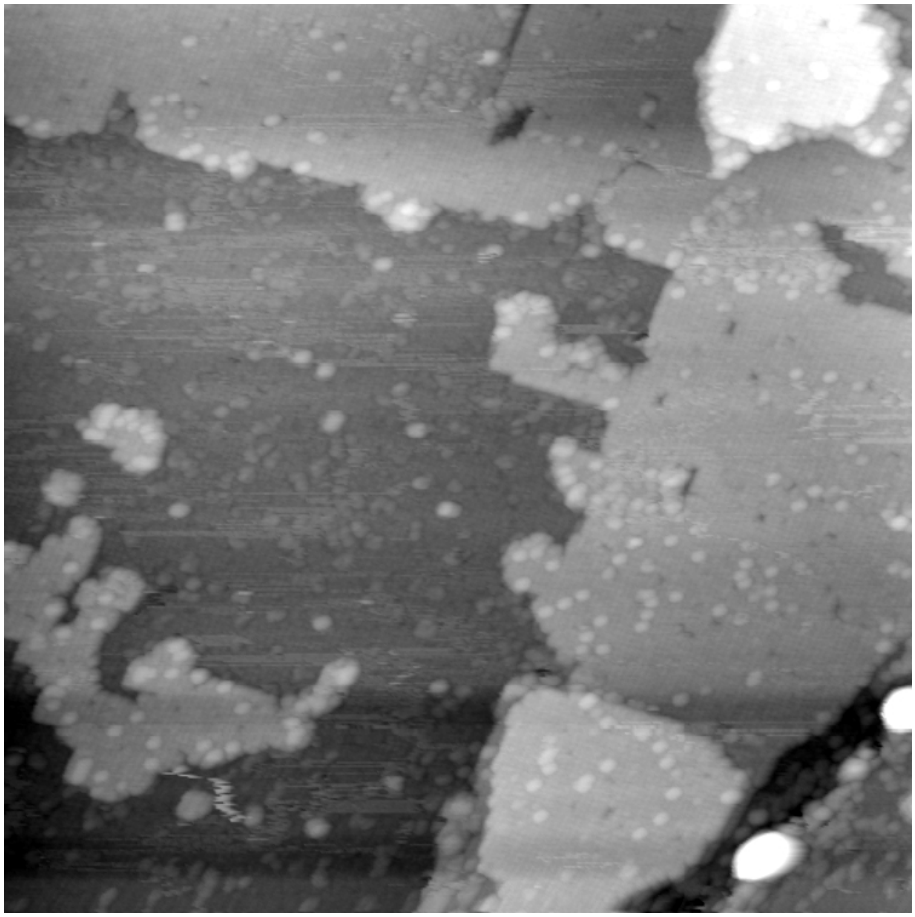
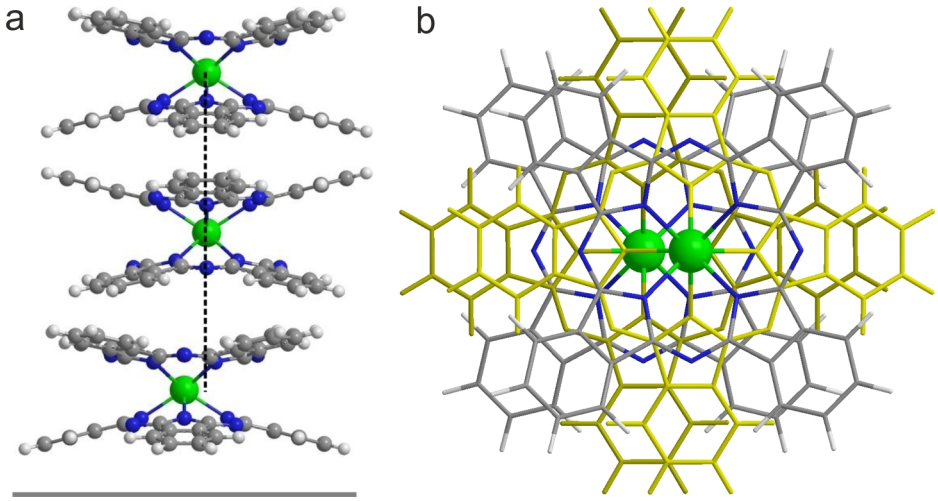
Island growth at multilayer coverage:



Supplementary figure S1. Overview STM image (200 x 200 nm^2) at a coverage of about 1 nm of $LuPc_2$ on HOPG

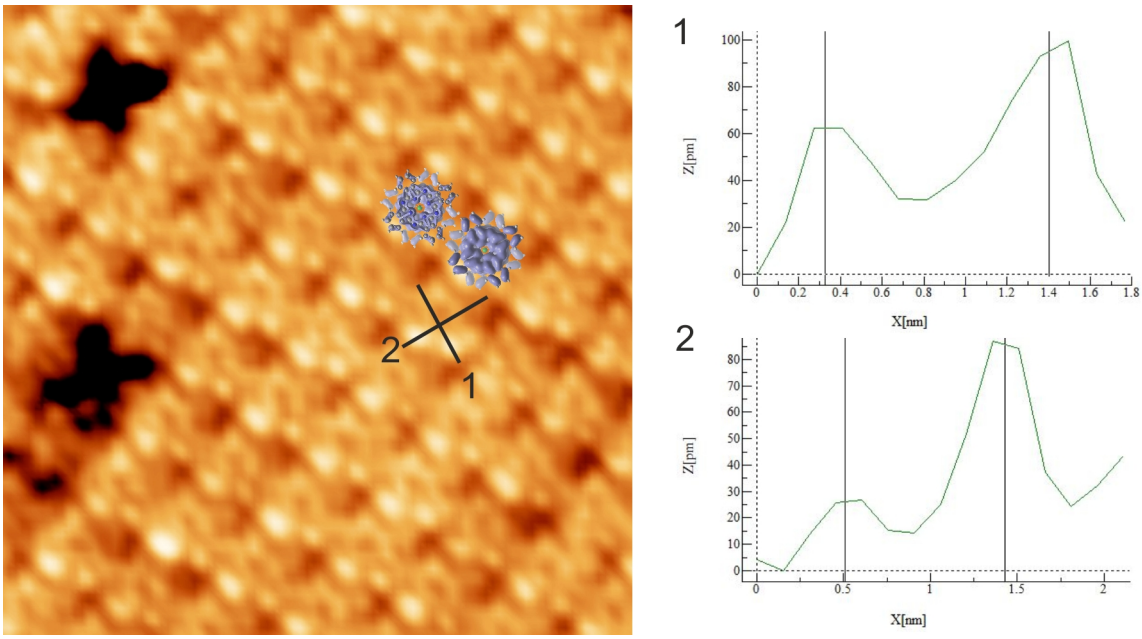
Stacking of $LuPc_2$ molecules:



Supplementary figure S2. Model for the stacking of $LuPc_2$ molecules **a:** side view of a stack of three $LuPc_2$ molecules, the second molecule is shifted perpendicular to the plane of projection relatively to the top molecule **b:** top view of two stacked $LuPc_2$ molecules which are slightly shifted relative to each other along one axis of the adjacent Pc ligands

Tilt of $LuPc_2$ molecules in the 2nd ML:

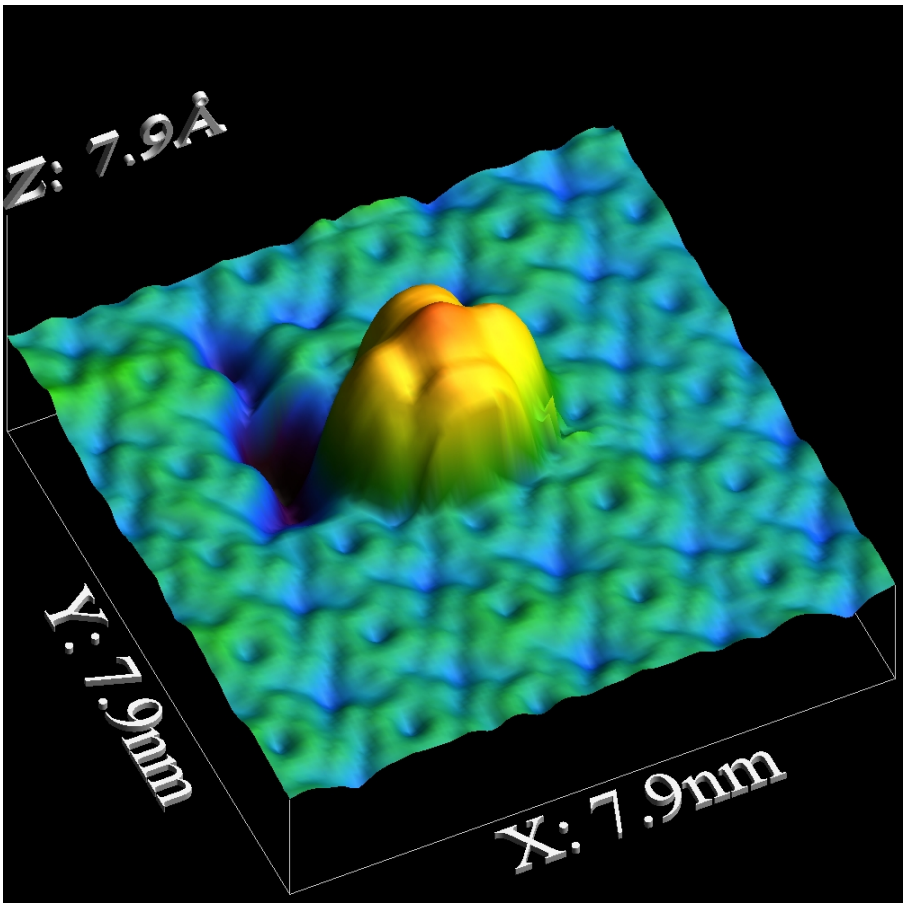
The tilt of the $LuPc_2$ molecules in the 2nd monolayer relative to the plane of the layer is shown in figure S3. Thereby from profile line 1 a tilt angle of 1.7° for one axis of the Pc ligand and from profile line 2 a tilt angle of 3.7° is calculated. The average tilt angle for axis 2 of the upper Pc ligand of the molecules in the 2nd ML was measured to be (3.5 ± 0.5)° which is about half of the value found for the tilt angle of the molecules in the 3rd ML.



Supplementary figure S3. STM image (12.2 x 12.2 nm^2, V = 0.46 V, I = 100) of tilted $LuPc_2$ molecules in the 2nd monolayer with profile lines along the molecular axes of the top Pc ligand

Lu_2Pc_2 molecules:

Seldom individual double decker molecules with an central protrusion 80 pm higher than the upper Pc were found as shown in figure S4. The protrusion does not originate from an electronic effect due to the adsorption on the molecular layer and therefore it is believed to be Lu_2Pc_2. These molecules most likely result from Lu impurities present in the evaporant since a clear evidence of decomposition of $LuPc_2$ during the deposition on graphite could not be found.



Supplementary figure S4. STM image (7.9 x 7.9 nm^2) of an individual double-decker phthalocyanine molecule with a central protrusion (Lu_2Pc_2) adsorbed on top of an ordered monolayer of $LuPc_2$, V = -1.5 V and I = 100 pA

xyz-coordinates of an geometry optimised $LuPc_2$ molecule with mPW1PW91/SDD :

Lu	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	6.95772450
C	1.40388735	0.00000000	6.81489633
C	2.00440746	0.14506662	5.55339856
C	-0.84244714	0.14523188	5.84320250
C	-0.23927584	0.27366703	4.59252110
C	1.16183432	0.27370562	4.45010987
C	-0.78950652	0.46417432	3.24575772
C	1.42993532	0.46333027	3.01999891

N	0.23766593	0.51463706	2.32156285
N	2.66126041	0.66485819	2.54592248
C	6.60084918	2.02954431	0.85363166
C	6.46713289	2.52603229	-0.46048997
C	5.22540243	2.51481586	-1.11702236
C	5.49668079	1.50826758	1.54791280
C	4.27045376	1.48667906	0.88423517
C	4.13714480	1.98220797	-0.42728078
C	2.93206966	1.04911632	1.29661463
C	2.72091794	1.83336868	-0.78116136
N	2.04072327	1.21726380	0.25298778
C	0.17865076	4.55900996	-5.25242975
C	-1.22509286	4.56166335	-5.10848435
C	-1.84633237	3.88526319	-4.04563008
C	1.00031549	3.88012852	-4.33755069
C	0.37559880	3.19849081	-3.29371172
C	-1.02543564	3.20123386	-3.15014762
C	0.90296861	2.42164299	-2.16620094
C	-1.31635876	2.42502197	-1.93929077
N	-0.14170226	1.92443570	-1.40898125
N	-2.54279865	2.35017006	-1.41799108
N	2.20923343	2.34350344	-1.90345064
C	-6.42153089	2.53910743	0.85475052
C	-6.28789713	2.04288106	2.16895263
C	-5.06713231	1.51919223	2.62567646
C	-5.33819850	2.52580391	-0.03925052
C	-4.13383545	1.99072660	0.41645153
C	-4.00061023	1.49549567	1.72812219
C	-2.81839930	1.83951618	-0.21586583
C	-2.60748426	1.05451015	1.86166487
N	-1.94480712	1.22146122	0.65961438
N	-2.09095653	0.66771073	3.02991603
C	-5.53239160	-0.81922017	-4.13573893
C	-4.63351962	-0.47230568	-5.16662952
C	-3.26015505	-0.32410932	-4.91196875
C	-5.08271358	-1.02843125	-2.82156973
C	-3.72033525	-0.86490394	-2.57331770
C	-2.82339068	-0.51750599	-3.60215719
C	-2.91219832	-1.02088746	-1.35851096
C	-1.49190379	-0.46779787	-2.98767174
N	-1.59138475	-0.71697393	-1.63121024
N	-0.37892060	-0.31237031	-3.70797328
C	3.49350560	-0.47927474	-5.99467467
C	4.57967152	-0.83529216	-5.16726955
C	4.40342850	-1.04630036	-3.78984946
C	2.20063459	-0.32512402	-5.46771588
C	2.03624666	-0.52154941	-4.09698979
C	3.12059348	-0.87584120	-3.27109264
C	0.85600060	-0.47003629	-3.22662076
C	2.57437431	-1.02842350	-1.91781207
N	1.22617554	-0.72055500	-1.91828920
C	5.35267376	-3.71229948	2.43839317

C	4.45353905	-4.06558070	3.46688121
C	3.10087040	-3.69177558	3.40773776
C	4.92390443	-2.97602466	1.32166630
C	3.58310522	-2.59564718	1.27714710
C	2.68594687	-2.94740917	2.30433723
C	2.79799888	-1.85964804	0.27960427
C	1.37756611	-2.41448829	1.90811861
N	1.49483674	-1.71837356	0.71911085
N	0.25965207	-2.69360285	2.58180830
N	3.30074671	-1.50701563	-0.90552442
C	-3.67244986	-4.05165532	4.29767077
C	-4.75899256	-3.70139753	3.46827986
C	-4.56236596	-2.96837582	2.28637778
C	-2.35889916	-3.67926151	3.96773851
C	-2.17326171	-2.93885392	2.80077287
C	-3.25789765	-2.58841007	1.97362531
C	-0.97026616	-2.41040913	2.14750885
C	-2.68888872	-1.85283812	0.83868034
N	-1.32316781	-1.71459727	1.00602883
N	-3.42009739	-1.49817592	-0.22003671
H	-0.43199369	-0.10967105	7.94688461
H	2.02622014	-0.10988221	7.69675899
H	3.08091790	0.15551820	5.43212380
H	-1.92126034	0.15649872	5.94160132
H	7.57327977	2.05679080	1.33398124
H	7.33915230	2.92597330	-0.96713185
H	5.10841129	2.90130721	-2.12232382
H	5.58508196	1.13325510	2.56043224
H	0.62728766	5.09511526	-6.08212201
H	-1.83077754	5.09952127	-5.83023071
H	-2.92233677	3.88752270	-3.91954548
H	2.07953076	3.87920511	-4.43219663
H	-7.37712849	2.94091088	0.53465368
H	-7.14314131	2.07187945	2.83586319
H	-4.94983067	1.14363180	3.63508349
H	-5.42609335	2.91275685	-1.04732772
H	-6.58663654	-0.92982959	-4.36680588
H	-5.01254759	-0.32234029	-6.17207250
H	-2.55940848	-0.06712824	-5.69720982
H	-5.76172554	-1.30450186	-2.02383151
H	3.66287571	-0.32758406	-7.05552114
H	5.56489113	-0.95099140	-5.60661237
H	5.22798118	-1.32875256	-3.14639815
H	1.35718379	-0.06144021	-6.09437619
H	6.39032973	-4.02022734	2.51266738
H	4.81576915	-4.63889419	4.31373359
H	2.39947950	-3.96518581	4.18684122
H	5.60265463	-2.70718636	0.52124029
H	-3.85816816	-4.62201512	5.20170890
H	-5.76082217	-4.00865016	3.74935259
H	-5.38762122	-2.70160831	1.63717535
H	-1.51563895	-3.95042717	4.59145672