Supporting Information

Reaction of Thin Films of Solid-State Benzene and Pyridine with Calcium

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Table S1 presents vibrational peak frequencies and assignments for the reaction of Ca with thin, solid-state films of benzene. Proposed species in the film after reaction include unreacted benzene, phenyl radical anion, phenyl radical, benzyne, and CaH_2. **Table S2** summarizes the observed Raman bands for the Ca/benzene reaction and their molecular assignments. **Table S3** includes vibrational peak frequencies and assignments for the reaction of Ca with thin, solid-state films of pyridine. Proposed species in the film after reaction include unreacted pyridine, pyridyl radicals, and pyridyne. **Table S4** includes vibrational assignments for the proposed ring opening products shown in **Figure S1**. **Table S5** summarizes the observed Raman bands for the Ca/pyridine reaction and their molecular assignments. **Table S6** presents vibrational peak frequencies and assignments for the reaction of Ca with thin, solid-state films of pyridine-d_5. **Table S7** presents the observed peak frequencies for a pristine thin, solid-state film of benzene-d_6 before and after deposition of 20 Å Ca.

Table S1. Vibrational peak frequencies and assignments for benzene and the proposed reaction products after Ca deposition: phenyl radical anion, phenyl radical, benzyne, and CaH_2.

	Observed Frequency (cm^{-1})	Benzene[a]			Phenyl Radical[b]			Phenyl Radical Anion[b]			Benzyne[c]		CaH_2[d]	
		Frequency (cm^{-1})	Wilson Number	Vibrational Mode	Frequency (cm^{-1})	Wilson Number	Vibrational Mode	Frequency (cm^{-1})	Wilson Number	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode
Region I	606	605	ν_6	δ(C-C-C)$_{ip}$	582	ν_{27}	δ(C-C-C)$_{ip}$	578	ν_{10}	δ(C-C-C)$_{ip}$	472	δ(C-C-C)$_{ip}$		
					603	ν_{10}	δ(C-C-C)$_{ip}$	617	ν_{27}	δ(C-C-C)$_{ip}$	589	δ(C-C-C)$_{ip}$		
					646	ν_{17}	δ(C-H)$_{oop}$	661	ν_{17}	δ(C-H)$_{oop}$				
	729				706	ν_{16}	δ(C-H)$_{oop}$	705	ν_{16}	δ(C-H)$_{oop}$				
					781	ν_{12}		817	ν_{15}	δ(C-H)$_{ip}$				
	854	846	ν_{10}	δ(C-H)$_{oop}$	857	ν_{15}	δ(C-H)$_{ip}$	838	ν_{12}		838	δ(C-H)$_{ip}$		
Region II	975				945	ν_{11}	δ(C-H)$_{oop}$	924	ν_9	δ(C-C-C)$_{ip}$	982	ν(C-H)$_{ring}$		
	993	982	ν_1	ν(C-H)$_{ring}$	973	ν_9	δ(C-C-C)$_{ip}$	980	ν_8	ν(C-H)$_{ring}$	1039	ν(C-H)		
					990	ν_{14}	δ(C-H)$_{oop}$	1009	ν_{26}	δ(C-H)$_{oop}$	1094	δ(C-H)$_{oop}$		
					998	ν_8	ν(C-H)$_{ring}$	1027	ν_7	δ(C-H)$_{ip}$	1271	δ(C-H)$_{ip}$		
					1028	ν_7	δ(C-H)$_{ip}$	1129	ν_{25}	δ(C-H)$_{ip}$	1307	δ(C-H)$_{ip}$		
Region III	1176	1177	ν_9	ν(C-H)$_{ip}$	1151	ν_6	δ(C-H)$_{ip}$	1165	ν_6	δ(C-H)$_{ip}$	1394	δ(C-H)$_{ip}$	1185	ν(CaH_2)
					1159	ν_{25}	δ(C-H)$_{ip}$	1225	ν_{24}	δ(C-H)$_{ip}$	1415	δ(C-H)$_{ip}$	1194	ν(CaH_2)
	1270				1281	ν_{24}	δ(C-H)$_{ip}$	1310	ν_{23}	δ(C-H)$_{ip}$	1451	ν(C-C)	1215	ν(CaH_2)
	1480	1473	ν_{19}	ν(C-C)$_{ip}$	1310	ν_{23}	δ(C-H)$_{ip}$	1396	ν_{22}	δ(C-H)$_{ip}$			1250	ν(Ca-H)
	1541				1497	ν_4	ν(C-C)	1414	ν_5	ν(C-C)			1290	ν(Ca-H)
	1583	1587	ν_8	ν(C-C)$_{ip}$				1525	ν_4	δ(C-H)$_{ip}$				
	1602	1602						1526	ν_{21}	ν(C-C)				
	1843										1846	ν(C=C)		
	2550													
	2790													
	3046	3047	ν_7	ν(C-H)	3083	ν_3	ν(C-H)	2858	ν_{20}	ν(C-H)	3049	ν(C-H)		
	3062	3062	ν_2	ν(C-H)	3089	ν_{20}	ν(C-H)	2860	ν_3	ν(C-H)	3086	ν(C-H)		
		3062	ν_{13}	ν(C-H)	3102	ν_2	ν(C-H)	2936	ν_2	ν(C-H)	3071	ν(C-H)		
	3100	3073	ν_{20}	ν(C-H)	3104	ν_{19}	ν(C-H)	2940	ν_{19}	ν(C-H)	3094	ν(C-H)		
					3117	ν_1	ν(C-H)	3031	ν_1	ν(C-H)				

[a] Benzene assignments taken from reference S1.
[b] Phenyl radical and phenyl radical anion assignments taken from reference S2.
[c] *o*-Benzyne assignments taken from reference S3.
[d] CaH and CaH_2 assignments taken from reference S4.

Table S2. Summary of observed Raman bands and assignments for proposed products from reaction of Ca with thin, solid-state films of benzene.

Observed Frequency (cm^{-1})			
Pristine		+ 20 Å Ca	Assignments[a]
Region I	606	606	Bz, $Ph^{\bullet-}$, $Ph^{\bullet}$
		729	Bz
	846		$Ph^{\bullet-}$, $Bz^{\bullet\bullet}$
		854	Bz
Region II		975	$Ph^{\bullet-}$, $Ph^{\bullet}$, $Bz^{\bullet\bullet}$
	993	993	Bz
Region III	1178	1176	Bz, $Ph^{\bullet-}$, CaH_2
		1270	$Bz^{\bullet\bullet}$, CaH_2
	1482	1480	Bz, $Ph^{\bullet-}$, $Ph^{\bullet}$, $Bz^{\bullet\bullet}$
		1541	$Ph^{\bullet-}$, $Ph^{\bullet}$
	1582	1583	Bz
	1602	1602	Bz, $Ph^{\bullet-}$
		1843	$Bz^{\bullet\bullet}$
2550		2550	Bz
		2790	$Ph^{\bullet-}$
3046		3046	Bz
3062		3062	Bz, $Ph^{\bullet-}$, $Bz^{\bullet\bullet}$
3073		3100	Bz, $Ph^{\bullet}$

[a] Assignment abbreviations: Bz = benzene, $Ph^{\bullet-}$ = phenyl radical anion, $Ph^{\bullet}$ = phenyl radical, and $Bz^{\bullet\bullet}$ = benzyne.

Table S3. Vibrational assignments of pyridine and proposed reaction products post-Ca deposition, including *o*-, *m*-, *p*-pyridyl, 2,3- and 3,4-pyridyne, and CaH_2.

Observed		Pyridine[a]			*o*-Pyridyl[b]		*m*-Pyridyl[c]		*p*-Pyridyl[d]		2,3-Pyridyne[e]		3,4-Pyridyne[f]		CaH_2[g]	
Frequency (cm^{-1})		Frequency (cm^{-1})	Wilson Number	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode	Frequency (cm^{-1})	Vibrational Mode
Region I		338	ν_{16a}	$\delta(ring)_{oop}$	377	$\delta(mol)_{oop}$	381	$\delta(mol)_{oop}$	370	$\delta(mol)_{oop}$	411	$\delta(mol)_{oop}$	403	$\delta(mol)_{oop}$		
	417	406	ν_{16b}	$\delta(ring)_{oop}$	417	$\delta(ring)_{oop}$	414	$\delta(ring)_{oop}$	436	$\delta(ring)_{oop}$	432	$\delta(ring)_{ip}$	451	$\delta(C\text{-}C)_{ip}$		
	523	603	ν_{6a}	$\delta(ring)_{ip}$	572	$\delta(ring)_{ip}$	572	$\delta(ring)_{ip}$	612	$\delta(ring)_{ip}$	465	$\delta(C\text{-}C\text{-}C\text{-}C)_{oop}$				
											478	$\delta(C\text{-}C)_{oop}$	637	$\delta(mol)_{oop}$		
Region I	654	654	ν_{6b}	$\delta(ring)_{ip}$	655	$\delta(ring)_{ip}$	654	$\delta(ring)_{ip}$	636	$\delta(ring)_{ip}$	651	$\delta(mol)$	658	$\delta(ring)$		
		703	ν_{11}	$\delta(C\text{-}H)_{oop}$	700	$\delta(C\text{-}H)_{oop}$	674	$\delta(C\text{-}H)_{oop}$	697	$\delta(C\text{-}H)_{oop}$	712	$\delta(mol)_{ip}$	818	$\delta(C\text{-}H)_{oop}$		
	750	747	ν_4	$\delta(ring)_{oop}$	739	$\delta(ring)_{oop}$	770	$\delta(ring)_{oop}$	754	$\delta(ring)_{oop}$	814	$\delta(C\text{-}H)_{oop}$	848	$\delta(N\text{-}C\text{-}C)$		
		884	ν_{10a}	$\delta(C\text{-}C)_{oop}$	871	$\delta(C\text{-}H)$	902	$\delta(C\text{-}H)$	810	$\delta(C\text{-}H)$	884	$\delta(C\text{-}C)_{oop}$	915	$\delta(C\text{-}H)$		
				$\delta(mol)$	939	$\delta(C\text{-}H)_{oop}$	925	$\delta(C\text{-}H)_{oop}$	940	$\delta(C\text{-}H)_{oop}$		$\delta(mol)$	944	$\delta(C\text{-}H)_{oop}$		
	949	941	ν_{17b}	$\delta(C\text{-}H)_{oop}$	950	$\nu(C\text{-}H)_{ring}$	972	$\nu(C\text{-}H)_{ring}$	961	$\nu(C\text{-}H)_{ring}$	926	$\delta(H\text{-}C\text{-}C\text{-}C\text{-}H)$	1009	$\delta(H\text{-}C\text{-}C\text{-}C\text{-}H)$		
	994	991	ν_1	$\nu(C\text{-}H)_{ring}$	998	$\nu(C\text{-}H)_{ring}$	973	$\nu(C\text{-}H)_{ring}$	963	$\nu(C\text{-}H)_{ring}$	975	$\delta(H\text{-}C\text{-}C\text{-}H)$		$\delta(H\text{-}C\text{-}C\text{-}H)$		
	1035	1030	ν_{12}	$\delta(ring)_{ip}$	1016	$\delta(C\text{-}H)_{ip}$	1025	$\delta(C\text{-}H)_{ip}$	1020	$\delta(C\text{-}H)_{ip}$	1025	$\delta(H\text{-}C\text{-}C\text{-}C\text{-}H)$				
							1036	$\delta(C\text{-}H)_{ip}$	1045	$\delta(C\text{-}H)_{ip}$						
Region III		1052	ν_{18b}	$\delta(C\text{-}H)_{ip}$	1047	$\delta(C\text{-}H)_{ip}$	1087		1056		1079	$\delta(C\text{-}H)$	1169	$\delta(C\text{-}H)_{ip}$	1185	$\nu(Ca\text{-}H_2)$
		1069	ν_{18a}		1093		1177	$\delta(C\text{-}H)_{ip}$	1209	$\delta(C\text{-}H)_{ip}$	1082	$\delta(mol)_{ip}$	1247	$\delta(C\text{-}H)_{ip}$	1194	$\nu(Ca\text{-}H_2)$
	1147	1146	ν_{15}	$\delta(C\text{-}H)$	1150	$\delta(C\text{-}H)_{ip}$	1222	$\delta(C\text{-}H)_{ip}$	1217	$\delta(C\text{-}H)_{ip}$	1134	$\delta(H\text{-}C\text{-}C\text{-}H)$	1292	$\delta(C\text{-}H)_{ip}$	1215	$\nu(Ca\text{-}H_2)$
		1217	ν_{9a}	$\nu(ring)_{ip}$	1228	$\delta(C\text{-}H)_{ip}$	1294	$\delta(C\text{-}H)_{ip}$	1291	$\delta(C\text{-}H)_{ip}$	1156	$\delta(H\text{-}C\text{-}C\text{-}H)$	1397	$\delta(mol)$	1250	$\nu(Ca\text{-}H)$
	1224	1227	ν_{14}	$\delta(C\text{-}H)_{ip}$	1305	$\delta(C\text{-}H)_{ip}$	1407	$\delta(C\text{-}H)$	1377	$\delta(C\text{-}H)$	1317	$\delta(H\text{-}C\text{-}C\text{-}C\text{-}H)_{ip}$	1387	$\delta(C\text{-}H)$	1290	$\nu(Ca\text{-}H)$
	1277	1355	ν_3	$\delta(C\text{-}H)_{ip}$	1389	$\delta(C\text{-}H)$									1394	$\nu(Ca\text{-}H)$
Region IV		1437	ν_{19b}	$\delta(C\text{-}H)_{ip}$	1464	$\delta(C\text{-}H)_{ip}$	1434	$\delta(C\text{-}H)_{ip}$	1436	$\delta(C\text{-}H)_{ip}$	1410	$\delta(C\text{-}H)$	1457	$\delta(C\text{-}H)$		
		1483	ν_{19a}	$\delta(C\text{-}H)_{ip}$	1526	$\delta(C\text{-}H)_{ip}$	1495	$\delta(C\text{-}H)_{ip}$	1491	$\delta(C\text{-}H)_{ip}$	1445	$\delta(H\text{-}C\text{-}C\text{-}H)_{ip}$				
	1565	1574	ν_{8b}	$\nu(ring)_{ip}$	1612	$\nu(ring)_{ip}$	1564	$\nu(ring)_{ip}$	1574	$\nu(ring)_{ip}$	1474	$\delta(H\text{-}C\text{-}C\text{-}H)_{ip}$				
		1581	ν_{8a}	$\nu(ring)_{ip}$												
1875											1863	$\nu(C\equiv C)_{ip}$	1971	$\nu(C\equiv C)_{ip}$		
2269																
2535																
2741																
2801		3094	ν_2	$\nu(C\text{-}H)$	3162	$\nu(C\text{-}H)$	3168	$\nu(C\text{-}H)$	3143	$\nu(C\text{-}H)$	3147	$\nu(C\text{-}H)$	3163	$\nu(C\text{-}H)$		
3058		3073	ν_{13}	$\nu(C\text{-}H)$	3173	$\nu(C\text{-}H)$	3185	$\nu(C\text{-}H)$	3145	$\nu(C\text{-}H)$	3190	$\nu(C\text{-}H)$	3205	$\nu(C\text{-}H)$		
3123		3030	ν_{20a}	$\nu(C\text{-}H)$	3194	$\nu(C\text{-}H)$	3190	$\nu(C\text{-}H)$	3183	$\nu(C\text{-}H)$	3211	$\nu(C\text{-}H)$	3209	$\nu(C\text{-}H)$		
3470					3200	$\nu(C\text{-}H)$	3202	$\nu(C\text{-}H)$	3184	$\nu(C\text{-}H)$						

[a] Pyridine assignments taken from references S5, S6.
[b] *o*-Pyridyl assignments taken from references S7, S8.
[c] *m*-Pyridyl assignments taken from references S9, S10.
[d] *p*-Pyridyl assignments taken from references S9, S10.
[e] 2,3-Pyridyne assignments taken from reference S7.
[f] 3,4-Pyridyne assignments taken from reference S7.
[g] CaH and CaH_2 assignments taken from reference S4.

Table S4. Vibrational peak frequencies and assignments for ring opening products proposed by Cheng et al.[S7,S9,S10] formed in the reaction of Ca with pyridine.

Observed Frequency (cm^{-1})		Literature Frequency (cm^{-1})	Vibrational Mode	Possible Open Ring Products (shown in Figure S1)
520		511	$\delta(C\text{-}H)_{oop}$[a]	DP5
		532	$\delta(mol)_{ip}$[a,b,c]	DP4, DP6
750		742	$\delta(C{\equiv}C\text{-}C{=}C\text{-}C{\equiv}N)$[a,b]	DP3
		746	$\delta(H\text{-}C{=}C\text{-}H)_{oop}$[b]	DP1
		753	$\delta(H\text{-}C{=}N\text{-}C)_{ip}$[c]	DP2
Region IV	1400-1600	~1410	$\delta(H\text{-}C{=}C\text{-}H)_{ip}$[a,b,c]	DP2, DP3
		~1420	$\delta(C\text{-}H)$[a,b]	DP1, DP5
		1462	$\nu(C{=}C)$[c]	DP2
		1607	$\nu(C{=}C\text{-}C{=}C)$[c]	DP5
		1610	$\delta(C\text{-}C\text{-}C{=}N)$[b]	DP1
		1637	$\nu(C{=}C)$[a,b]	DP3, DP6
2260		2200	$\nu(C{\equiv}C)$[a,b,c]	DP1, DP3, DP4, DP6
2700		~2700	2D Band[d]	Amorphous Carbon
2801				
3040		3034	$\nu(C\text{-}H)$[a]	DP5
3125		~3170	$\nu(C\text{-}H)$[a,b]	DP3, DP5
3473		3475	$\nu(C\text{-}H)$[a,b,c]	DP1, DP2, DP3, DP4, DP5, DP6

[a] Assignments taken from reference S7.
[b] Assignments taken from reference S9.
[c] Assignments taken from reference S10.
[d] Assignments taken from reference S11.

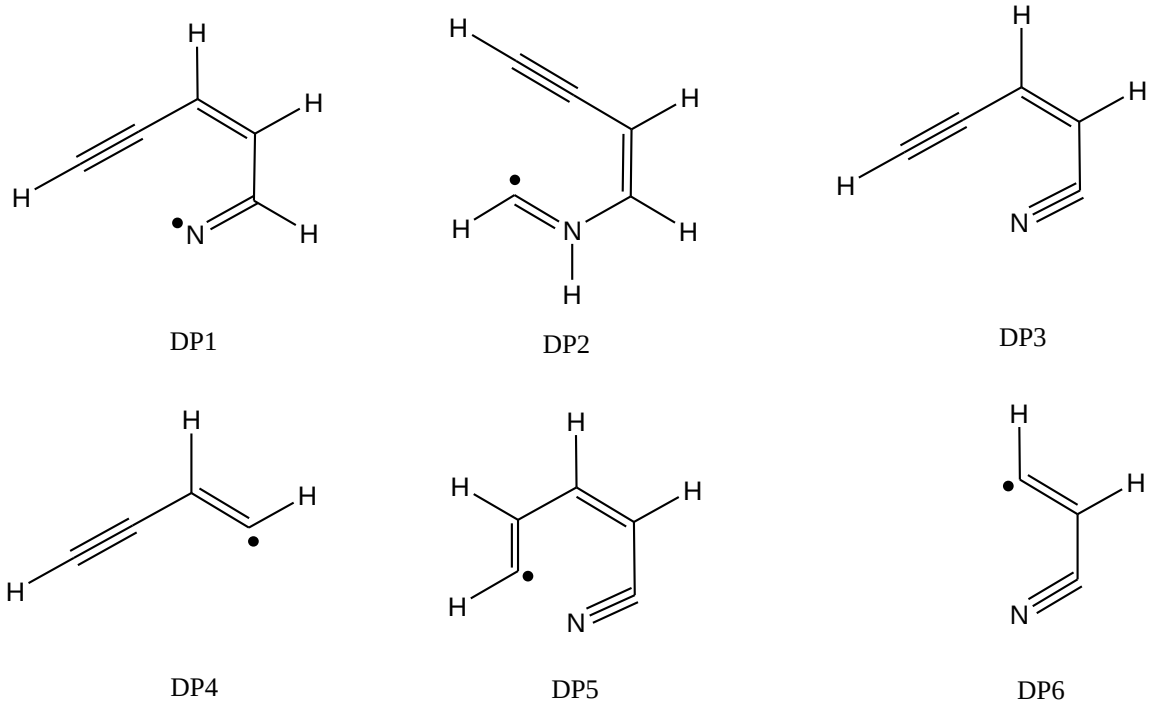

Figure S1. Six possible degradation products from pyridyl ring opening as proposed by Cheng et al. in references S7, S9, and S10.

Table S5. Summary of observed Raman bands and assignments for proposed products from reaction of Ca with thin, solid-state films of pyridine.

Observed Frequency (cm^{-1})			
Pristine		+ 20 Å Ca	Assignments[a]
Region I	409	417	Py, Py$^{\bullet}$, Py$^{\bullet\bullet}$
		523	Py$^{\bullet}$, Py$^{\bullet\bullet}$
Region I	623		Py
	653	654	Py, Py$^{\bullet}$, Py$^{\bullet\bullet}$
		750	Py$^{\bullet}$, Py$^{\bullet\bullet}$, DP
		949	Py$^{\bullet}$, Py$^{\bullet\bullet}$
	993	994	Py
	1034	1035	Py, Py$^{\bullet}$, Py$^{\bullet\bullet}$
Region III	1062		Py
	1146	1147	Py, Py$^{\bullet}$, Py$^{\bullet\bullet}$, CaH_2
	1205		Py
	1224	1224	Py, Py$^{\bullet}$, Py$^{\bullet\bullet}$, CaH_2
		1277	CaH_2
Region IV	1482		Py
	1571	1565	Py, Py$^{\bullet}$, DP, a-C:H
	1581		Py
	1599		Py
		1875	Py$^{\bullet\bullet}$
		2269	DP
		2535	DP
		2741	DP, a-C:H
		2801	DP, a-C:H
3058		3058	Py
3143		3123	Py, Py$^{\bullet}$, Py$^{\bullet\bullet}$
		3470	DP

[a] Assignment abbreviations: Py = pyridine, Py$^{\bullet}$ = *o*-, *m*-, and *p*-pyridyl radicals, Py$^{\bullet\bullet}$ = 2,3- and 3,4-pyridine, DP = degradation product, and a-C:H = amorphous carbon.

Table S6. Vibrational peak frequencies and assignment for pyridine-d_5 and amorphous carbon.

Observed Frequency (cm^{-1})		Pyridine-d_5[a]		Amorphous Carbon Assignment[b]
Pristine	+ 20 Å Ca	Frequency (cm^{-1})	Wilson Number	
	243			
	377			
	599			
622		624	ν_{6b}	
696		690	ν_{10a}	
	713			
774		768	ν_4	
821				
839	836	835	ν_{18b}	
893	894	886	ν_{10a}	
916				
964	975	965	ν_1	
1002	1005	1009	ν_{12}	
1033		1041	ν_{14}	
	1180			
	1312			
	1348			
1540		1537	ν_{8b}	
1555		1550	ν_{8a}	
	1524			G Band
	1776			
	2219			
2253		2248	ν_{20b}	
2275		2271	ν_2	
2300	2300	2294	ν_{13}	
	2415			
	2692			
	2775			
	2934			
3061	3061			
	3278			

[a] Assignments taken from reference S12.
[b] Assignments taken from reference S11.

Table S7. Vibrational peak frequencies and assignments for a pristine solid-state film of benzene-d_6 before and after deposition of 20 Å Ca.

Frequency (cm^{-1})			Wilson Number[a]
Observed		Literature[a]	
Pristine	+ 20 Å Ca		
579	579	579	ν_6
666	666	672	ν_{10}
854	854	837	ν_{15}
876	876	865	ν_9
936	936	936	ν_1
1554	1554	1550	ν_8
2261	2261	2260	ν_7
2289	2289	2290	ν_2

[a] Assignments taken from reference S1.

References

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