Spectroscopic Characterization of Fluorinated Benzylphosphonic Acid Monolayers on AlO_x/Al Surfaces

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SUPPORTING INFORMATION

Contents:

Section 1.

Table S1. Molecular coverage, surface area per molecule, molecular density *N*, and work function Φ based on XPS and LI-XPS data for phosphonic acid SAMs on AlO_x/Al substrates. Molecular dipole moments from DFT calculations (Data are from Ref [1]).

SAM	Coverage[a]	Area (Å^2)[b]	*N* (nm^{-2})	Φ (eV)	Φ_{norm}[c] (eV)	μ_z[d] (D)	μ_z-μ_z^{ref} (D)
1	0.90_6	24.1	4.15	3.18	3.18	-2.664	0.000
2	1.22_9	17.7	5.64	3.57	3.47	-3.506	-0.842
3	0.73_0	29.6	3.38	3.62	3.72	-2.804	-0.140
4	0.91_7	23.8	4.20	3.41	3.41	-2.071	+0.592
5	0.56_3	38.4	2.61	3.55	3.77	-2.674	-0.010
6	0.77_7	28.2	3.55	3.27	3.29	-2.634	+0.030
7	0.51_5	42.8	2.34	3.50	3.75	-3.438	-0.774
8	0.77_1	28.0	3.57	3.58	3.64	-2.440	+0.224
9	0.50_3	42.9	2.33	4.08	4.78	-5.560	-2.896
10	0.74_2	29.1	3.43	4.09	4.28	-4.708	-2.044
11	0.67_2	32.1	3.11	3.71	3.89	-3.041	-0.377

[a]Coverage as determined from XPS data, relative to a SAM of $C_{12}H_{25}SH$ on Au(111). [b]Surface area per molecule, assuming a value of 21.6 Å^2/molecule for a reference SAM of $C_{12}H_{25}SH$ on Au.[2] [c]Work function from LI-XPS data, normalized for molecular density, *N*. [d]Molecular dipole moment from DFT calculations of a coupled phosphonic acid/Al_6O_{10} cluster system[1].

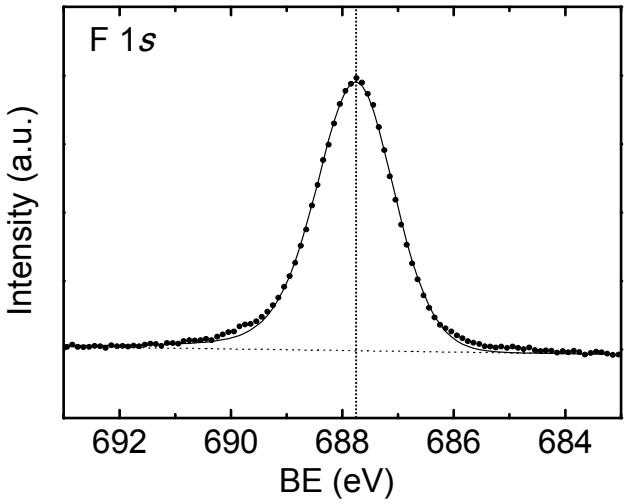
Table S2: Elemental composition of the SAMs based on XPS data.

Name	Position	FWHM	R.S.F.	Area	% Conc.	%P/%Al
SAM **1**						
P 2*s*	193.1	2.46	0.34	71	1.80	0.061
O 1*s*	533.0	2.73	0.78	3784	42.18	
C 1*s*	286.7	1.21	0.33	1010	26.39	
F 1*s*	687.2	0.90	1.00	21	0.18	
Al 2*p*	76.0	1.71	0.29	996	29.45	
SAM **2**						
P 2*s*	192.1	2.22	0.34	91	3.39	0.083
O 1*s*	532.4	2.56	0.78	499	8.23	
C 1*s*	285.6	1.32	0.33	1193	46.08	
F 1*s*	689.2	1.78	1.00	122	1.57	
Al 2*p*	75.5	1.66	0.29	931	40.74	
SAM **3**						
P 2*s*	191.9	2.43	0.34	63	1.38	0.050
O 1*s*	532.6	2.63	0.78	4858	46.72	
C 1*s*	285.5	1.49	0.33	1067	24.03	
F 1*s*	687.0	0.14	1.00	23	0.17	
Al 2*p*	75.5	1.66	0.29	1086	27.70	
SAM **4**						
P 2*s*	192.1	2.46	0.34	87	1.89	0.062
O 1*s*	532.5	2.60	0.78	5342	51.07	
C 1*s*	285.6	1.69	0.33	709	15.89	
F 1*s*	686.1	1.64	1.00	85	0.63	
Al 2*p*	75.3	1.65	0.29	1203	30.52	

SAM **5**						
P 2*s*	192.2	2.44	0.34	54	1.19	0.038
O 1*s*	532.5	2.52	0.78	4977	48.33	
C 1*s*	288.0	3.65	0.33	547	12.45	
F 1*s*	688.4	1.68	1.00	934	7.07	
Al 2*p*	75.3	1.73	0.29	1202	30.96	
SAM **6**						
P 2*s*	192.6	2.53	0.34	73	1.67	0.052
O 1*s*	532.6	2.52	0.78	4828	48.54	
C 1*s*	286.1	1.56	0.33	633	14.91	
F 1*s*	688.4	1.70	1.00	382	3.00	
Al 2*p*	75.6	1.66	0.29	1196	31.89	
SAM **7**						
P 2*s*	191.9	2.19	0.34	45	1.03	0.034
O 1*s*	532.4	2.51	0.78	4515	45.58	
C 1*s*	285.8	1.56	0.33	762	18.01	
F 1*s*	688.4	1.56	1.00	697	5.49	
Al 2*p*	75.4	1.69	0.29	1116	29.89	
SAM **8**						
P 2*s*	191.9	2.48	0.34	60	1.34	0.053
O 1*s*	532.4	2.57	0.78	4154	40.72	
C 1*s*	285.4	3.40	0.33	1089	25.00	
F 1*s*	688.2	1.55	1.00	975	7.46	
Al 2*p*	75.3	1.69	0.29	980	25.48	
SAM **9**						
P 2*s*	192.1	2.17	0.34	50	1.05	0.034
O 1*s*	532.4	2.44	0.78	5115	46.89	
C 1*s*	288.6	1.33	0.33	622	13.37	
F 1*s*	688.6	1.71	1.00	1130	8.08	
Al 2*p*	75.2	1.72	0.29	1259	30.61	
SAM **10**						
P 2*s*	192.2	2.44	0.34	64	1.35	0.051
O 1*s*	532.4	2.49	0.78	4534	42.43	
C 1*s*	285.7	1.57	0.33	961	21.07	
F 1*s*	688.9	1.56	1.00	1163	8.49	
Al 2*p*	75.5	1.70	0.29	1074	26.66	
SAM **11**						
P 2*s*	191.4	2.54	0.34	57	1.22	0.046
O 1*s*	532.5	2.49	0.78	4583	43.24	
C 1*s*	285.5	1.47	0.33	981	21.69	
F 1*s*	688.3	1.52	1.00	984	7.24	
Al 2*p*	75.3	1.67	0.29	1063	26.61	
Blank (Aluminum only)						
P 2*s*	191.8	1.52	0.34	17	0.37	0.013
O 1*s*	532.4	2.51	0.78	4791	46.34	
C 1*s*	285.9	1.41	0.33	869	19.69	
F 1*s*	689.0	1.67	1.00	564	4.25	
Al 2*p*	75.4	1.61	0.29	1144	29.35	

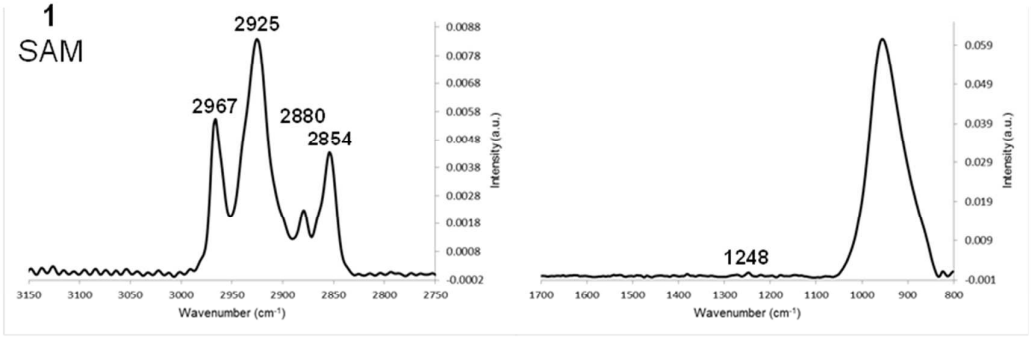
Section 2.

Figure S1: XPS F 1*s* spectrum of SAM **10**, with a single component at 687.76 eV, resulting from the fluorinated ring.

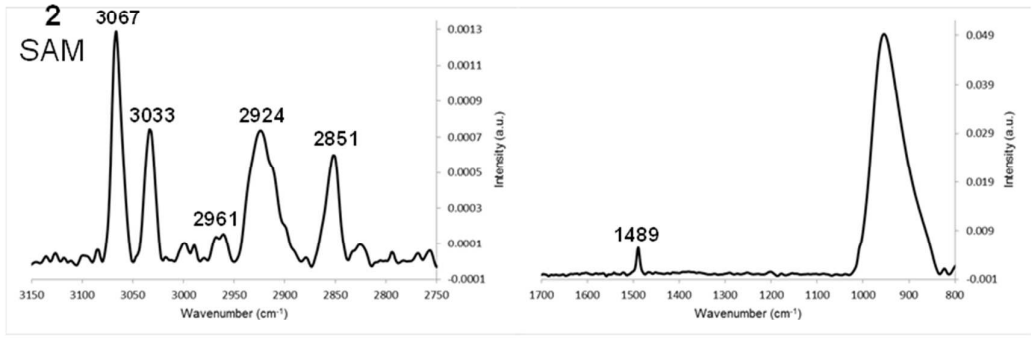


Section 3.

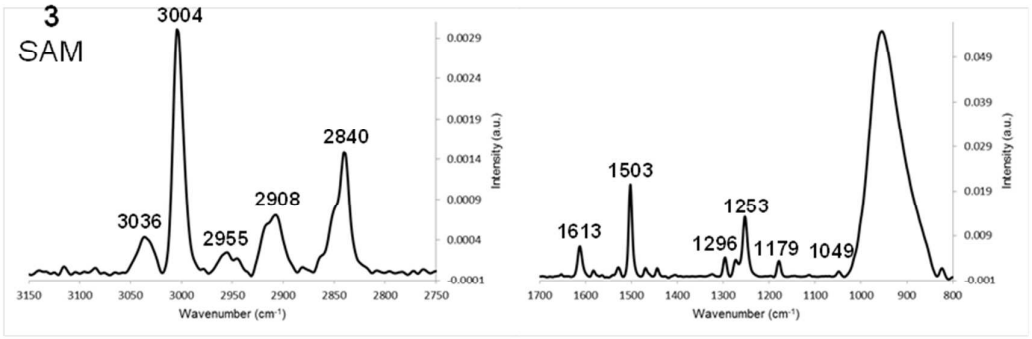
Figure S2: PM-IRRAS (SAM) spectra for **1**−**11** (all peak positions and amplitudes are also listed).



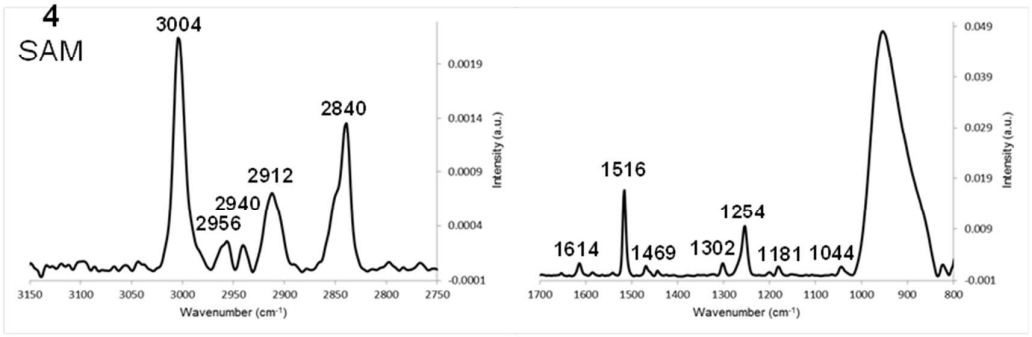
1_SAM	
2967	0.0056
2925	0.0084
2880	0.0023
2854	0.0043
1248	0.0009
956	0.0606
824	0.0012



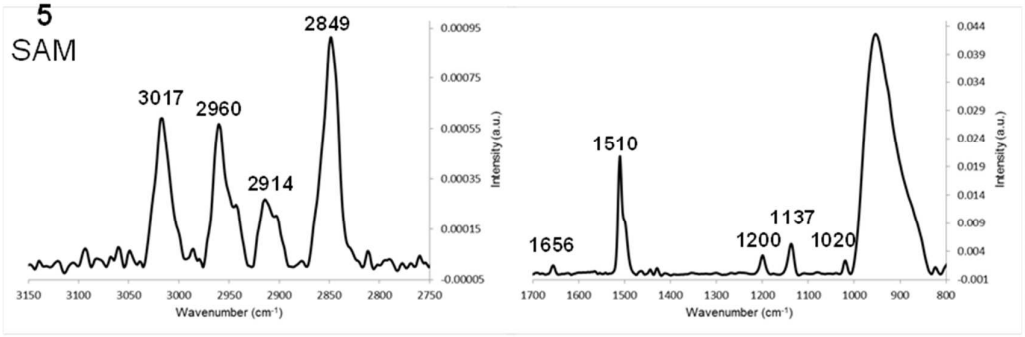
2_SAM	
3330	0.0001
3067	0.0013
3033	0.0007
2999	0.0001
2989	0.0001
2961	0.0002
2924	0.0007
2851	0.0006
2826	0.0001
1489	0.0055
954	0.0492



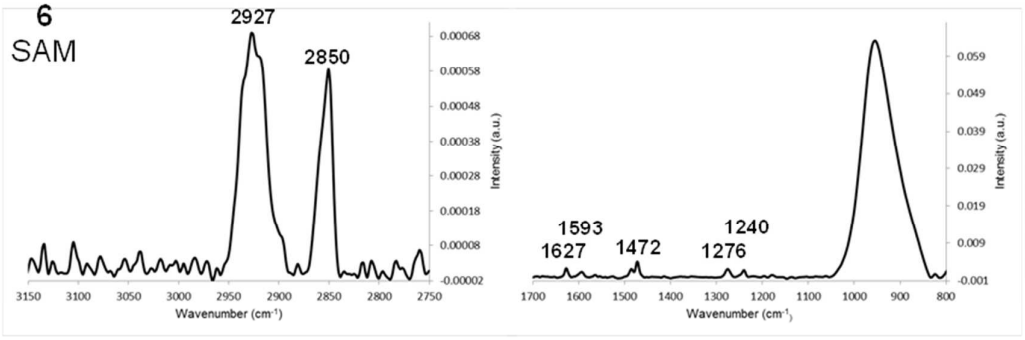
3_SAM	
3036	0.0004
3004	0.0030
2955	0.0002
2908	0.0007
2840	0.0015
1613	0.0067
1583	0.0013
1529	0.0020
1503	0.0205
1470	0.0018
1444	0.0018
1296	0.0042
1273	0.0037
1253	0.0133
1179	0.0034
1049	0.0011
955	0.0549
824	0.0018



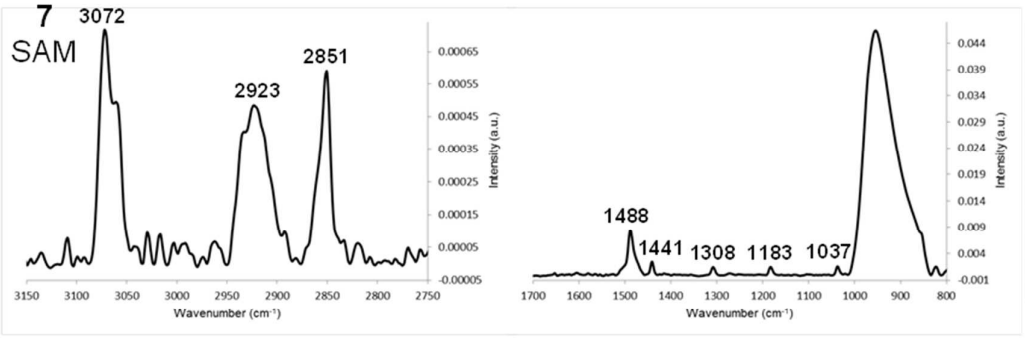
4_SAM	
3004	0.0022
2956	0.0003
2940	0.0002
2912	0.0007
2840	0.0014
1614	0.0023
1516	0.0168
1469	0.0018
1444	0.0009
1302	0.0023
1254	0.0096
1181	0.0017
1044	0.0017
954	0.0481
823	0.0021



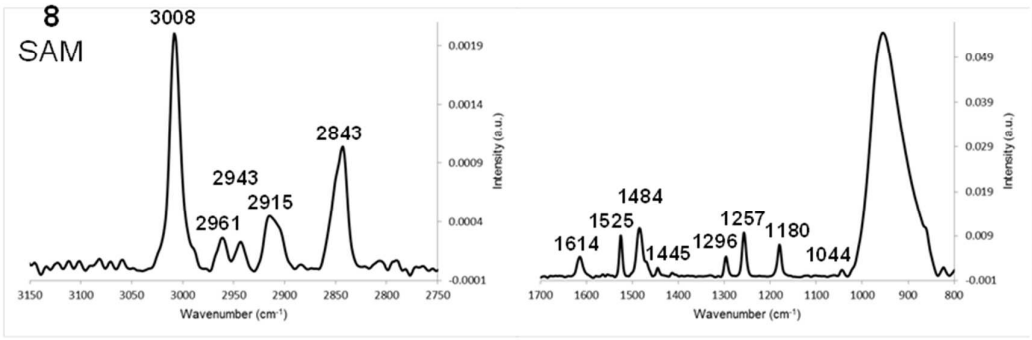
5_SAM	
3017	0.0006
2960	0.0006
2914	0.0003
2849	0.0009
1656	0.0015
1510	0.0209
1444	0.0008
1429	0.0010
1200	0.0033
1137	0.0053
1020	0.0024
954	0.0426
823	0.0012



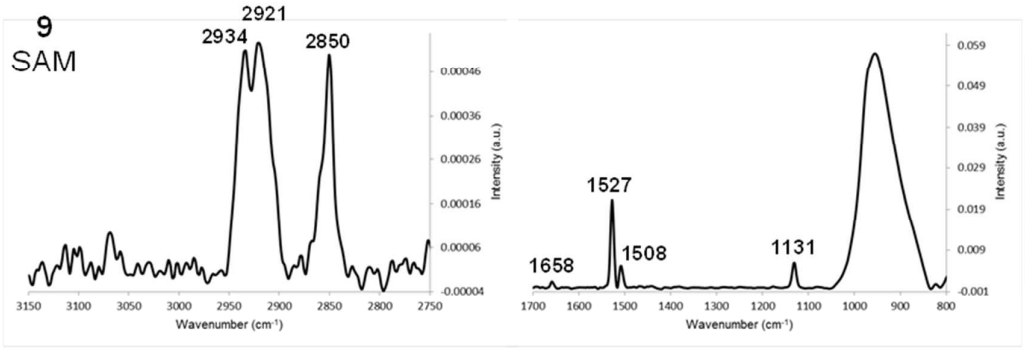
6_SAM	
2927	0.0007
2851	0.0006
1627	0.0023
1593	0.0014
1472	0.0041
1276	0.0021
1240	0.0018
955	0.0631



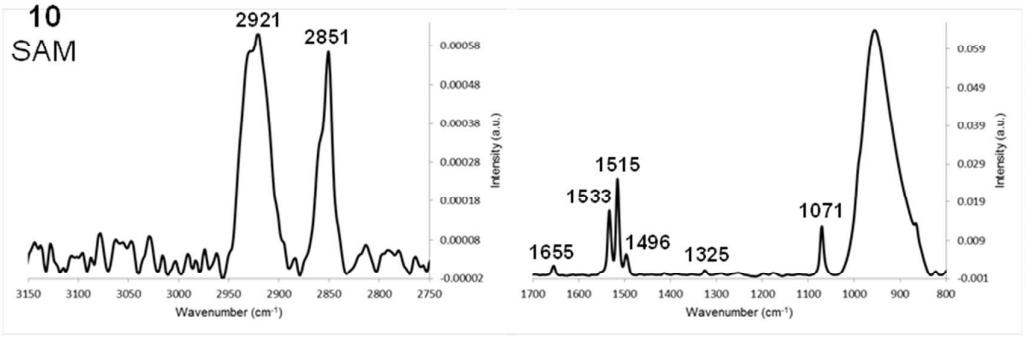
7_SAM	
3072	0.0007
2923	0.0005
2851	0.0006
1488	0.0084
1441	0.0025
1308	0.0015
1183	0.0015
1037	0.0016
955	0.0464
823	0.0015



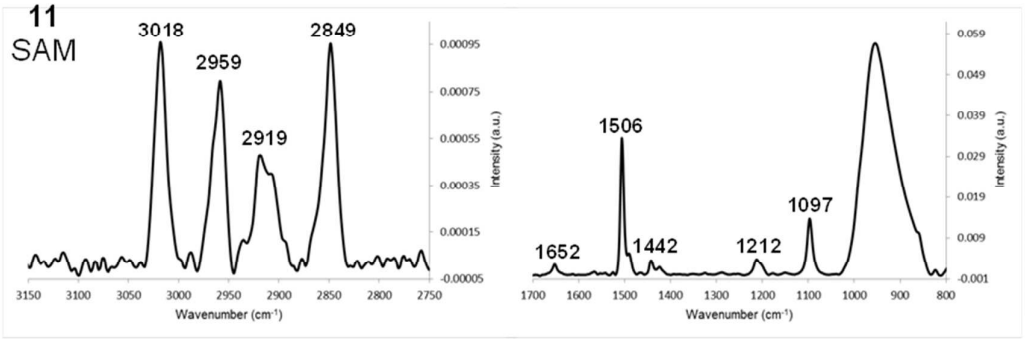
8_SAM	
3008	0.0020
2961	0.0003
2943	0.0002
2915	0.0005
2843	0.0010
1614	0.0043
1525	0.0092
1484	0.0108
1445	0.0018
1296	0.0044
1257	0.0097
1180	0.0071
1044	0.0014
955	0.0546
823	0.0019



9_SAM	
2934	0.0005
2921	0.0005
2850	0.0005
1658	0.0014
1527	0.0213
1508	0.0052
1131	0.0060
955	0.0570



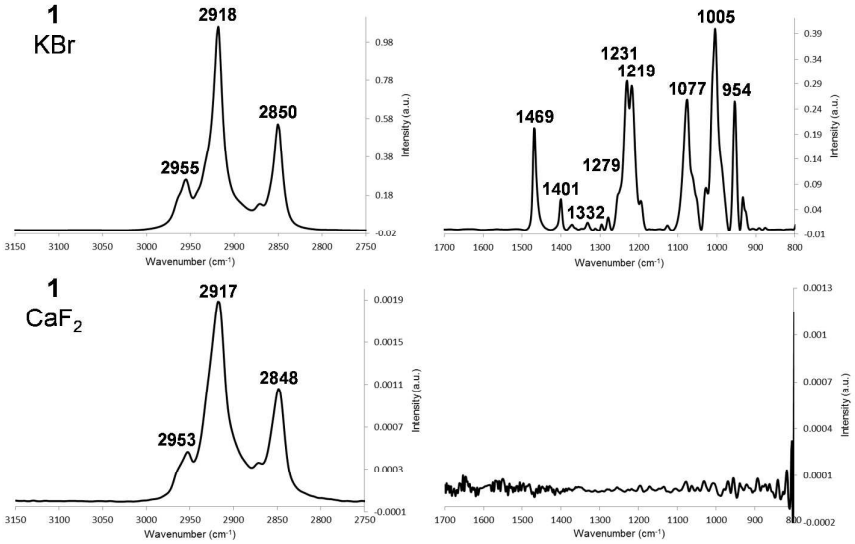
10_SAM	
2921	0.0006
2851	0.0006
1655	0.0025
1533	0.0167
1515	0.0252
1496	0.0055
1325	0.0013
1071	0.0127
956	0.0640



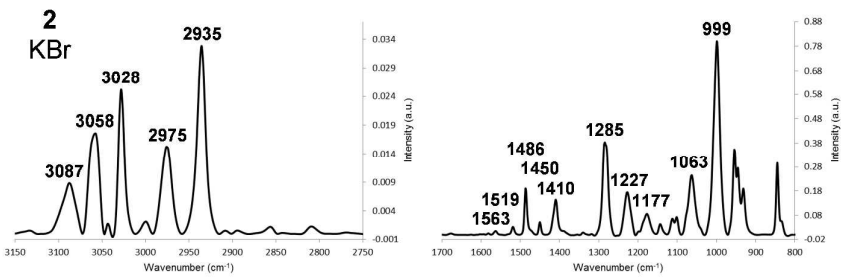
11_SAM	
3018	0.0010
2959	0.0008
2919	0.0005
2849	0.0010
1652	0.0024
1506	0.0337
1442	0.0035
1212	0.0037
1097	0.0138
955	0.0565
824	0.0011

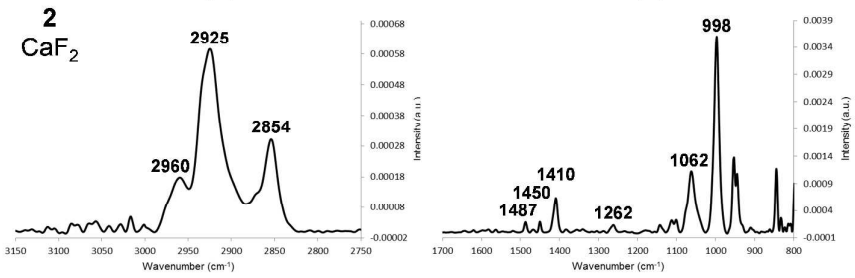
Section 4.

Figure S3: TIR (KBr, CaF_2) spectra for **1**−**11** (all peak positions and amplitudes are also listed).

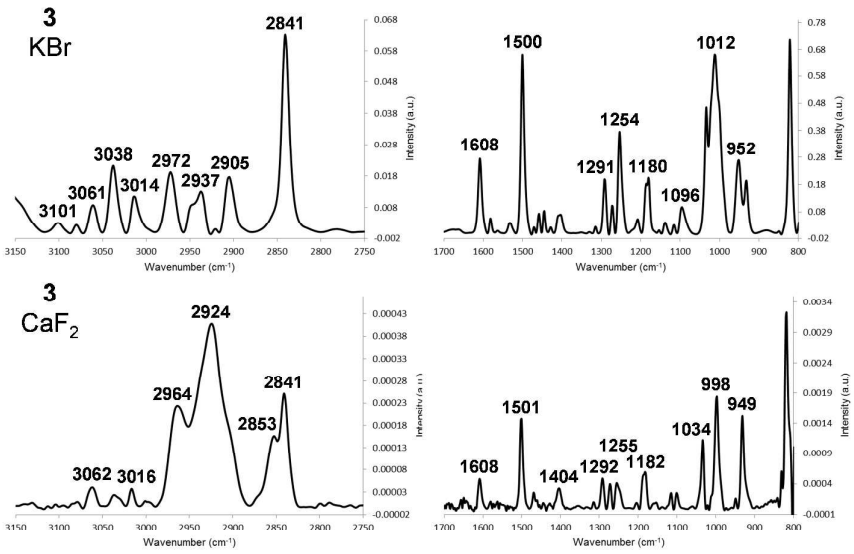


1_KBr		1_CaF_2	
2955	0.264	2953	0.0005
2919	1.063	2917	0.0019
2850	0.555	2848	0.0011
1469	0.208		
1401	0.061		
1372	0.010		
1332	0.014		
1296	0.011		
1279	0.025		
1231	0.297		
1219	0.286		
1195	0.057		
1127	0.009		
1077	0.260		
1028	0.083		
1005	0.399		
954	0.256		
933	0.064		

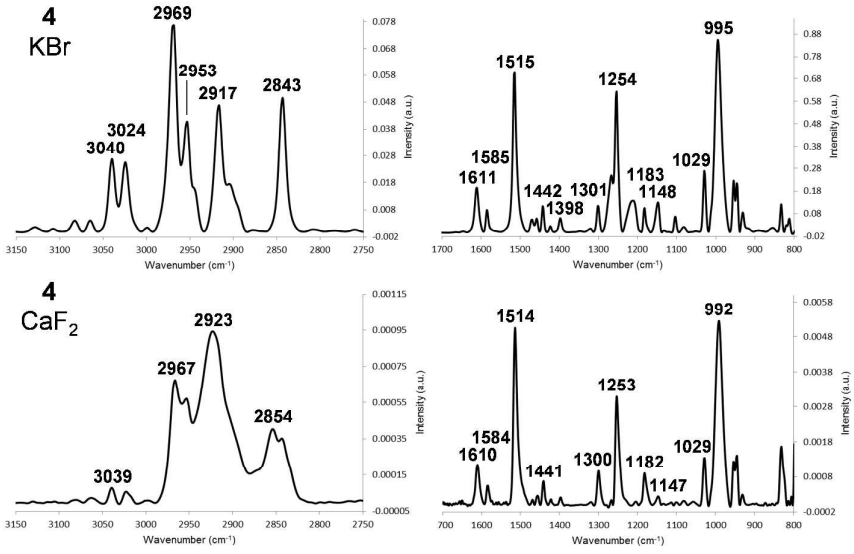




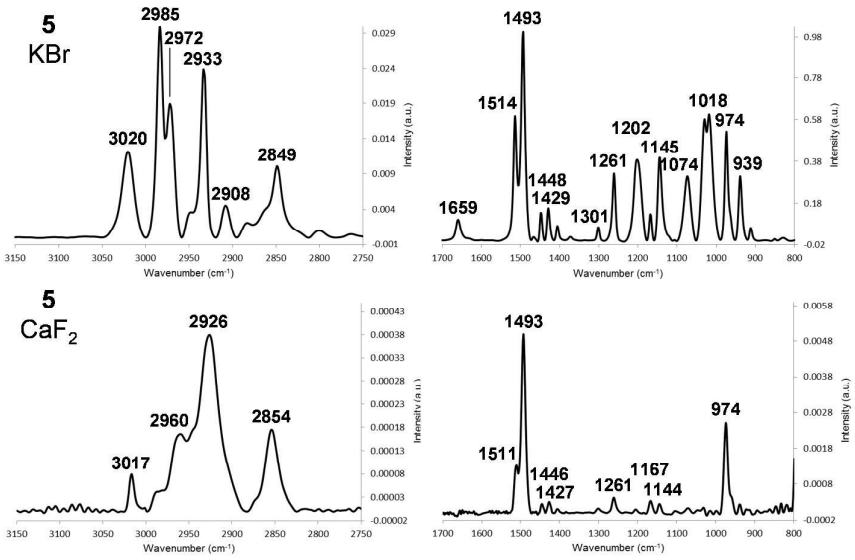
2_KBr		2_CaF_2	
3427	0.024		
3087	0.009		
3058	0.018		
3028	0.025		
2975	0.015	2960	0.0002
2935	0.033	2925	0.0006
		2854	0.0003
1563	0.015		
1519	0.033		
1486	0.194	1487	0.0002
1450	0.052	1450	0.0002
1410	0.144	1410	0.0006
1285	0.384	1262	0.0001
1227	0.176		
1177	0.086		
1143	0.044	1143	0.0001
1112	0.066	1113	0.0002
1101	0.073	1101	0.0002
1063	0.246	1062	0.0011
999	0.801	998	0.0036
954	0.360	954	0.0014
945	0.276	945	0.0011
931	0.190		
845	0.297	844	0.0012
		833	0.0003
		808	0.0002



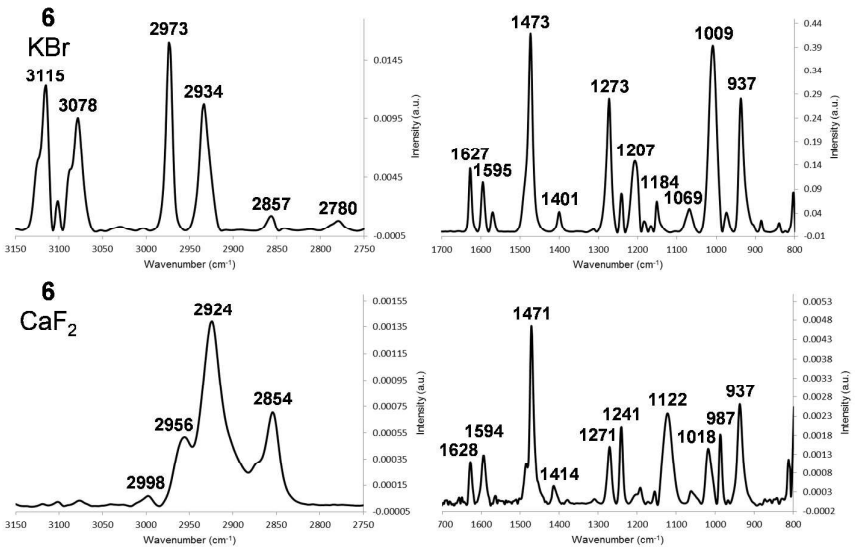
3_KBr		3_CaF_2	
3205	0.033		
3101	0.003		
3080	0.002		
3061	0.009	3062	0.0000
3038	0.021	3037	0.0000
3014	0.012	3016	0.0000
2972	0.019	2964	0.0002
2937	0.013	2924	0.0004
2905	0.018	2853	0.0002
2841	0.063	2841	0.0003
1663	0.013	1650	0.0002
1608	0.276	1608	0.0005
1581	0.056		
1532	0.039		
1500	0.662	1501	0.0015
1471	0.022	1469	0.0003
1458	0.074		
1445	0.086		
1429	0.021		
1404	0.070	1404	0.0003
1315	0.024		
1291	0.203	1292	0.0005
1272	0.106	1272	0.0004
1254	0.376	1255	0.0004
1208	0.053		
1180	0.205	1182	0.0006
1138	0.040		
1116	0.030	1115	0.0003
1096	0.098	1101	0.0003
1034	0.466	1034	0.0011
1012	0.665	998	0.0019
952	0.271	949	0.0002
932	0.197	932	0.0015
821	0.720	819	0.0033



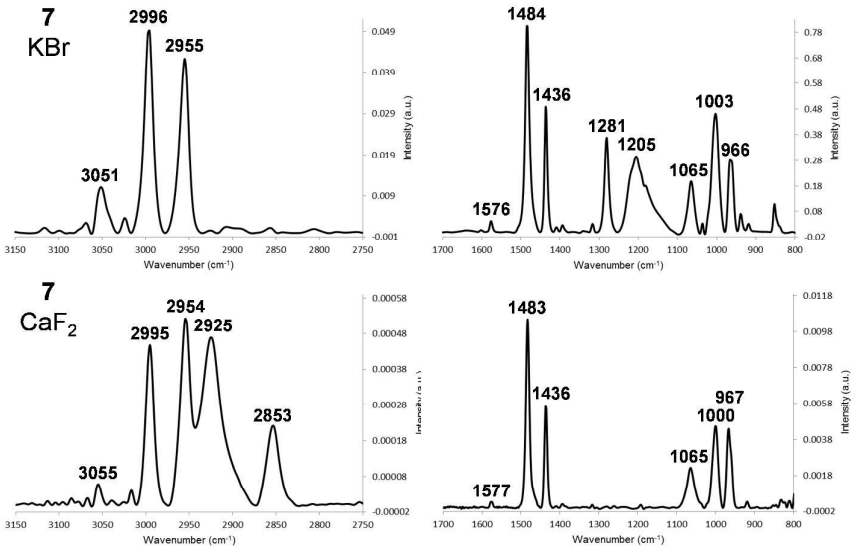
4_KBr		4_CaF_2	
3425	0.012		
3083	0.004		
3065	0.004		
3040	0.027	3039	0.0001
3024	0.026	3023	0.0001
2969	0.078	2967	0.0007
2953	0.041	2953	0.0006
2917	0.047	2923	0.0009
		2854	0.0004
2843	0.050	2843	0.0004
1611	0.197	1610	0.0012
1585	0.097	1584	0.0006
1515	0.725	1514	0.0051
1470	0.055		
1458	0.058	1456	0.0003
1442	0.114	1441	0.0007
1423	0.024		
1398	0.061	1397	0.0002
1320	0.014		
1301	0.117	1300	0.0010
1267	0.249		
1254	0.632	1253	0.0031
1212	0.138		
1183	0.106	1182	0.0009
1148	0.130	1147	0.0002
1104	0.069		
1082	0.021		
1029	0.272	1029	0.0014
995	0.856	992	0.0052
955	0.226	954	0.0013
946	0.219	946	0.0014
931	0.086	931	0.0003
855	0.017		
833	0.121	832	0.0017
813	0.059	805	0.0003



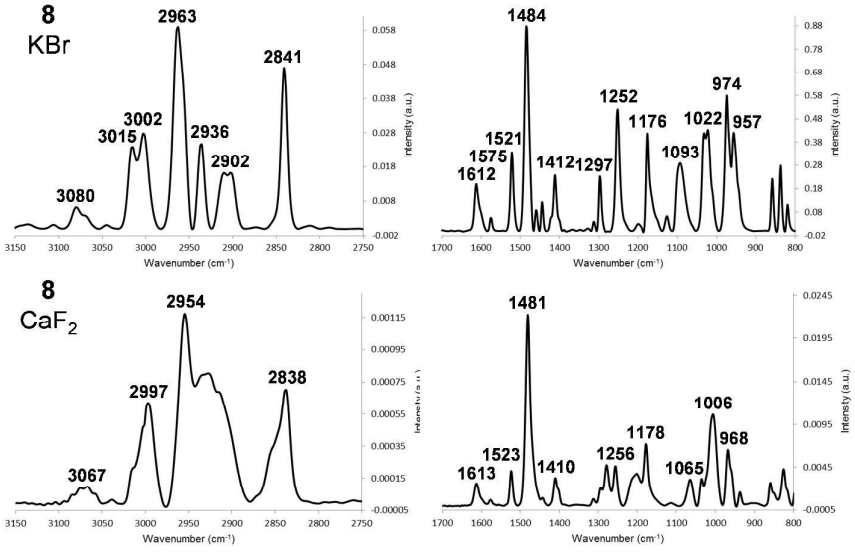
5_KBr		5_CaF_2	
3439	0.010		
3020	0.012	3017	0.0001
2983	0.030		
2972	0.019	2960	0.0002
2933	0.024	2926	0.0004
2908	0.005		
2849	0.010	2854	0.0002
1659	0.101		
1514	0.599	1511	0.0013
1493	1.017	1493	0.0050
1448	0.138	1446	0.0003
1429	0.156	1427	0.0003
1406	0.071		
1301	0.065		
1261	0.323	1261	0.0004
1202	0.388		
1168	0.130	1167	0.0003
1145	0.405	1144	0.0003
1074	0.309		
1030	0.583		
1018	0.607		
974	0.524	974	0.0025
939	0.309	938	0.0002
912	0.061		
		846	0.0002
		832	0.0003
		818	0.0002



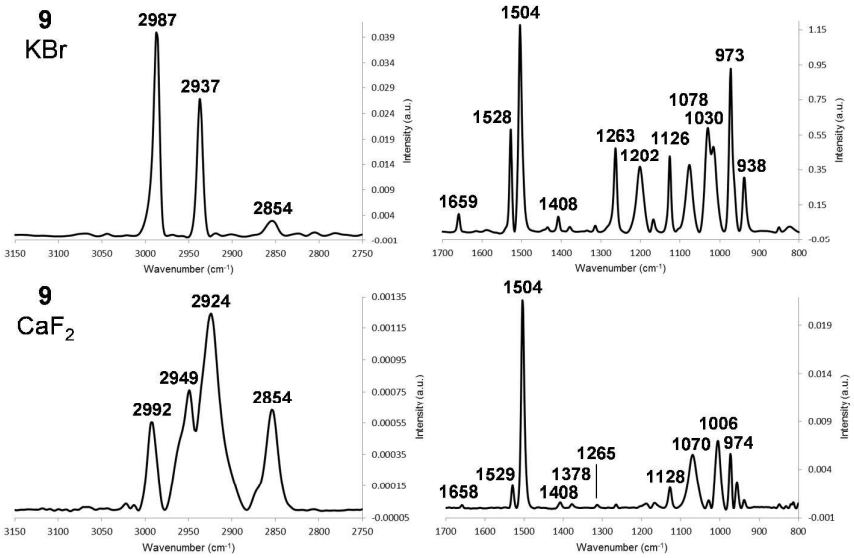
6_KBr		6_CaF_2	
3422	0.025		
3266	0.001		
3115	0.012		
3102	0.003	3102	0.0000
3078	0.010	3077	0.0000
		2998	0.0001
2973	0.016	2956	0.0005
2934	0.011	2924	0.0014
2857	0.001	2854	0.0007
		1657	0.0002
		1650	0.0002
1627	0.135	1628	0.0011
1595	0.105	1594	0.0013
1570	0.042	1563	0.0002
		1485	0.0011
1473	0.419	1471	0.0047
1401	0.043	1414	0.0005
		1309	0.0001
1273	0.281	1271	0.0015
1241	0.082	1241	0.0021
1207	0.149		
1184	0.023	1192	0.0004
1167	0.013	1155	0.0003
1151	0.064	1122	0.0024
1069	0.049	1062	0.0003
1009	0.394	1018	0.0015
974	0.041	987	0.0019
937	0.281	937	0.0026
885	0.025	873	0.0001
840	0.020	842	0.0002
		812	0.0012



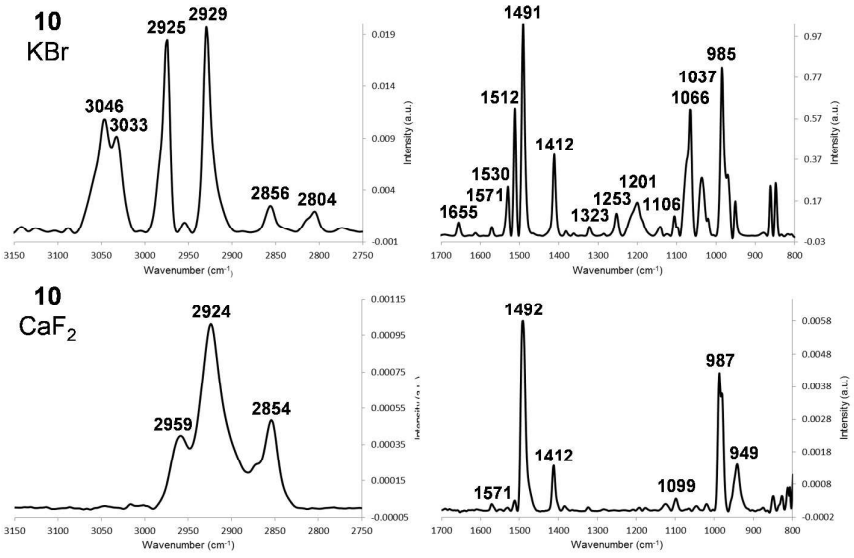
7_KBr		7_CaF_2	
3426	0.029		
3116	0.001		
3068	0.002		
3051	0.011	3055	0.0001
3024	0.004	3017	0.0000
2996	0.050	2995	0.0004
2955	0.042	2954	0.0005
2907	0.001	2925	0.0005
2857	0.001	2853	0.0002
1576	0.043	1577	0.0003
1484	0.823	1483	0.0105
1436	0.496	1436	0.0058
1409	0.018		
1394	0.026		
1317	0.031		
1281	0.371		
1206	0.296		
1065	0.199	1065	0.0022
1036	0.034		
1003	0.462	1000	0.0046
966	0.282	967	0.0044
939	0.071		
919	0.032	919	0.0004
853	0.109	832	0.0005
		811	0.0004



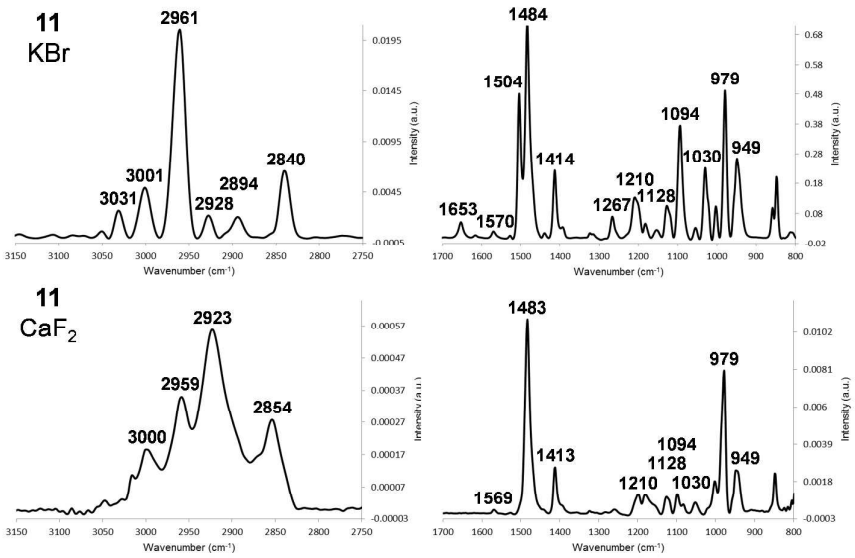
8_KBr		8_CaF_2	
3424	0.021		
3080	0.006	3067	0.0001
3015	0.024		
3002	0.028	2997	0.0006
2963	0.059	2954	0.0012
2936	0.025	2927	0.0008
2902	0.016		
2841	0.047	2838	0.0007
1612	0.200	1613	0.0026
1575	0.057	1576	0.0007
1521	0.339	1523	0.0041
1484	0.888	1481	0.0223
1460	0.090		
1444	0.123		
1412	0.238	1410	0.0033
1313	0.040	1313	0.0008
1297	0.238	1279	0.0048
1252	0.525	1256	0.0047
1199	0.030	1202	0.0038
1176	0.418	1178	0.0073
1127	0.063		
1093	0.289	1065	0.0031
1032	0.420	1035	0.0032
1022	0.433	1006	0.0107
974	0.580	968	0.0065
957	0.422	937	0.0016
858	0.222	859	0.0027
837	0.280		
819	0.112	825	0.0043



9_KBr		9_CaF_2	
3425	0.010		
2987	0.041	2992	0.0006
		2949	0.0008
2937	0.027	2924	0.0012
2854	0.003	2854	0.0006
1659	0.100	1658	0.0003
1528	0.583	1529	0.0023
1504	1.180	1504	0.0221
1408	0.085	1408	0.0006
		1378	0.0004
1263	0.478	1265	0.0003
1202	0.368	1188	0.0004
1168	0.070	1167	0.0005
1126	0.433	1128	0.0021
1077	0.379	1070	0.0055
1030	0.592	1029	0.0008
1016	0.486	1006	0.0070
973	0.936	973	0.0057
		957	0.0027
938	0.314	939	0.0008
		849	0.0004
		813	0.0006



10_KBr		10_CaF_2	
3418	0.038		
3046	0.011		
3033	0.009		
2975	0.019		
2954	0.001	2959	0.0004
2929	0.020	2924	0.0010
2856	0.003	2854	0.0005
1655	0.068		
1612	0.014		
1571	0.047	1571	0.0002
1530	0.241		
1512	0.619	1511	0.0007
1491	1.040	1492	0.0065
1412	0.395	1412	0.0014
1382	0.024		
1323	0.047		
1253	0.111		
1201	0.164		
1142	0.047		
1106	0.101	1099	0.0004
1066	0.631		
1037	0.283		
985	0.829	987	0.0044
951	0.171	981	0.0037
862	0.247	942	0.0012
848	0.262	849	0.0006
		812	0.0011



11_KBr		11_CaF_2	
3429	0.017		
3051	0.001	3048	0.0000
3031	0.003	3016	0.0001
3001	0.005	3000	0.0002
2961	0.021	2959	0.0004
2928	0.002	2923	0.0006
2894	0.002		
2840	0.007	2854	0.0003
1653	0.051		
1570	0.021	1569	0.0002
1504	0.482		
1484	0.724	1483	0.0109
1440	0.015		
1414	0.223	1413	0.0027
1324	0.015		
1267	0.070	1260	0.0002
1210	0.133	1199	0.0011
1183	0.047	1181	0.0011
1154	0.026		
1128	0.106	1126	0.0009
1094	0.379	1099	0.0011
1055	0.033	1052	0.0006
1030	0.232		
1003	0.104	1002	0.0019
979	0.494	978	0.0081
949	0.264	948	0.0025
858	0.099		
848	0.207	848	0.0023
813	0.018	805	0.0007

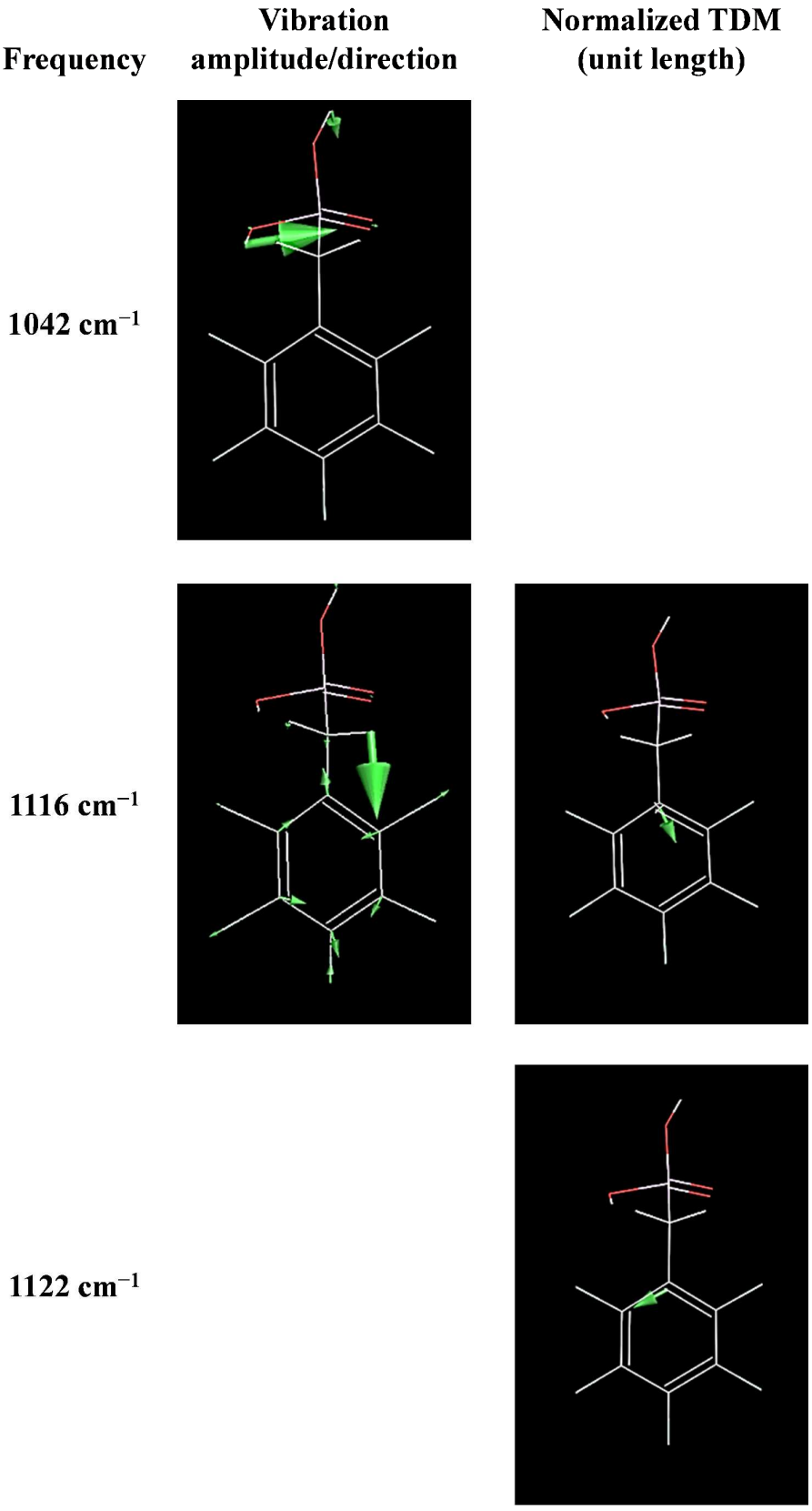
Section 5.

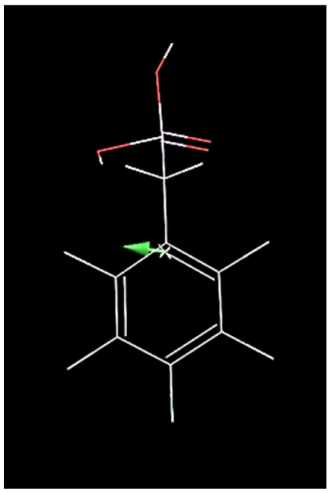
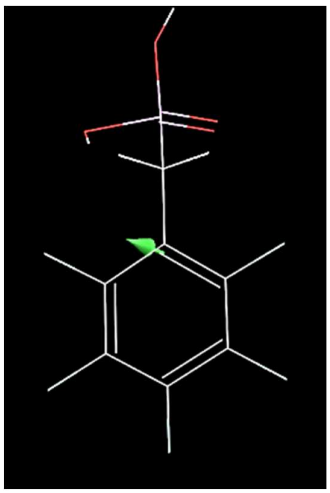
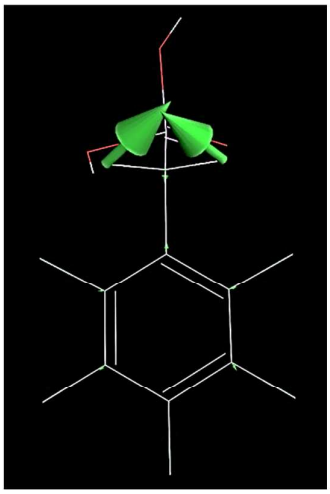
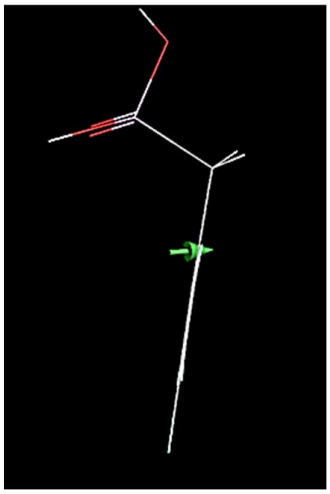
Vibrational modes from DFT calculations for PA derivatives **9**, **10**, **2**, and **11**.

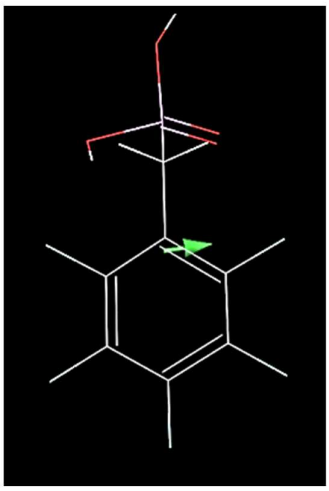
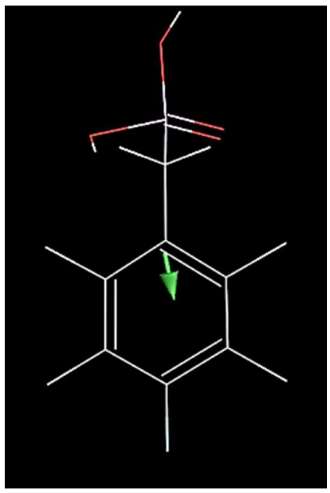
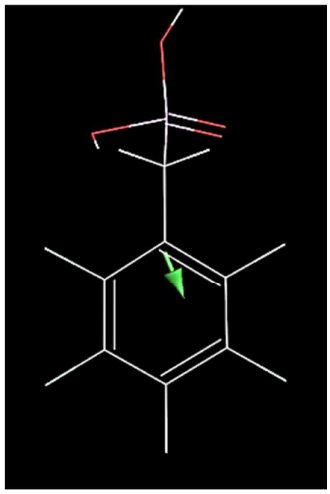
Table S3.

PA **9**			PA **10**			PA **2**			PA **11**		
mode	cm^{-1}	km/mol	mode	cm^{-1}	km/mol	mode	cm^{-1}	km/mol	mode	cm^{-1}	km/mol
37	806	146.5	50	834	20.3	40	822	4.1	52	820	34.6
38	837	135.9	51	835	195.5	41	833	216.8	53	837	83.5
39	878	231.2	52	859	27.4	42	838	10.4	54	843	161.5
40	960	116.3	53	874	256.8	43	868	202.6	55	848	10.5
41	972	209.2	54	931	1.7	44	897	3.2	56	879	234.1
42	1005	45.0	55	952	0.8	45	949	0.2	57	934	9.4
43	1044	50.7	56	979	204.7	46	951	0.5	58	939	19.1
44	1116	53.5	57	994	44.5	47	962	2.4	59	965	17.8
45	1122	27.6	58	1019	33.4	48	968	0.0	60	972	185.7
46	1166	24.2	59	1019	0.3	49	995	0.0	61	1014	0.1
47	1230	34.2	60	1053	127.9	50	1006	7.4	62	1018	48.9
48	1273	176.8	61	1086	2.3	51	1020	3.4	63	1043	30.0
49	1298	10.2	62	1127	4.0	52	1024	32.0	64	1077	234.8
50	1328	2.9	63	1132	6.0	53	1042	2.6	65	1092	1.8
51	1402	10.7	64	1175	2.6	54	1055	49.3	66	1105	2.7
52	1416	5.2	65	1185	7.5	55	1085	12.3	67	1135	7.7
53	1485	375.6	66	1201	0.7	56	1089	2.2	68	1139	9.4
54	1496	233.7	67	1221	32.2	57	1125	8.3	69	1176	4.7
55	1610	3.7	68	1265	198.0	58	1163	0.0	70	1185	1.7
56	1620	17.9	69	1298	9.2	59	1171	0.9	71	1190	0.7
57	2997	3.1	70	1313	8.1	60	1178	0.9	72	1196	37.2
58	3085	1.4	71	1315	3.7	61	1186	1.4	73	1224	44.3
59	3696	125.7	72	1338	2.0	62	1219	32.8	74	1267	201.8
60	3699	140.1	73	1407	7.2	63	1263	186.9	75	1279	18.1
			74	1409	21.7	64	1279	4.9	76	1299	8.6
			75	1414	34.2	65	1291	0.5	77	1307	0.8
			76	1475	322.1	66	1306	1.6	78	1335	2.7
			77	1489	313.5	67	1330	0.4	79	1387	62.0
			78	1511	5.5	68	1347	0.1	80	1413	54.7
			79	1566	8.1	69	1405	6.7	81	1417	14.1
			80	1594	8.7	70	1413	10.7	82	1429	195.3
			81	1616	2.2	71	1445	2.7	83	1452	97.3
			82	1625	20.8	72	1480	45.7	84	1457	139.7
			83	2981	9.6	73	1509	3.9	85	1461	46.3
			84	3054	1.7	74	1551	1.6	86	1473	164.4
			85	3110	10.4	75	1580	1.4	87	1505	5.9
			86	3130	3.5	76	1605	0.7	88	1543	5.9
			87	3164	6.2	77	1612	6.5	89	1562	1.0
			88	3171	2.8	78	3002	11.2	90	1608	13.8
			89	3705	116.5	79	3064	1.2	91	1616	8.3
			90	3708	155.0	80	3097	14.4	92	2984	72.7
						81	3113	6.3	93	2994	10.2
						82	3121	3.7	94	3069	1.8
						83	3129	0.9	95	3070	20.9
						84	3137	10.1	96	3122	10.9
						85	3145	17.2	97	3131	14.4
						86	3146	23.9	98	3138	3.4
						87	3153	18.7	99	3158	7.5
						88	3154	4.3	100	3179	5.0
						89	3695	130.2	101	3715	125.8
						90	3708	88.1	102	3718	146.0

Figure S4. Vibrational modes for **9**.



Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1166 cm^{-1}		
1273 cm^{-1}		
1402 cm^{-1}		

Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1485 cm^{-1}		
1496 cm^{-1}		
1610 cm^{-1}		

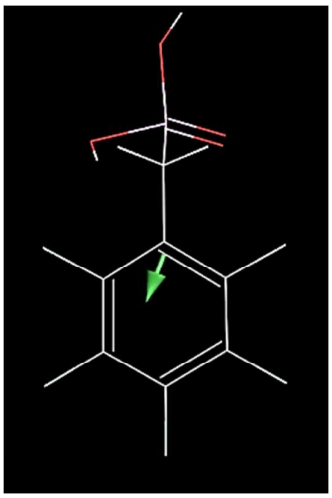
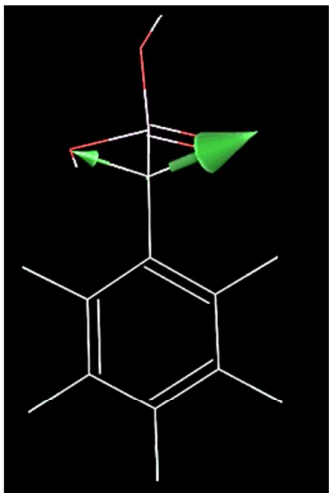
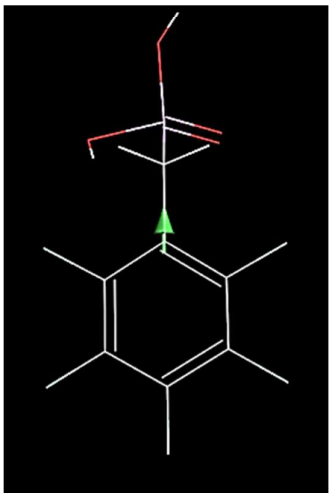
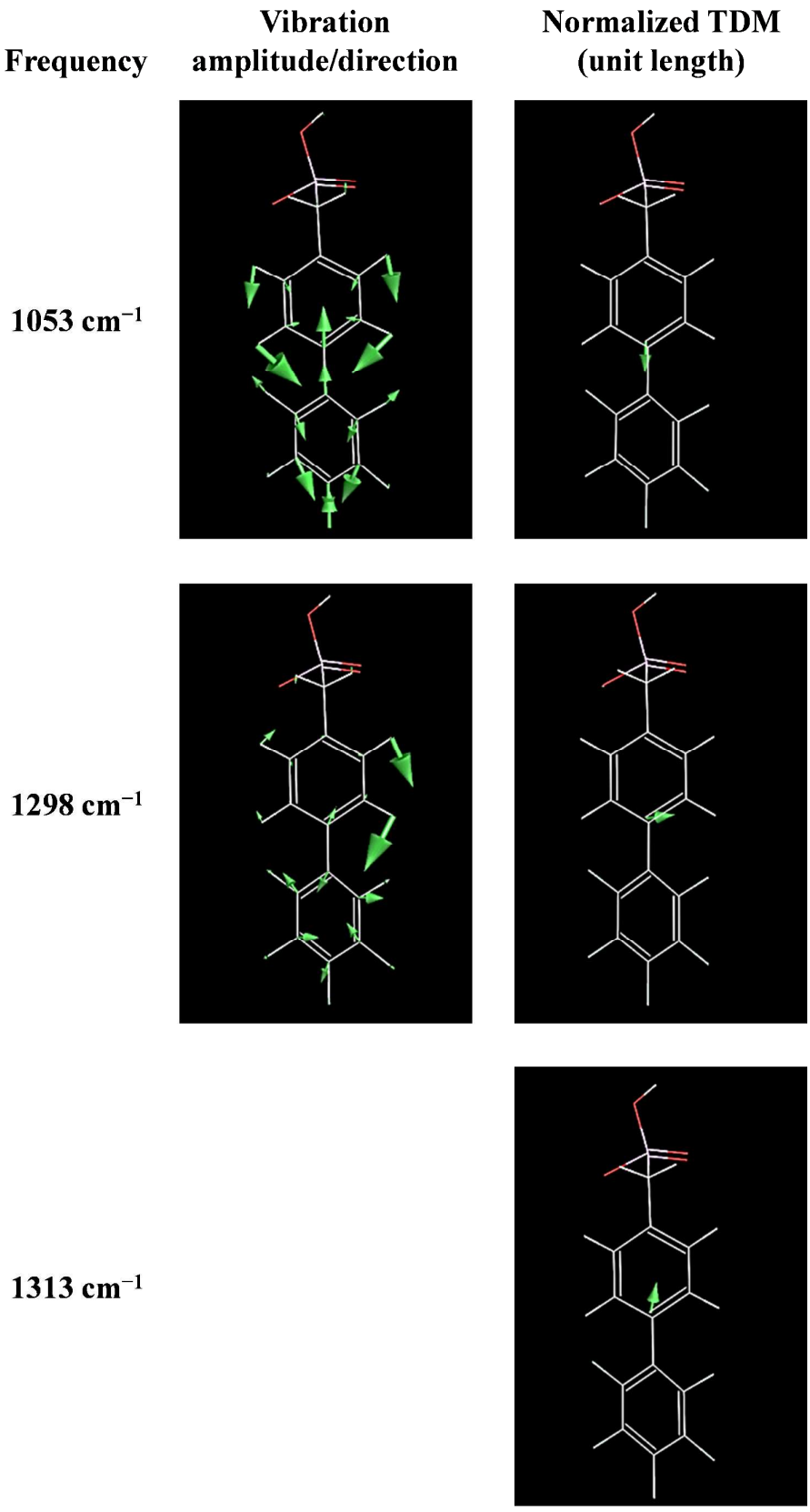
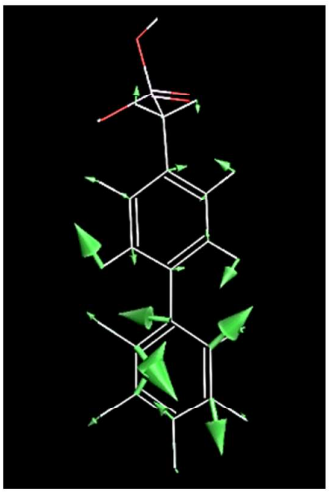
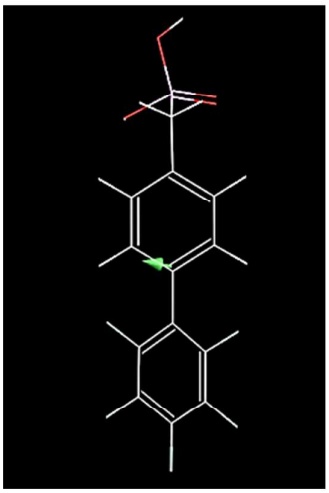
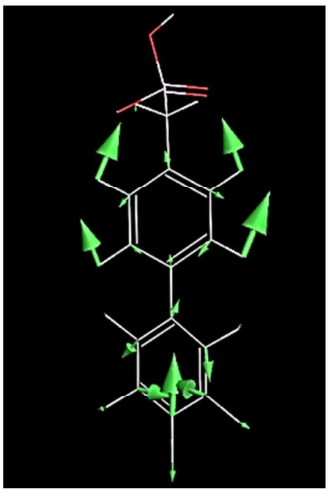
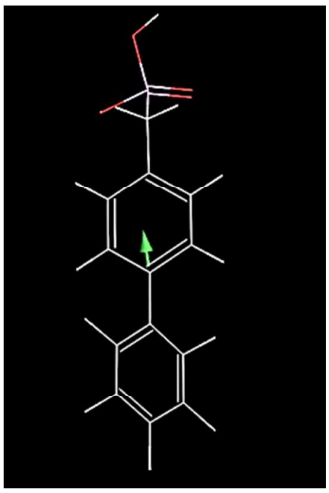
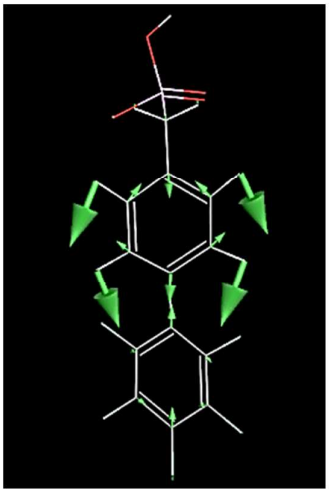
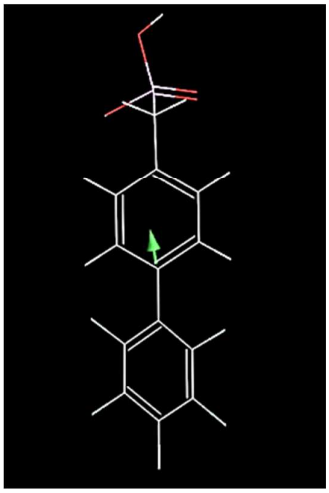
Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1620 cm^{-1}		
2997 cm^{-1}		

Figure S5. Vibrational modes for **10**.



Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1475 cm^{-1}		
1489 cm^{-1}		
1511 cm^{-1}		

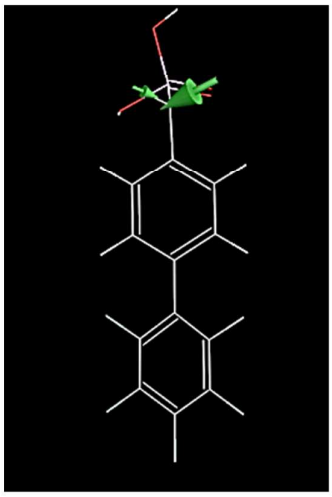
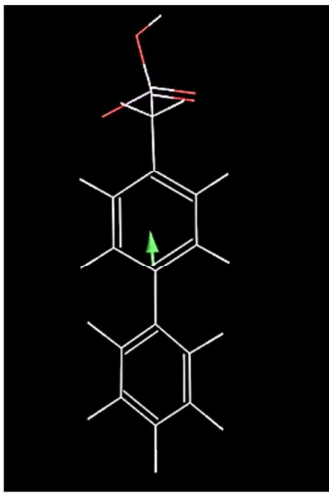
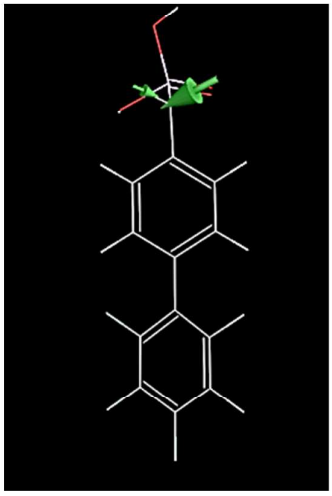
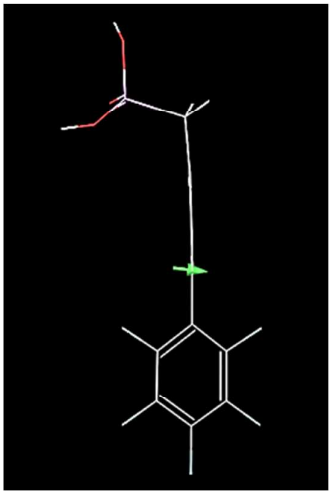
Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1625 cm^{-1}		
2981 cm^{-1}		

Figure S6. Vibrational modes for **2**.

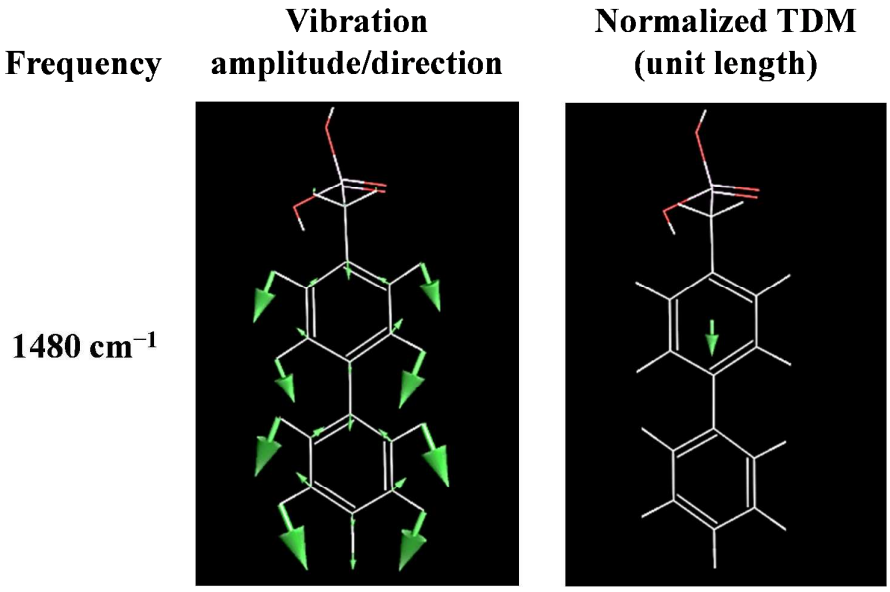
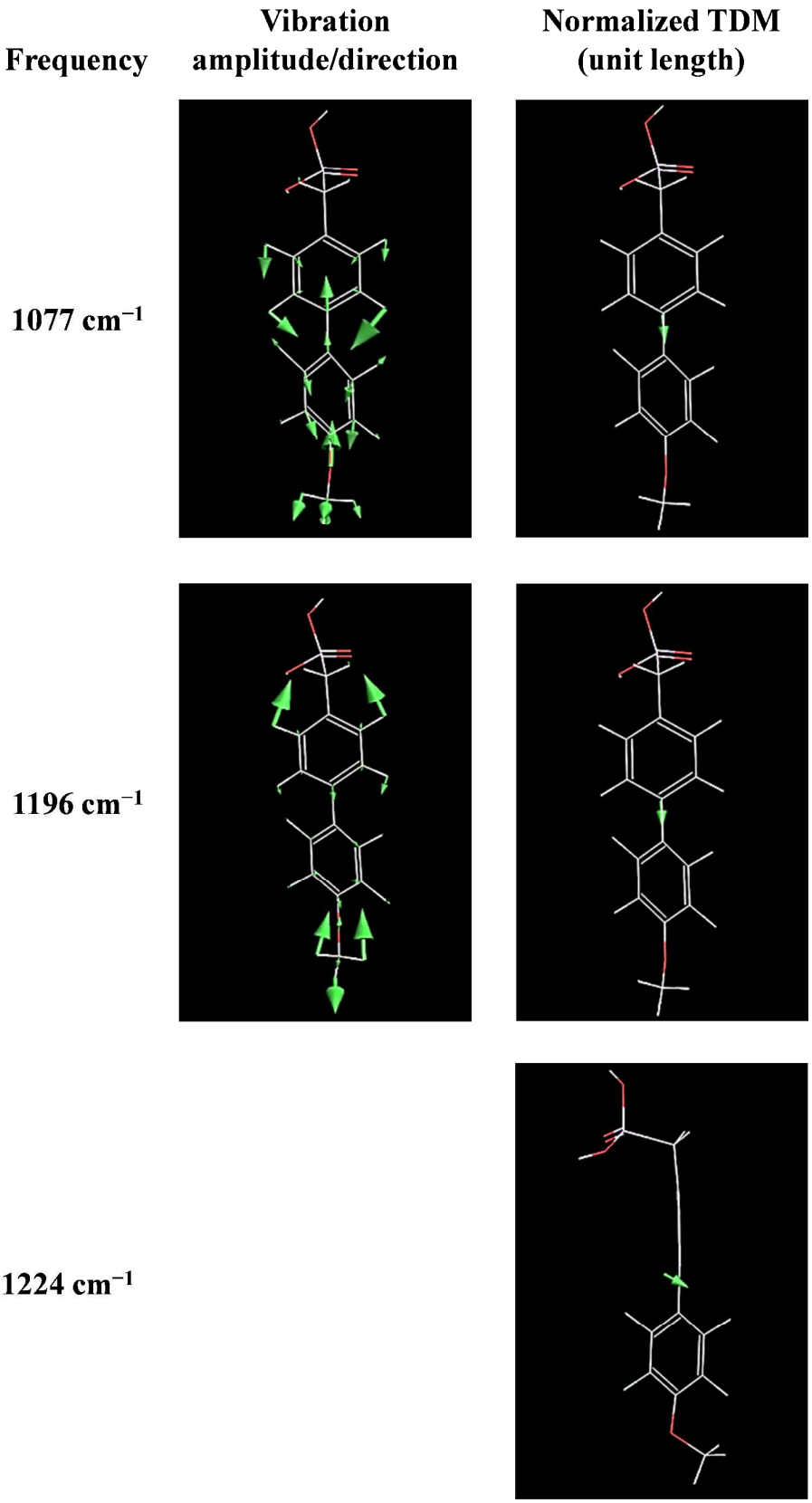
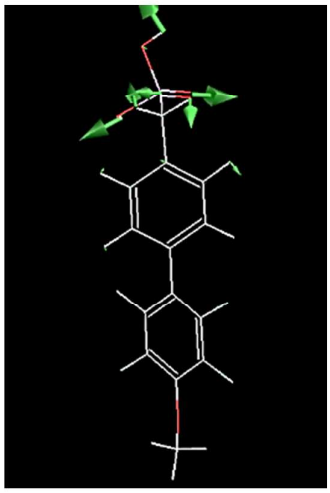
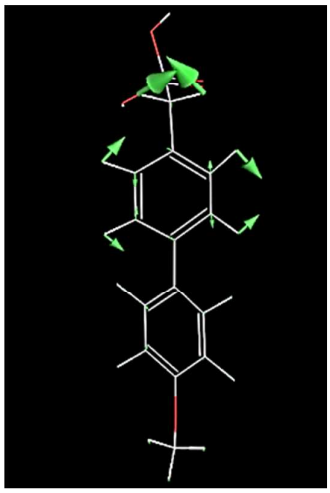
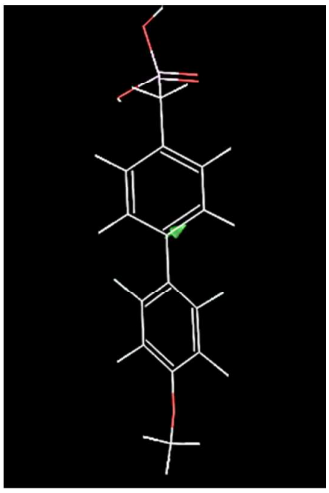
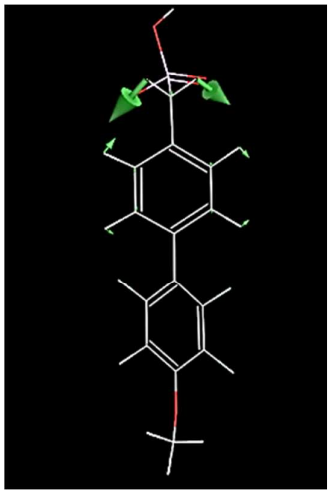
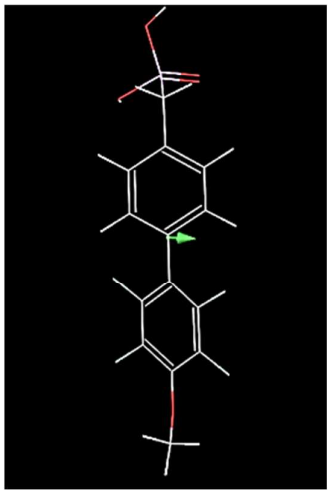
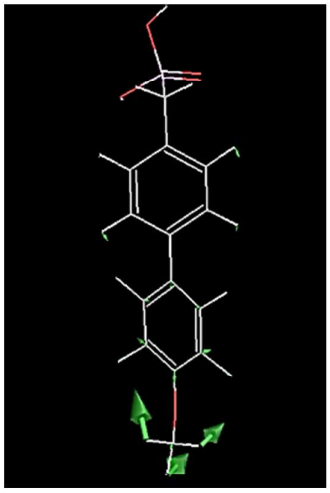
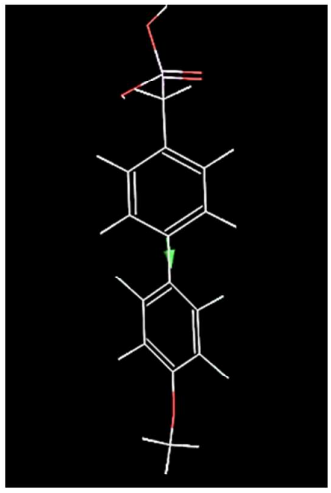
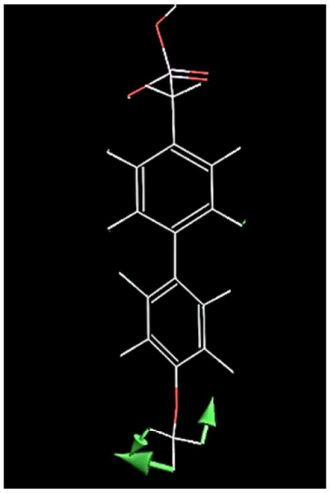
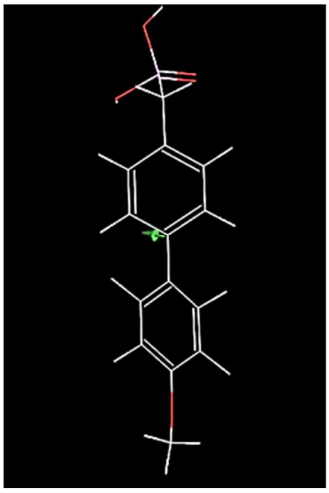
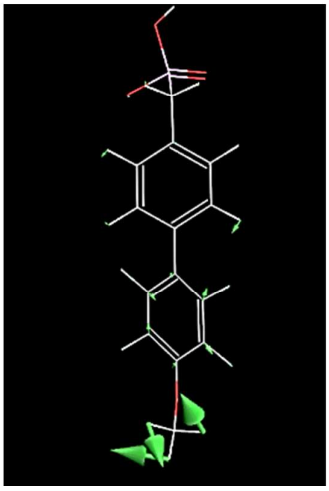
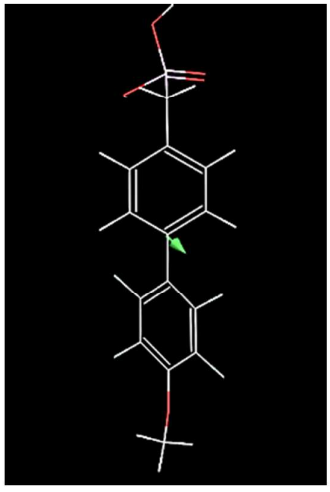
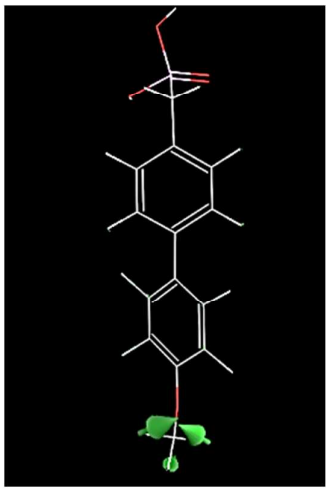
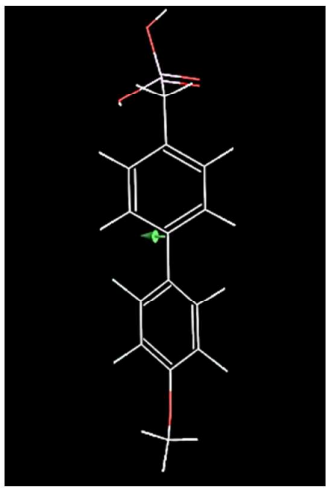
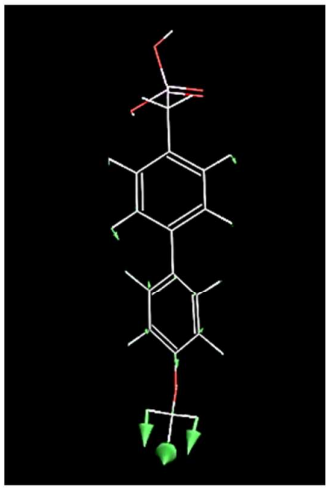
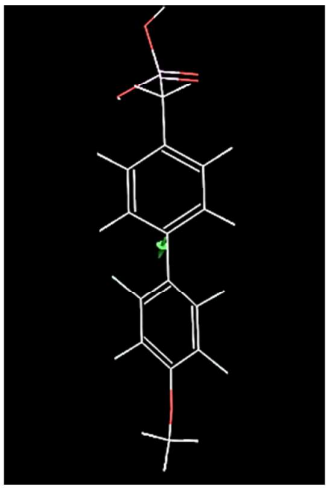
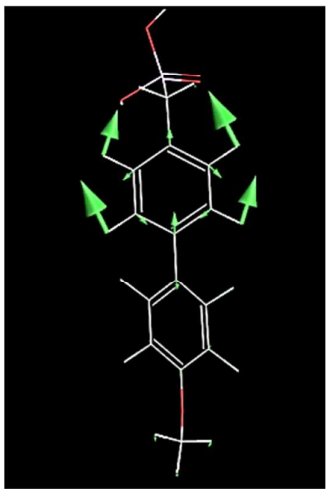
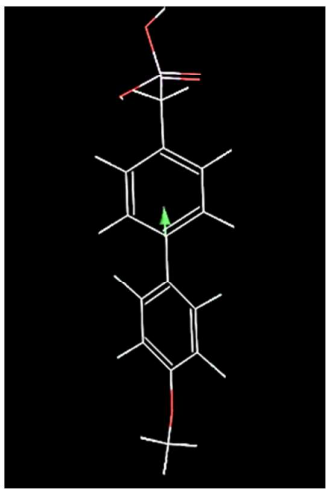


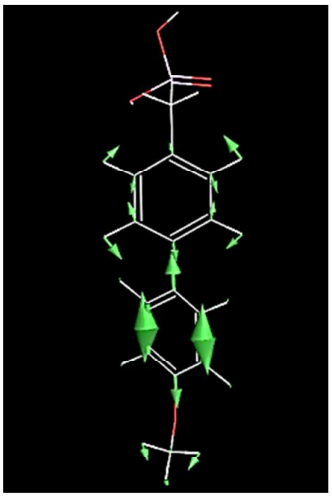
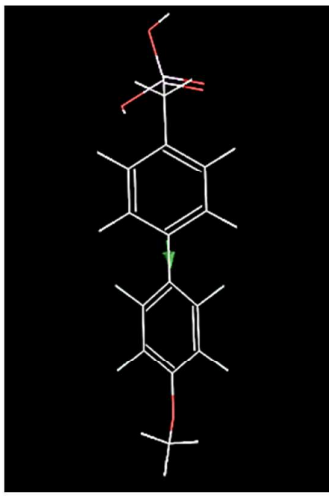
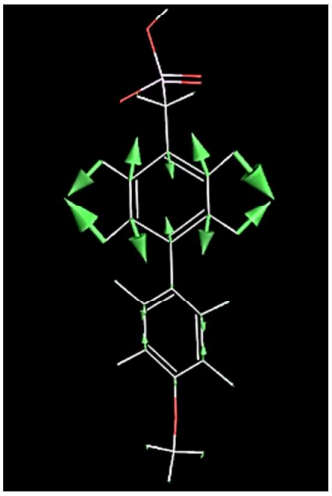
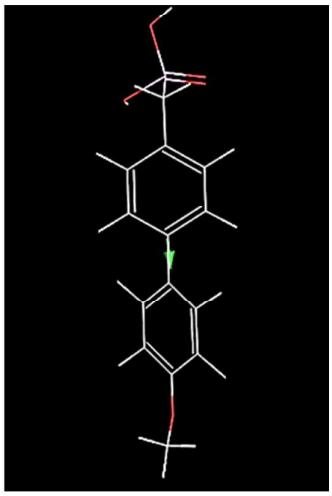
Figure S7. Vibrational modes for **11**.



Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1267 cm^{-1}		
1413 cm^{-1}		
1417 cm^{-1}		

Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1429 cm^{-1}		
1452 cm^{-1}		
1457 cm^{-1}		

Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1461 cm^{-1}		
1473 cm^{-1}		
1505 cm^{-1}		

Frequency	Vibration amplitude/direction	Normalized TDM (unit length)
1608 cm^{-1}		
1616 cm^{-1}		

Section 6.

Table S4. Literature IR results in the fingerprint region (1700−900 cm^{-1}) for systems related to **9**, **10**, **2**, and **11**. Band assignments are those provided in the cited references.

System											Ref
C_6F_5-CH_2PO_3/IZO	1658 ν_{8a}	1529 ν_{19a}	1508 ν_{19b}				1257 ν(P=O)	1131 ν_{7a}	1019 ν(P-O)	979 ν_{20a}	3
C_6H_5-CH_2PO_3/IZO	1603 ν_{8a}		1496 ν_{19a}	1455 ν_{19b}			1259 ν(P=O)		1077 β(C-C)		3
C_6H_5-CH_2S/Au			1495 ν_{19a}						1028 ν_{18a}		4
NC-C_6H_4-CH_2S/Au	1605 ν_{8a}		1502 ν_{19a}						1020 ν_{18a}		4
C_6H_5-CH_2Se/Au	1595 8a					1265 3	1181 9a	1101 7a	1074 15	1020 18a	5
C_6H_5-CH_2SeH	1598 8a		1492 19a	1452 19b	1408 CH_2 sci	1280 3	1173 9a	1101 7a	1065 15	1028 18a	5
C_6F_5-C_6F_4-C_6F_4-$(CH_2)_3S$/Au	1658 C=C	1543 C=C	1517 C=C	1485 C=C		1259 C-F		1150 C-F	1090 C-F	~940 C-F	6
C_6F_5-CH_2F	1658 C=C	1523 C=C	1510 C-F		1432 CH_2 δ			1134 C-F	1016 C-F	965 C-F	7
C_6F_5-CH_3	1656 ν_1	1519 ν_2	1503 ν_{22}					1124 ν_5		958 ν_6	8
C_6F_5-SH		1514 ip, 1,4	1496 ip, 3,5					1090 ip, 1,4			9
C_6F_5-C_6H_4-CH_3	1649 C=C	1526 C=C	1510 C=C	1494 C-F		1322 C-F		1141 C-F	1064 C-F	991 C-F	10
C_6H_5-C_6H_5-SH			1480 ip, par	1403 ip, perp		1259 ip, perp		1105 ip, perp	1076 op		11

References: Sang *et al.* (2015)[3]; Rajalingam *et al.* (2010)[4]; Azzam et al. (2014)[5];Chesneau *et al.* (2010)[6]; Mooney (1968)[7]; Frankiss and Harrison (1975)[8]; Azzam *et al.* (2012)[9], Brown and Mooney (1968)[10]; Azzam *et al.* (2002)[11].

Table S5. Literature IR results in the aromatic C−H stretch region (3150−3000 cm^{-1}) for systems related to **9**, **10**, **2**, and **11**. Band assignments are those provided in the cited references.

System						Ref
C_6H_5-CH_2PO_3/IZO			3067 ν_2	3034 ν_{20b}		3
C_6H_5-$CH_2PO_3H_2$		3071 ν_{20a}	3051 ν_2	3038 ν_{20b}		3
C_6H_5-CH_2S/Au			3063 ν_2			4
C_6H_5-CH_2SH	3102	3084 ν_{20b}	3062 ν_2	3027 ν_{20a}	3003	4
C_6H_5-PO_3/IZO			3061 ν_2	3031 ν_{20b}		12
C_6H_5-PO_3H_2		3083 ν_{20a}	3055 ν_2	3016 ν_{20b}		12

References: Sang *et al.* (2015)[3]; Rajalingam *et al.* (2010)[4]; Gliboff *et al.* (2013)[12]

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