Supplemental Information (SI)

for

Pyridine on γ-CuI: Synergy between Molecular Dynamic and Molecular Orbital Approaches to Molecule/Surface Interactions

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Figure S1. Optimized ground state structures of various DFT methods.

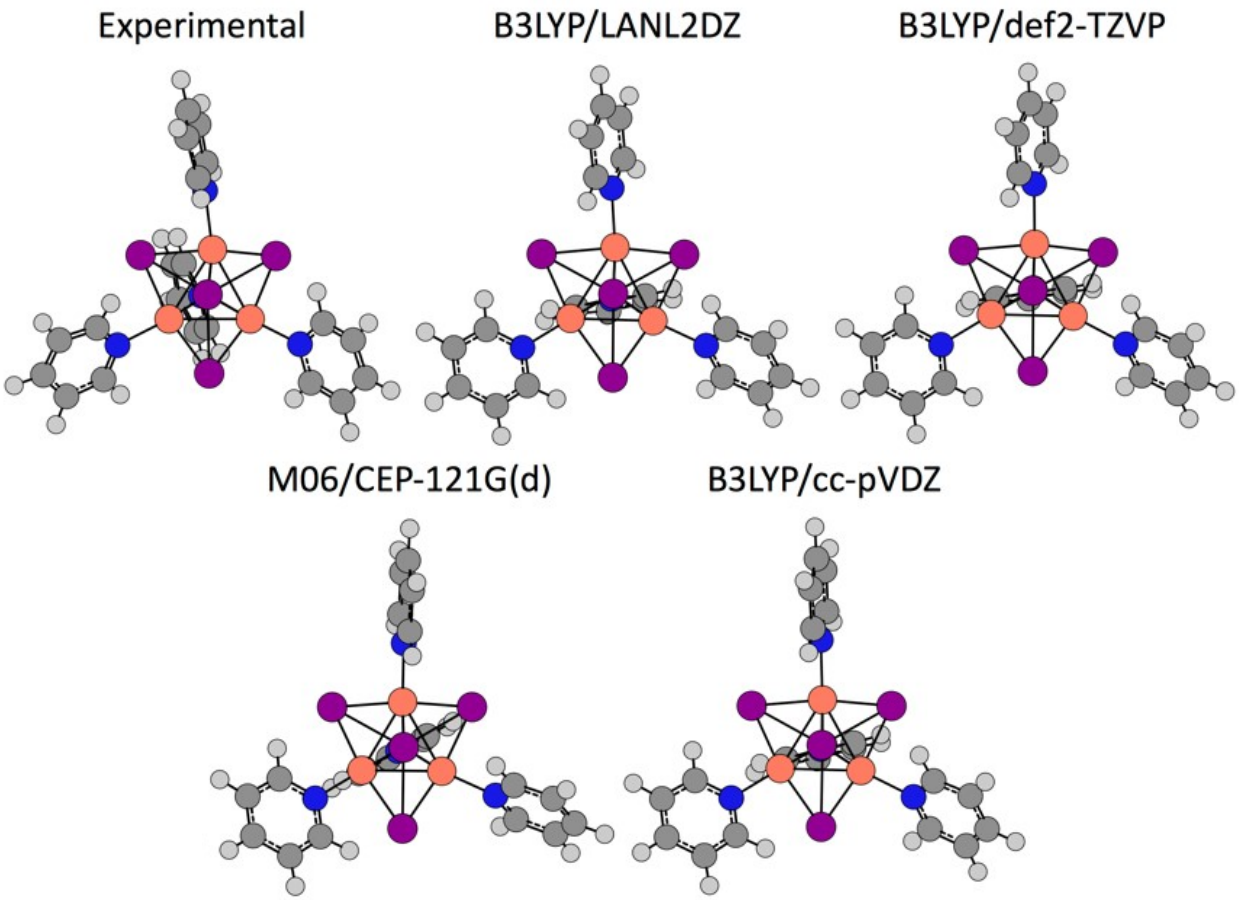

Table S1. Calculated ground state parameters for various DFT methods. Values represent averages whereas percentages represent deviations from reported experimental values.

Method	Experimental	B3LYP/LANL2DZ	B3LYP/def2-ZVP	M06/CEP-121G(d)	B3LYP/cc-pVDZ
Cu-I	2.7030 Å	2.8354 Å (4.9%)	2.7724 Å (2.6%)	2.7532 Å (1.9%)	2.7757 Å (2.7%)
Cu-N	2.0403 Å	2.0583 Å (0.9%)	2.1116 Å (3.5%)	2.0202 Å (1.0%)	2.0733 Å (1.6%)
Cu…Cu	2.6900 Å	2.6761 Å (0.5%)	2.7365 Å (1.7%)	2.6311 Å (2.2%)	2.6861 Å (0.1%)
I-Cu-I	113.0242°	113.7075° (0.6%)	113.3250° (0.3%)	114.3417° (1.2%)	113.9675° (0.8%)
Cu-I-Cu	59.6700°	58.3883° (2.1%)	59.1408° (0.9%)	57.0717° (4.4%)	57.8592° (3.0%)
I-Cu-N	105.4458°	104.6850° (0.7%)	105.2358° (0.2%)	103.8892° (1.5%)	104.4150° (1.0%)

Table S2. B3LYP/lanl2dz derived atomic force tensor (APT) values used in Molecular Dynamics simulations.

Atom	APT Value		Atom	APT Value
C	0.129369		Cu	0.610953
C	-0.133756		Cu	0.612731
C	0.078063		Cu	0.613975
C	-0.113638		Cu	0.607597
C	0.091553		I	-0.675793
C	0.106050		I	-0.673237
C	-0.097594		I	-0.676475
C	0.053272		I	-0.675229
C	-0.093443		N	-0.314987
C	0.097598		N	-0.319787
C	0.104835		N	-0.324219
C	-0.109970		N	-0.307472
C	0.071392		H	0.037698
C	-0.111066		H	0.051284
C	0.119832		H	0.082412
C	0.093762		H	0.088514
C	-0.082759		H	0.039650
C	0.049266		H	0.049679
C	-0.084829		H	0.039090
C	0.089957		H	0.092535
H	0.074370		H	0.047362
H	0.067685		H	0.045338
H	0.033830		H	0.090158
H	0.057384		H	0.083799
H	0.093705		H	0.055540
H	0.086384		H	0.047633

Atom	Avg APT Values
C	0.0128947
Cu	0.611314
N	-0.3166163
H	0.0632025
I	-0.6751835

Figure S2. B3LYP/lanl2dz ideal surface model. The model contains one pyridine molecule and 4 CuI layers (241 atoms) used for NBO calculations.

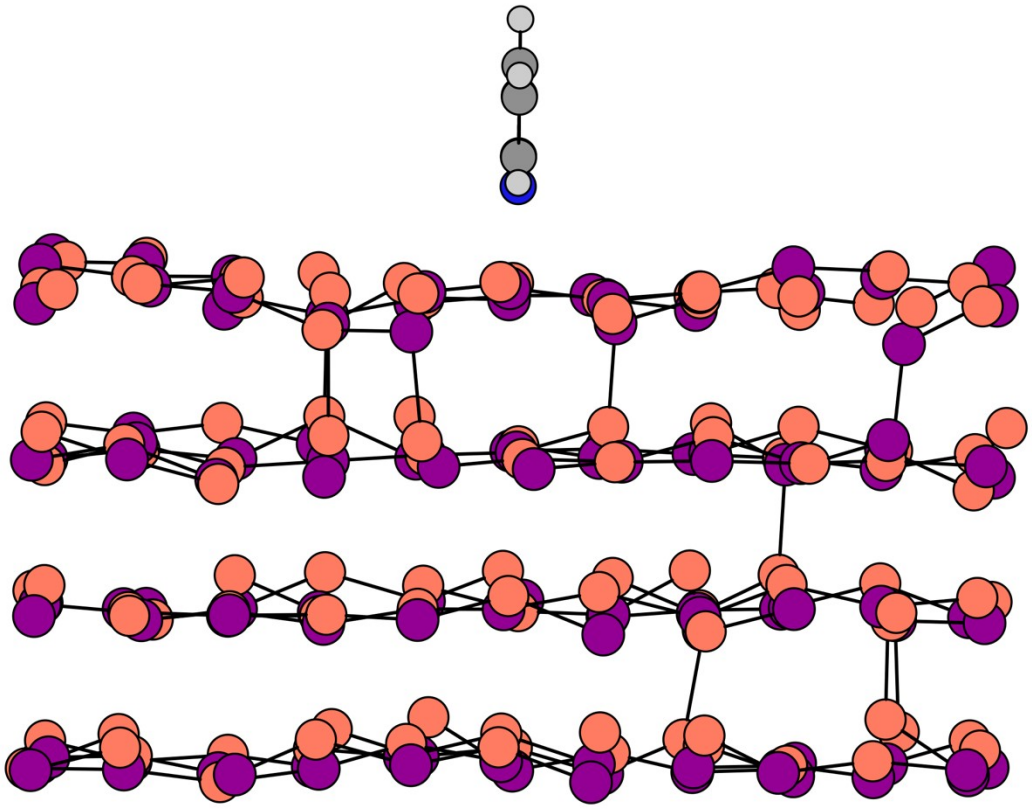

Table S3. NBO determined orbital interactions and stabilization energies for the ideal surface model where the Py molecule is perpendicular to the surface.

Donor Orbital			Acceptor Orbital			Stabilization Energy (Kcal mol^{-1})
1454	BD	C5-H125	1630	BD*	Cu99-I208	0.09
1444	LP	N241	1554	LV	Cu711	4.64
1445	BD	C1-C2	1554	LV	Cu71	0.38
1446	BD	C1-H121	1554	LV	Cu71	0.74
1447	BD	C1-N241	1554	LV	Cu71	0.85
1449	BD	C2-H122	1554	LV	Cu71	0.07
1452	BD	C4-C5	1554	LV	Cu71	0.34
1453	BD	C4-H124	1554	LV	Cu71	0.06
1454	BD	C5-H125	1554	LV	Cu71	0.17
1455	BD	C5-N241	1554	LV	Cu71	1.32
1454	BD	C5-H125	1562	LV	Cu87	0.16
794	LP	Cu71	1644	3C*	C1-C2-N241	0.06
796	LP	Cu71	1644	3C*	C1-C2-N241	0.05
1334	LP	I208	1644	3C*	C1-C2-N241	0.09
1334	LP	I208	1645	3C*	C3-C4-C5	0.05
1335	LP	I208	1644	3C*	C1-C2-N241	0.08
1334	LP	I208	1643	3Cn	C3-C4-C5	0.06
1501	BD	Cu99-I208	1643	3Cn	C3-C4-C5	0.07
1227	LP	I178	1574	BD*	C1-C2	0.22
1227	LP	I178	1575	BD*	C1-H121	1.73
1229	LP	I178	1574	BD*	C1-C2	0.07
1229	LP	I178	1575	BD*	C1-H121	0.08
792	LP	Cu71	1574	BD*	C1-C2	0.08
792	LP	Cu71	1584	BD*	C5-N241	0.14
794	LP	Cu71	1584	BD*	C5-N241	0.10
1334	LP	I208	1576	BD*	C1-N241	0.14
1334	LP	I208	1581	BD*	C4-C5	0.08
1334	LP	I208	1584	BD*	C5-N241	0.12
1501	BD	Cu99-I208	1581	BD*	C4-C5	0.07
1377	LP	I221	1583	BD*	C5-H125	0.43
1380	LP	I221	1583	BD*	C5-H125	0.10

Figure S3. B3LYP/lanl2dz 16 atom defect surface model. The model contains five Py molecules and three CuI layers (273 atoms) used for NBO calculations. The CuI layer contains 109 Cu atoms and 109 I atoms. The roughly square defect site (l x w x h) is approximately 14.02066 A x 15.90416 A x 2.90590 A, respectively.

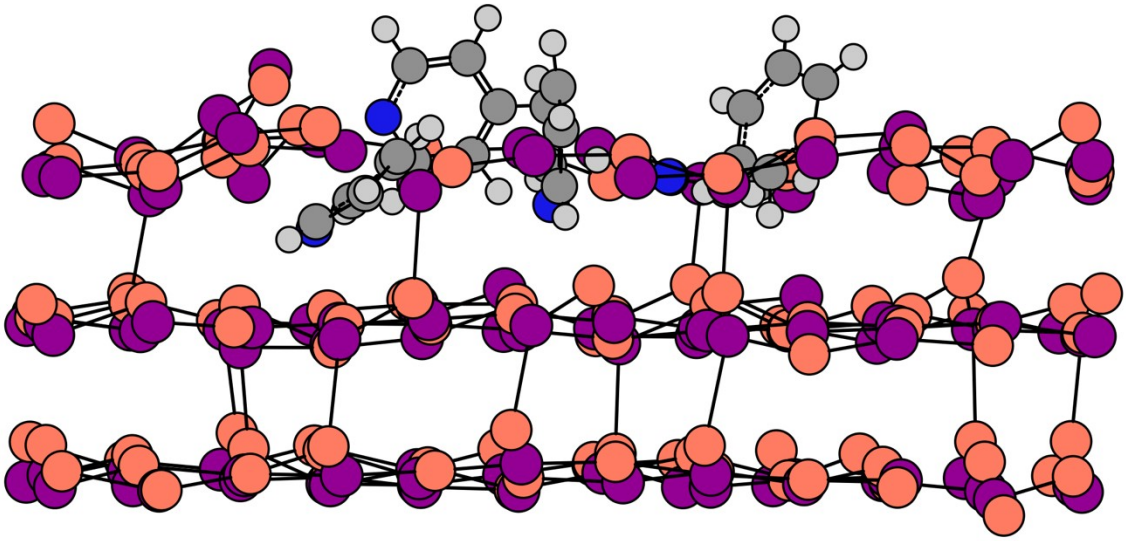

Figure S4. B3LYP/lanl2dz defect surface model as viewed from above (bottom three CuI layers removed for clarity) showing the Py positioned over a Cu atom.

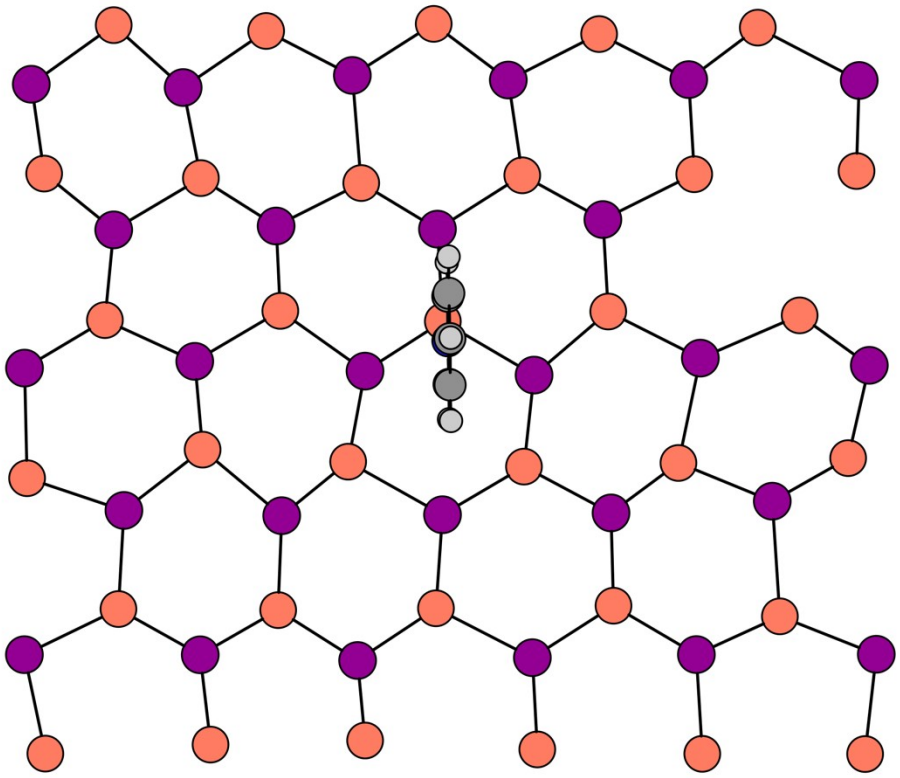

Figure S5. Angular distribution of Py molecules (i.e. flat orientation = 0°; upright orientation = 90°) for an ideal and kinked surface.

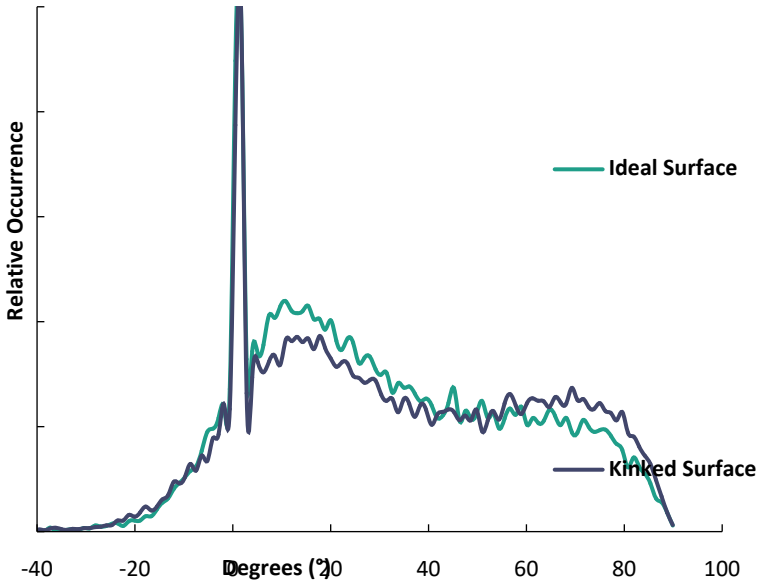

Table S4. NBO determined orbital interactions and stabilization energies for the defect surface model.

Donor Orbital			Acceptor Orbital			Stabilization Energy (Kcal mol^{-1})
1443	BD	C24-H158	1680	BD*	Cu128-I248	0.52
1444	BD	C25-H159	1680	BD*	Cu128-I248	0.06
1436	BD	C21-H155	1604	BD*	C16-H150	0.05
1436	BD	C21-H155	1542	LV	Cu62	0.39
1444	BD	C25-H159	1545	LV	Cu68	0.06
1444	BD	C25-H159	1551	LV	Cu80	0.49
1390	LP	N273	1542	LV	Cu62	6.36
1390	LP	N273	1551	LV	Cu80	0.09
1517	3C	C23-C24-C25	1598	BD*	C13-H147	0.06
1522	3Cn	C21-C22-N273	1598	BD*	C13-H147	0.1
1522	3Cn	C21-C22-N273	1542	LV	Cu62	0.16
1435	BD	C21-C22	1542	LV	Cu62	0.27
1437	BD	C21-N273	1542	LV	Cu62	0.24
1442	BD	C24-C25	1542	LV	Cu62	0.19
1445	BD	C25-N273	1542	LV	Cu62	0.54
1517	3C	C23-C24-C25	1680	BD*	Cu128-I248	0.15
1522	3Cn	C21-C22-N273	1650	BD*	Cu78-I216	0.06
1516	3C	C21-C22-N273	1689	3Cn	C12-C13-C14	0.14
1522	3Cn	C21-C22-N273	1689	3Cn	C12-C13-C14	0.07
1522	3Cn	C21-C22-N273	1592	BD*	C11-C12	0.05
1522	3Cn	C21-C22-N273	1597	BD*	C13-C14	0.06
981	LP	Cu128	1622	BD*	C24-H158	0.22
739	LP	Cu80	1623	BD*	C25-H159	0.12
647	LP	Cu62	1614	BD*	C21-C22	0.06
647	LP	Cu62	1624	BD*	C25-N273	0.12
1389	LP	N272	1700	3C	C21-C22-N273	0.63
1090	LP	I182	1615	BD*	C21-H155	0.45
1092	LP	I182	1615	BD*	C21-H155	0.14
1116	LP	I189	1615	BD*	C21-H155	0.06
1156	LP	I200	1623	BD*	C25-H159	0.12
1177	LP	I207	1623	BD*	C25-H159	0.92
1218	LP	I219	1623	BD*	C25-H159	0.07
1289	LP	I239	1622	BD*	C24-H158	0.64
1290	LP	I239	1622	BD*	C24-H158	0.07
1291	LP	I239	1622	BD*	C24-H158	0.06
1292	LP	I239	1622	BD*	C24-H158	0.29

1090	LP	I182	1614	BD*	C21-C22	0.08
1153	LP	I200	1700	3C*	C21-C22-N273	0.08
1153	LP	I200	1616	BD*	C21-N273	0.08
1177	LP	I207	1691	3Cn	C23-C24-C25	0.08
1177	LP	I207	1621	BD*	C24-C25	0.12
1289	LP	I239	1619	BD*	C23-C24	0.15
1518	3Cn	C1-C2-N269	1691	3Cn	C23-C24-C25	0.09

Figure S6. Angular distribution of Py molecules (i.e. flat orientation = 0°; upright orientation = 90°) for the cratered surface MD simulations.

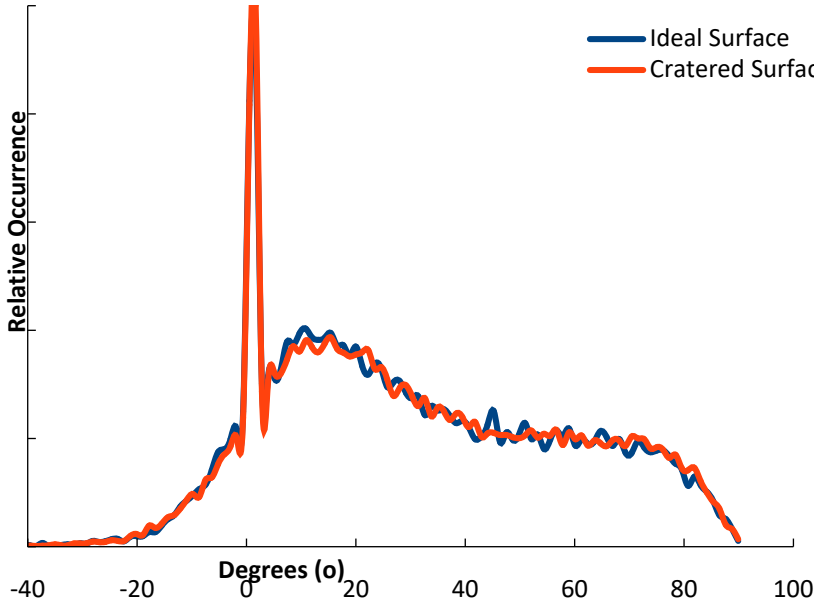

Figure S7. B3LYP/lanl2dz ideal surface model for a Py molecule nearly parallel to the surface. The model contains one pyridine molecule and 4 CuI layers (241 atoms) used for NBO calculations.

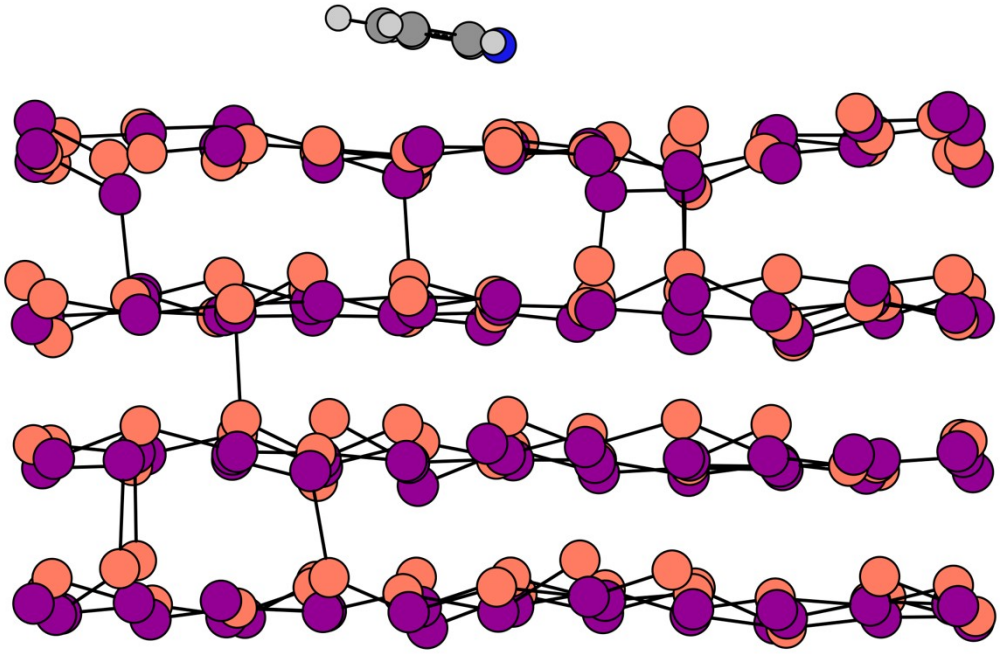

Table S5. NBO determined orbital interactions and stabilization energies for the ideal surface model where a Py molecule is nearly parallel to the surface.

Donor Orbital			Acceptor Orbital			Stabilization Energy (Kcal mol^{-1})
1227	LP	I178	1644	3C*	C1-C2-C3	0.24
1229	LP	I178	1644	3C*	C1-C2-C3	0.31
792	LP	Cu71	1644	3C*	C1-C2-C3	0.06
793	LP	Cu71	1644	3C*	C1-C2-C3	0.12
794	LP	Cu71	1645	3C*	C4-C5-N241	0.09
795	LP	Cu71	1644	3C*	C1-C2-C3	0.24
795	LP	Cu71	1645	3C*	C4-C5-N241	0.66
796	LP	Cu71	1644	3C*	C1-C2-C3	0.18
796	LP	Cu71	1645	3C*	C4-C5-N241	0.18
1241	LP	I182	1644	3C*	C1-C2-C3	0.07
1286	LP	I194	1645	3C*	C4-C5-N241	0.19
1337	LP	I208	1645	3C*	C4-C5-N241	0.06
1381	LP	I221	1645	3C*	C4-C5-N241	0.08
1227	LP	I178	1643	3Cn	C1-C2-C3	1.15
1228	LP	I178	1643	3Cn	C1-C2-C3	0.08
1229	LP	I178	1643	3Cn	C1-C2-C3	0.91
792	LP	Cu71	1643	3Cn	C1-C2-C3	0.39
793	LP	Cu71	1643	3Cn	C1-C2-C3	0.27
795	LP	Cu71	1643	3Cn	C1-C2-C3	0.77
796	LP	Cu71	1643	3Cn	C1-C2-C3	1.29
819	LP	Cu76	1643	3Cn	C1-C2-C3	0.23
1286	LP	I194	1643	3Cn	C1-C2-C3	0.07
1336	LP	I208	1643	3Cn	C1-C2-C3	0.14
1227	LP	I178	1575	BD*	C1-C2	0.07
1227	LP	I178	1576	BD*	C1-H121	0.94
1229	LP	I178	1577	BD*	C1-N241	0.07
1288	LP	I194	1583	BD*	C4-H124	0.06
1334	LP	I208	1577	BD*	C1-N241	0.21
1334	LP	I208	1582	BD*	C4-C5	0.07
1334	LP	I208	1585	BD*	C5-N241	0.1
1336	LP	I208	1577	BD*	C1-N241	0.06
1336	LP	I208	1582	BD*	C4-C5	0.11
1378	LP	I221	1584	BD*	C5-H125	0.31
1450	BD	C2-H122	1547	LV	Cu60	0.07
1514	3C	C1-C2-C3	1547	LV	Cu60	0.06
1445	LP	N241	1554	LV	Cu71	5.91

1446	BD	C1-C2	1554	LV	Cu71	0.93
1447	BD	C1-H121	1554	LV	Cu71	1.4
1448	BD	C1-N241	1554	LV	Cu71	1.03
1449	BD	C2-C3	1554	LV	Cu71	0.22
1450	BD	C2-H122	1554	LV	Cu71	0.24
1451	BD	C3-C4	1554	LV	Cu71	0.13
1452	BD	C3-H123	1554	LV	Cu71	0.11
1453	BD	C4-C5	1554	LV	Cu71	0.53
1454	BD	C4-H124	1554	LV	Cu71	0.14
1455	BD	C5-H125	1554	LV	Cu71	0.49
1456	BD	C5-N241	1554	LV	Cu71	0.87
1514	3C	C1-C2-C3	1554	LV	Cu71	0.74
1515	3C	C4-C5-N241	1554	LV	Cu71	1.44
1516	3Cn	C4-C5-N241	1554	LV	Cu71	1.78
1446	BD	C1-C2	1557	LV	Cu76	0.09
1450	BD	C2-H122	1557	LV	Cu76	0.13
1451	BD	C3-C4	1557	LV	Cu76	0.09
1452	BD	C3-H123	1557	LV	Cu76	0.29
1453	BD	C4-C5	1557	LV	Cu76	0.08
1514	3C	C1-C2-C3	1557	LV	Cu76	0.66
1451	BD	C3-C4	1562	LV	Cu87	0.08
1454	BD	C4-H124	1562	LV	Cu87	0.3
1455	BD	C5-H125	1562	LV	Cu87	0.21
1456	BD	C5-N241	1562	LV	Cu87	0.09
1515	3C	C4-C5-N241	1562	LV	Cu87	0.32
1516	3Cn	C4-C5-N241	1562	LV	Cu87	0.98