Supporting Information for "Influence of the d Orbital Occupation on the Nature and Strength of Copper Cation-π Interactions: Threshold Collision-Induced Dissociation and Theory Studies " C. Ruan, Z. Yang, and M. T. Rodgers*

Table S1. Vibrational Frequencies and Average Internal Energies of the Neutral π-Ligands and Cu^+(π-ligand) Complexes [a]

Species	E_{int} (eV)[b]	Vibrational Frequencies (cm^{-1}) [c]
C_6H_5F	0.11 (0.02)	235, 396, 416, 501, 515, 616, 684, 753, 807, 815, 889, 952, 971, 999, 1018, 1068, 1152, 1156, 1227, 1296, 1318, 1458, 1496, 1609, 1612, 3108, 3116, 3128, 3137, 3139
$Cu^+(C_6H_5F)$	0.16 (0.02)	72, 96, 214, 339, 399, 410, 484, 506, 600, 604, 803, 812, 836, 928, 949, 964, 985, 998, 1057, 1145, 1158, 1259, 1298, 1336, 1434, 1476, 1547, 1594, 3094, 3108, 3135, 3147, 3148
C_6H_5Br	0.13 (0.02)	162, 242, 293, 407, 457, 614, 655, 688, 731, 823, 895, 958, 982, 990, 1014, 1055, 1074, 1159, 1175, 1293, 1313, 1446, 1474, 1585, 1595, 3107, 3115, 3129, 3142, 3144
$Cu^+(C_6H_5Br)$	0.18 (0.02)	53, 93, 162, 247, 300, 325, 403, 456, 583, 601, 651, 788, 845, 933, 952, 967, 975, 997, 1049, 1058, 1151, 1179, 1301, 1321, 1420, 1455, 1526, 1562, 3095, 3106, 3132, 3146, 3149
C_6H_5Cl	0.12 (0.02)	183, 292, 406, 409, 470, 616, 689, 695, 739, 825, 899, 959, 983, 996, 1022, 1076, 1076, 1159, 1174, 1292, 1317, 1449, 1479, 1592, 1596, 3107, 3116, 3129, 3139, 3141
$Cu^+(C_6H_5Cl)$	0.17 (0.02)	58, 91, 179, 298, 327, 403, 409, 467, 581, 602, 697, 796, 846, 933, 952, 970, 981, 999, 1060, 1086, 1151, 1178, 1300, 1325, 1424, 1459, 1528, 1570, 3096, 3107, 3134, 3145, 3149
C_6H_6	0.09 (0.01)	404, 405, 611(2), 675, 709, 844, 846, 961, 962, 994, 996, 1003, 1040(2), 1152, 1174(3), 1310, 1355, 1483, 1484, 1606(2), 3094, 3103, 3104, 3119(2), 3130
$Cu^+(C_6H_6)$	0.15 (0.01)	93, 94, 214, 383, 385, 598, 605(2), 708, 852, 853, 943, 944, 957, 967, 987, 1015(2), 1149, 1163(2), 1266, 1342, 1452(2), 1544, 1545, 3132, 3138(2), 3147, 3148, 3154
C_6H_5I	0.14 (0.01)	148, 216, 249, 404, 451, 614, 646, 690, 729, 828, 900, 960, 984, 990, 1010, 1054, 1075, 1160, 1181, 1287, 1317, 1442, 1474, 1583, 1589, 3104, 3113, 3127, 3136, 3138
$Cu^+(C_6H_5I)$	0.19 (0.01)	22, 23, 136, 192, 211, 228, 404, 425, 604, 632, 668, 724, 812, 906, 964, 970, 1005, 1009, 1045, 1080, 1170, 1182, 1294, 1317, 1448, 1465, 1563, 1594, 3123, 3130, 3140, 3146, 3148
C_6H_5OH	0.12 (0.02)	227, 336, 398, 413, 506, 526, 621, 685, 746, 803, 813, 867, 942, 964, 993, 1023, 1072, 1154, 1167, 1175, 1262, 1323, 1344, 1473, 1501, 1606, 1619, 3084, 3104, 3113, 3127, 3134, 3757
$Cu^+(C_6H_5OH)$	0.17 (0.02)	69, 82, 189, 351, 392, 409, 453, 494, 519, 604, 624, 800, 811, 819, 918, 937, 963, 987, 994, 1052, 1151, 1171, 1173, 1308, 1337, 1356, 1452, 1488, 1545, 1597, 3084, 3109, 3121, 3131, 3146, 3725
$C_6H_5CH_3$	0.14 (0.02)	31, 204, 337, 406, 467, 519, 625, 699, 730, 784, 837, 893, 956, 980, 981, 998, 1032, 1042, 1090, 1158, 1180, 1206, 1303, 1330, 1387, 1442, 1462, 1475, 1501, 1596, 1618, 2961, 3014, 3040, 3091, 3092, 3105, 3113, 3126
$Cu^+(C_6H_5CH_3)$	0.19 (0.02)	81, 93, 107, 191, 229, 334, 387, 453, 513, 598, 618, 742, 772, 843, 878, 937, 946, 977, 979, 1006, 1026, 1071, 1152, 1167, 1197, 1257, 1315, 1394, 1411, 1457, 1458, 1465, 1533, 1555, 2980, 3039, 3065, 3128, 3129, 3138, 3142, 3151
$C_{10}H_8$	0.16 (0.02)	169, 182, 358, 387, 471, 476, 508, 510, 622, 624, 713, 758, 770, 783, 793, 830, 878, 932, 937, 954, 973, 980, 1016, 1026, 1128, 1147, 1149, 1162, 1209, 1246, 1262, 1365, 1372, 1390, 1462, 1463, 1519, 1583, 1610, 1639, 3094, 3096, 3098, 3102, 3112, 3113, 3125, 3126
$Cu^+(C_{10}H_8)$	0.21 (0.02)	41, 142, 184, 313, 357, 374, 426, 445, 457, 499, 504, 615, 651, 743, 749, 784, 825, 827, 861, 922, 925, 947, 970, 974, 1007, 1020, 1110, 1144, 1148, 1168, 1212, 1243, 1267, 1353, 1375, 1384, 1442, 1449, 1494, 1556, 1563, 1622, 3106, 3116, 3117, 3120, 3124, 3129, 3132, 3142

Table S1. Vibrational Frequencies and Average Internal Energies of the Neutral π-Ligands and Cu^+(π-ligand) complexes [a]

Species	E_{int} (eV)[b]	Vibrational Frequencies (cm^{-1}) [c]
$C_6H_5OCH_3$	0.16 (0.02)	92, 205, 252, 269, 417, 438, 510, 550, 618, 690, 752, 784, 812, 878, 948, 967, 990, 1022, 1047, 1081, 1147, 1155, 1171, 1181, 1251, 1309, 1331, 1447, 1459, 1463, 1478, 1500, 1595, 1614, 2941, 2996, 3070, 3101, 3108, 3124, 3132, 3139
$Cu^+(C_6H_5OCH_3)$	0.21 (0.02)	46, 62, 111, 179, 224, 244, 358, 389, 435, 509, 542, 600, 635, 778, 808, 831, 915, 937, 959, 974, 987, 1017, 1058, 1143, 1150, 1174, 1181, 1301, 1312, 1345, 1444, 1453, 1467, 1470, 1490, 1524, 1593, 2976, 3050, 3081, 3109, 3114, 3129, 3144, 3157
C_4H_5N	0.07 (0.01)	465, 618, 628, 673, 713, 814, 861, 864, 884, 1014, 1046, 1071, 1136, 1151, 1283, 1390, 1428, 1471, 1546, 3166, 3177, 3194, 3199, 3604
$Cu^+(C_4H_5N)$	0.12 (0.01)	72, 130, 337, 578, 611, 709, 725, 800, 850, 868, 895, 899, 973, 1042, 1089, 1120, 1155, 1281, 1348, 1387, 1468, 1518, 3152, 3160, 3204, 3208, 3539
C_8H_7N	0.14 (0.02)	208, 240, 383, 396, 421, 541, 573, 605, 606, 710, 735, 760, 765, 837, 846, 869, 893, 915, 955, 1013, 1066, 1088, 1119, 1151, 1198, 1243, 1273, 1338, 1355, 1418, 1452, 1496, 1520, 1587, 1629, 3098, 3104, 3114, 3126, 3172, 3192, 3603
$Cu^+(C_8H_7N)$	0.19 (0.02)	68, 94, 203, 218, 354, 395, 416, 519, 528, 532, 595, 606, 653, 750, 757, 784, 855, 887, 892, 921, 943, 956, 996, 1070, 1091, 1104, 1157, 1195, 1243, 1278, 1346, 1360, 1423, 1436, 1469, 1501, 1555, 1592, 3091, 3102, 3124, 3142, 3186, 3203, 3572
$C_6H_5NH_2$	0.13 (0.02)	214, 334, 372, 409, 503, 529, 624, 688, 743, 798, 820, 851, 936, 955, 987, 1003, 1028, 1099, 1156, 1176, 1301, 1317, 1337, 1470, 1505, 1590, 1609, 1629, 3088, 3089, 3105, 3110, 3129, 3567, 3684
$Cu^+(C_6H_5NH_2)$	0.19 (0.02)	44, 67, 162, 362, 378, 383, 391, 499, 506, 544, 606, 679, 806, 813, 816, 897, 933, 957, 984, 996, 1004, 1073, 1160, 1190, 1336, 1359, 1360, 1480, 1499, 1519, 1609, 1645, 3054, 3116, 3117, 3131, 3132, 3522, 3634
$C_4H_4NCH_3$	0.12 (0.01)	80, 186, 352, 606, 616, 660, 667, 710, 802, 854, 873, 966, 1040, 1057, 1084, 1087, 1121, 1269, 1294, 1371, 1392, 1425, 1462, 1485, 1509, 1525, 2965, 3030, 3060, 3162, 3173, 3185, 3193
$Cu^+(C_4H_4NCH_3)$	0.17 (0.01)	46, 93, 97, 225, 356, 363, 576, 621, 645, 716, 786, 856, 877, 891, 966, 1006, 1045, 1080, 1094, 1125, 1250, 1264, 1350, 1357, 1425, 1443, 1462, 1488, 1511, 3001, 3077, 3100, 3148, 3160, 3197, 3201
$C_6H_5NHCH_3$	0.17 (0.02)	99, 180, 232, 247, 381, 412, 456, 510, 584, 621, 690, 746, 794, 803, 858, 939, 960, 986, 1025, 1062, 1078, 1123, 1155, 1157, 1181, 1270, 1322, 1334, 1428, 1442, 1457, 1490, 1499, 1517, 1594, 1620, 2908, 2989, 3048, 3085, 3098, 3107, 3125, 3133, 3546
$Cu^+(C_6H_5NHCH_3)$	0.22 (0.02)	45, 68, 113, 141, 199, 227, 365, 396, 436, 492, 533, 561, 602, 683, 785, 805, 811, 895, 932, 959, 979, 990, 1041, 1053, 1121, 1140, 1169, 1193, 1294, 1342, 1368, 1442, 1449, 1463, 1478, 1488, 1520, 1564, 1614, 2973, 3029, 3051, 3087, 3110, 3121, 3130, 3151, 3549
$C_6H_5N(CH_3)_2$	0.21 (0.02)	69, 102, 156, 190, 273, 276, 394, 416, 464, 510, 543, 621, 690, 739, 749, 798, 856, 940, 942, 962, 985, 1035, 1059, 1091, 1111, 1121, 1161, 1169, 1193, 1239, 1321, 1344, 1344, 1421, 1456, 1457, 1459, 1464, 1489, 1502, 1513, 1580, 1618, 2901, 2909, 2989, 2991, 3049, 3061, 3096, 3102, 3125, 3144, 3145
$Cu^+(C_6H_5N(CH_3)_2)$	0.27 (0.02)	80, 88, 132, 133, 269, 330, 379, 405, 463, 492, 523, 593, 641, 720, 776, 790, 918, 924, 973, 984, 1002, 1008, 1035, 1060, 1097, 1119, 1149, 1164, 1199(2), 1330, 1345, 1362, 1415, 1430, 1448, 1460, 1461, 1469, 1484, 1488, 1528, 1579, 2978, 2982, 3066, 3070, 3106, 3108, 3133, 3140, 3148, 3165(2)

[a]Obtained from vibrational analyses of the B3LYP/6-311G(d,p) geometry optimized structures and scaled by 0.9804.
[b]Uncertainties are listed in parenthesis. [c]Degeneracies are listed in parentheses.

Table S2. Rotational Constants of the Ground State Conformations of the Cu^+(π-ligand) Complexes and PSL Transition States for Dissociation

Species	Energized Molecule		Products	Transition State		
	1-D[a]	2-D[b]		1-D[c]	2-D[c]	2-D[d]
$Cu^+(C_6H_5F)$	0.105	0.033	Cu^+	0.19	0.071	0.0026
$Cu^+(C_6H_5Br)$	0.092	0.015	Cu^+	0.19	0.030	0.0028
	0.092	0.015	$C_6H_5^+$	0.23	0.094, 0.14	0.0066
$Cu^+(C_6H_5Cl)$	0.097	0.024	Cu^+	0.19	0.046	0.0023
	0.097	0.024	$C_6H_5^+$	0.23	0.17, 0.14	0.0069
$Cu^+(C_6H_6)$	0.093	0.086	Cu^+	0.10	0.191	0.0014
$Cu^+(C_6H_5I)$	0.053	0.016	Cu^+	0.19	0.023	0.0022
	0.090	0.011	$C_6H_5^+$	0.23	0.068, 0.14	0.0059
	0.090	0.011	$Cu(C_6H_5)^+$	0.13	0.054	0.0079
$Cu^+(C_6H_5OH)$	0.109	0.033	Cu^+	0.19	0.072	0.0021
$Cu^+(C_6H_5CH_3)$	0.086	0.053	Cu^+	0.19	0.070	0.0014
$Cu^+(C_{10}H_8)$	0.058	0.020	Cu^+	0.10	0.035	0.0015
$Cu^+(C_6H_5OCH_3)$	0.090	0.023	Cu^+	0.17	0.046	0.0022
$Cu^+(C_4H_5N)$	0.192	0.067	Cu^+	0.15	0.30	0.0025
$Cu^+(C_8H_7N)$	0.069	0.025	Cu^+	0.13	0.046	0.0016
	0.069	0.025	$C_8H_7N^+$	0.13	0.046	0.0038
$Cu^+(C_6H_5NH_2)$	0.115	0.030	Cu^+	0.18	0.073	0.0040
	0.115	0.030	$C_6H_5NH_2^+$	0.19	0.072	0.0022
$Cu^+(C_4H_4NCH_3)$	0.152	0.042	Cu^+	0.29	0.10	0.0025
	0.152	0.042	$C_4H_4NCH_3^+$	0.30	0.098	0.0037
$Cu^+(C_6H_5NHCH_3)$	0.098	0.021	Cu^+	0.17	0.044	0.0021
	0.098	0.021	$C_6H_5NHCH_3^+$	0.16	0.045	0.0039
$Cu^+(C_6H_5N(CH_3)_2)$	0.079	0.017	$C_6H_5N(CH_3)_2^+$	0.12	0.035	0.0037

[a]Active external. [b]Inactive external. [c]Rotational constants of the transition state treated as free internal rotors. [d]Treated variationally and statistically, value cited is obtained at the threshold energy for dissociation.

Table S3. B3LYP/6-311G(d,p) Optimized Geometries of the Ground State Neutral π-Ligands and Cu^+(π-ligand) Complexes[a]

	C_6H_5F				$Cu^+(C_6H_5F)$ π34				C_6H_5Br		
	x, y, z				x, y, z				x, y, z		
C	-1.13419	-1.20610	0.00000	C	0.25946	1.66943	0.15908	C	-0.12823	0.00001	0.00002
C	0.25918	-1.21443	0.00000	C	1.45798	1.16042	-0.30060	C	-0.80274	1.21422	0.00001
C	0.92901	-0.00006	-0.00008	C	1.77324	-0.18402	-0.05445	C	-2.19706	1.20521	-0.00000
C	0.25918	1.21443	-0.00004	C	0.92288	-1.03484	0.62866	C	-2.89538	0.00001	-0.00002
C	-1.13408	1.20616	0.00004	C	-0.29931	-0.52658	1.10836	C	-2.19703	-1.20524	-0.00001
C	-1.83302	0.00000	-0.00000	C	-0.64864	0.84253	0.87135	C	-0.80275	-1.21420	0.00003
H	-1.67244	-2.14690	0.00002	H	0.02358	2.71598	0.00972	H	-0.25361	2.14643	0.00004
H	0.82655	-2.13676	0.00002	H	2.17391	1.77975	-0.82670	H	-2.73358	2.14719	0.00001
F	2.28129	-0.00000	0.00004	F	2.93887	-0.64879	-0.49027	H	-3.97898	-0.00003	-0.00003
H	0.82668	2.13669	-0.00001	H	1.22684	-2.05490	0.82675	H	-2.73367	-2.14713	-0.00002
H	-1.67248	2.14687	0.00006	H	-0.86049	-1.10847	1.83313	H	-0.25367	-2.14645	0.00002
H	-2.91646	0.00007	0.00001	H	-1.43879	1.30638	1.45510	Br	1.83122	-0.00000	-0.00001
				Cu	-1.66788	-0.28832	-0.46069				
	$Cu^+(C_6H_5Br)$ π34				C_6H_5Cl				$Cu^+(C_6H_5Cl)$ π34		
	x, y, z				x, y, z				x, y, z		
C	-1.00271	1.78707	-0.03734	C	0.17912	-1.21326	-0.00001	C	-0.29504	1.75805	0.02887
C	0.31177	1.43823	-0.28765	C	1.57235	-1.20504	0.00002	C	0.98096	1.33686	-0.29306
C	0.82355	0.22395	0.20374	C	2.27150	0.00000	-0.00001	C	1.42872	0.06613	0.11562
C	0.03416	-0.64316	0.94386	C	1.57232	1.20505	0.00001	C	0.60730	-0.78508	0.84188
C	-1.30666	-0.29961	1.21454	C	0.17912	1.21326	0.00000	C	-0.69351	-0.36672	1.18652
C	-1.84293	0.93161	0.71837	C	-0.50098	-0.00002	-0.00002	C	-1.16369	0.92075	0.77336
H	-1.38293	2.73992	-0.38550	H	-0.37296	-2.14420	0.00001	H	-0.62270	2.75087	-0.25477
H	0.95662	2.10520	-0.84490	H	2.10876	-2.14702	0.00002	H	1.65234	1.98575	-0.84069
H	0.45105	-1.55621	1.34834	H	3.35507	0.00003	-0.00001	H	0.97980	-1.74296	1.18127
H	-1.84839	-0.85988	1.97073	H	2.10875	2.14702	0.00001	H	-1.24287	-0.92836	1.93609
H	-2.77208	1.32072	1.12467	H	-0.37301	2.14417	0.00002	H	-2.04624	1.34993	1.23884
Cu	-2.44044	-0.57109	-0.51081	Cl	-2.26278	-0.00000	0.00000	Cu	-1.91708	-0.47314	-0.49652
Br	2.66473	-0.22334	-0.14095					Cl	3.04039	-0.42789	-0.28123
	C_6H_6				$Cu^+(C_6H_6)$ πc				C_6H_5I		
	x, y, z				x, y, z				x, y, z		
C	1.20688	0.69694	0.00000	C	-1.01325	-1.08673	-0.54289	C	1.26061	-1.21268	-0.00000
C	1.20688	-0.69684	0.00000	C	-1.49730	0.23593	-0.45948	C	2.65501	-1.20440	0.00002
C	0.00009	1.39359	0.00000	C	-0.61062	1.32285	-0.61206	C	3.35430	0.00001	-0.00001
H	2.14603	1.23897	0.00000	C	0.76092	1.08734	-0.84750	C	2.65497	1.20441	0.00000
C	0.00011	-1.39359	0.00000	C	1.24549	-0.23588	-0.93083	C	1.26060	1.21268	0.00001
C	-1.20695	0.69673	0.00000	C	0.35800	-1.32298	-0.77882	C	0.57817	-0.00002	-0.00000
H	2.14605	-1.23883	0.00000	H	-1.69728	-1.92021	-0.44802	H	0.71971	-2.14997	0.00000
H	-0.00036	2.47794	0.00000	H	-2.55259	0.41678	-0.30064	H	3.19059	-2.14713	0.00000
C	-1.20695	-0.69684	0.00000	H	1.43732	1.92092	-0.98592	H	4.43799	0.00004	-0.00001
H	-0.00001	-2.47794	0.00000	H	2.29330	-0.41671	-1.13310	H	3.19056	2.14714	-0.00000
H	-2.14604	1.23881	0.00000	H	0.72568	-2.33737	-0.86472	H	0.71964	2.14993	0.00001
H	-2.14603	-1.23896	0.00000	H	-0.98584	2.33726	-0.57007	I	-1.56303	0.00000	0.00000
				Cu	0.18345	-0.00013	1.01145				

Table S3. B3LYP/6-311G(d,p) Optimized Geometries of the Ground State Neutral π-Ligands and Cu^+(π-ligand) Complexes[a]

	$Cu^+(C_6H_5I)$ πx				C_6H_5OH				$Cu^+(C_6H_5OH)$ π34		
	x, y, z				x, y, z				x, y, z		
C	-1.53188	1.78661	-0.06889	C	1.16947	-1.18831	0.00000	C	-0.19121	1.60676	0.27751
C	-0.20258	1.47324	-0.28831	C	-0.22014	-1.22099	0.00000	C	-1.40724	1.20566	-0.22035
C	0.34666	0.28724	0.23767	C	-0.93998	-0.02403	0.00005	C	-1.83366	-0.13682	-0.07623
C	-0.43561	-0.58341	0.98580	C	-0.26257	1.19689	0.00003	C	-1.00672	-1.07560	0.54620
C	-1.79143	-0.27796	1.22587	C	1.13078	1.21646	-0.00003	C	0.23266	-0.67824	1.05893
C	-2.35803	0.92453	0.69436	C	1.85460	0.02737	0.00001	C	0.67358	0.67879	0.93073
H	-1.93521	2.71881	-0.44605	H	1.72188	-2.12141	-0.00001	H	0.10472	2.64637	0.20457
H	0.42296	2.15328	-0.85205	H	-0.76497	-2.15721	-0.00001	H	-2.07903	1.90585	-0.70112
H	-0.00630	-1.47658	1.42098	H	-0.82260	2.12785	-0.00003	H	-1.34214	-2.09831	0.67941
H	-2.32940	-0.84006	1.98341	H	1.64831	2.16927	-0.00004	H	0.77264	-1.35615	1.71178
H	-3.30534	1.29351	1.07693	H	2.93779	0.04579	0.00000	H	1.44916	1.05798	1.59180
Cu	-2.88208	-0.61350	-0.51895	O	-2.30449	-0.11067	-0.00005	O	-3.04535	-0.42301	-0.56390
I	2.38813	-0.14564	-0.09156	H	-2.67735	0.77679	0.00020	H	-3.29397	-1.34101	-0.39611
								Cu	1.72231	-0.24255	-0.47172
	$C_6H_5CH_3$				$Cu^+(C_6H_5CH_3)$ πc				$C_{10}H_8$		
	x, y, z				x, y, z				x, y, z		
C	1.19916	1.20252	0.00200	C	-0.15101	1.70085	0.08955	C	-1.83756	-0.00002	-1.73876
C	1.90120	-0.00019	0.00835	C	-1.37098	1.19123	-0.31104	C	-1.83627	-0.00008	-0.36549
C	-0.19362	1.19995	-0.00863	C	-1.76213	-0.13371	-0.00612	C	-0.61761	-0.00010	0.36152
H	1.73591	2.14485	0.00143	C	-0.88018	-0.93928	0.70807	C	0.61761	0.00010	-0.36152
C	1.19834	-1.20290	0.00198	C	0.36793	-0.44670	1.14584	C	0.57999	0.00025	-1.78020
C	-0.91204	0.00043	-0.01139	C	0.74867	0.89739	0.83380	C	-0.61689	0.00017	-2.45343
H	2.98526	-0.00052	0.01390	H	0.10684	2.73132	-0.12371	H	-1.51723	-0.00046	2.32712
H	-0.73153	2.14281	-0.01729	H	-2.05919	1.83008	-0.85357	H	-2.7759	-0.00007	-2.28173
C	-0.19399	-1.19992	-0.00863	H	-1.17169	-1.94665	0.98162	H	-2.77191	-0.00015	0.18415
H	1.73490	-2.14537	0.00140	H	0.92629	-1.00604	1.89077	C	-0.57999	-0.00025	1.78020
C	-2.42164	0.00022	0.00919	H	1.57279	1.36625	1.36368	C	1.83627	0.00008	0.36549
H	-0.73274	-2.14228	-0.01731	Cu	1.65565	-0.36244	-0.47623	H	1.51723	0.00046	-2.32712
H	-2.82743	-0.87851	-0.49782	C	-3.11490	-0.63562	-0.42953	H	-0.63111	0.00017	-3.53747
H	-2.80135	-0.01142	1.03687	H	-3.90488	0.00293	-0.02462	C	1.83756	0.00002	1.73876
H	-2.82744	0.88976	-0.47840	H	-3.21494	-0.61685	-1.51891	C	0.61689	-0.00017	2.45343
				H	-3.29322	-1.65519	-0.08808	H	2.77191	0.00015	-0.18415
								H	2.77593	0.00007	2.28173
								H	0.63111	-0.00017	3.53747

Table S3. B3LYP/6-311G(d,p) Optimized Geometries of the Ground State Neutral π-Ligands and Cu^+(π-ligand) Complexes[a]

	$Cu^+(C_{10}H_8)$ π12				$C_6H_5OCH_3$				$Cu^+(C_6H_5OCH_3)$ π34		
	x, y, z				x, y, z				x, y, z		
C	1.43199	0.84978	1.00971	C	-1.84988	-0.99857	0.00000	C	0.50283	1.73692	0.15709
C	0.26671	1.48482	0.59007	C	-0.49611	-1.30078	-0.00003	C	-0.78642	1.54244	-0.26781
C	-0.89595	0.74875	0.26432	C	0.45337	-0.27083	-0.00002	C	-1.46430	0.32219	-0.00303
C	-0.85847	-0.68970	0.32902	C	0.03081	1.06112	-0.00001	C	-0.80493	-0.71028	0.67468
C	0.33213	-1.33080	0.74089	C	-1.33601	1.34897	-0.00004	C	0.51068	-0.51909	1.11501
C	1.46566	-0.59576	1.10013	C	-2.28119	0.33036	0.00005	C	1.20127	0.70939	0.86116
H	-2.13629	2.47078	-0.16151	H	-2.57486	-1.80503	0.00001	H	0.98986	2.68974	-0.01227
H	2.25306	1.43230	1.41182	H	-0.14312	-2.32498	-0.00004	H	-1.33338	2.31985	-0.78667
H	0.22827	2.56811	0.56621	H	0.74567	1.87292	0.00004	H	-1.31096	-1.63616	0.90887
C	-2.10523	1.38823	-0.11527	H	-1.65510	2.38548	-0.00006	H	0.93691	-1.23480	1.81074
C	-2.03335	-1.42382	0.01661	H	-3.33931	0.56344	0.00012	H	2.06103	0.97960	1.46970
H	0.34282	-2.41043	0.84047	O	1.75833	-0.67016	0.00002	O	-2.72117	0.27149	-0.43709
H	2.29370	-1.08784	1.59933	C	2.77096	0.32478	0.00002	Cu	1.99641	-0.51601	-0.47293
C	-3.18505	-0.77025	-0.34136	H	2.71558	0.95650	0.89387	C	-3.53048	-0.88826	-0.17351
C	-3.22110	0.64530	-0.40768	H	3.71727	-0.21382	-0.00003	H	-4.49897	-0.66640	-0.61275
H	-2.00900	-2.50610	0.07330	H	2.71551	0.95653	-0.89382	H	-3.10370	-1.77455	-0.64984
H	-4.07980	-1.33612	-0.57109					H	-3.63913	-1.04491	0.90228
H	-4.14270	1.14066	-0.68866								
Cu	2.07125	-0.07278	-0.76512								

	C_4H_5N				$Cu^+(C_4H_5N)$ π34				C_8H_7N		
	x, y, z				x, y, z				x, y, z		
C	-0.33097	1.12433	-0.00009	C	1.28923	-1.12800	-0.03939	C	0.00000	0.71551	0.00000
C	0.98161	0.71179	0.00003	C	0.28715	-0.73378	0.84522	C	-0.49278	-0.61782	0.00000
C	0.98161	-0.71179	-0.00011	C	0.28810	0.73552	0.84438	C	0.42839	-1.67729	0.00000
C	-0.33097	-1.12433	0.00018	C	1.29074	1.12742	-0.04053	C	1.78443	-1.39228	0.00000
N	-1.12052	-0.00000	-0.00002	N	1.86743	-0.00099	-0.53936	C	2.24907	-0.06314	0.00000
H	-2.12605	-0.00000	0.00007	H	2.61642	-0.00182	-1.21957	C	1.36603	1.00644	0.00000
H	-0.76421	2.11113	-0.00017	H	1.64826	-2.11120	-0.29590	N	-1.09572	1.55312	0.00000
H	1.84520	1.35820	0.00003	H	-0.15418	-1.37428	1.59653	C	-2.25111	0.79524	0.00000
H	1.84520	-1.35820	-0.00020	H	-0.15263	1.37752	1.59473	C	-1.92621	-0.53287	0.00000
H	-0.76420	-2.11113	0.00031	H	1.65101	2.10964	-0.29904	H	0.08160	-2.70492	0.00000
				Cu	-1.29698	0.00000	-0.25032	H	2.50370	-2.20333	0.00000
								H	3.31617	0.12748	0.00000
								H	1.72589	2.02962	0.00000
								H	-1.06113	2.55795	0.00000
								H	-3.21814	1.27314	0.00000
								H	-2.62495	-1.35449	0.00000

Table S3. B3LYP/6-311G(d,p) Optimized Geometries of the Ground State Neutral π-Ligands and Cu^+(π-ligand) Complexes[a]

	$Cu^+(C_8H_7N)$ π45				$C_6H_5NH_2$				$Cu^+(C_6H_5NH_2)$ π4		
	x, y, z				x, y, z				x, y, z		
C	-0.48790	-0.48204	1.00519	C	1.17008	1.20014	0.00333	C	-0.01930	-1.22285	0.74666
C	-1.25869	0.72737	0.91463	C	-0.22027	1.20580	-0.00439	C	-1.26617	-1.22474	0.17386
C	0.82465	-0.48707	0.47133	C	-0.93833	0.00000	-0.00743	C	-1.93158	-0.00057	-0.11066
H	-0.79334	-1.26493	1.69350	C	-0.22027	-1.20580	-0.00440	C	-1.26774	1.22525	0.17074
Cu	-1.88000	-0.60262	-0.49638	C	1.17008	-1.20015	0.00333	C	-0.02091	1.22651	0.74347
C	-0.70963	1.89168	0.30693	C	1.87893	0.00000	0.00731	C	0.67107	0.00268	1.03781
C	0.57144	1.88863	-0.21071	H	1.70319	2.14483	0.00721	H	0.43948	-2.16325	1.02932
C	1.32193	0.70749	-0.13018	H	-0.75977	2.14794	-0.01283	H	-1.76852	-2.16263	-0.03344
C	1.87564	-1.44885	0.43259	N	-2.33315	-0.00000	-0.07609	N	-3.16587	-0.00203	-0.64562
H	-2.13753	0.83888	1.54321	H	-0.75980	-2.14794	-0.01283	H	-1.77133	2.16194	-0.03900
C	2.94389	-0.84119	-0.17601	H	1.70319	-2.14483	0.00721	H	0.43687	2.16826	1.02322
N	2.60772	0.44987	-0.51961	H	2.96226	0.00000	0.01386	H	1.40200	0.00427	1.84657
H	1.85571	-2.45800	0.81151	H	-2.77917	-0.83610	0.27175	H	-3.66889	0.85678	-0.80271
H	-1.29790	2.80022	0.28855	H	-2.77918	0.83610	0.27174	H	-3.66780	-0.86188	-0.80050
H	0.99056	2.78870	-0.64554					Cu	1.85404	-0.00093	-0.49226
H	3.23306	1.11250	-0.95241								
H	3.92835	-1.22659	-0.38912								

	$C_4H_4NCH_3$				$Cu^+(C_4H_4NCH_3)$ π34				$C_6H_5NHCH_3$		
	x, y, z				x, y, z				x, y, z		
C	-0.17511	-1.11845	-0.01376	C	0.87140	-1.04336	0.53340	C	0.44277	-0.27413	-0.05180
C	-1.49024	-0.71095	0.01544	C	-0.31594	-0.54617	1.07597	C	-0.52535	-1.29617	-0.00535
C	-1.49024	0.71095	0.01543	C	-0.28673	0.90425	0.85137	C	-1.87798	-0.99294	0.03824
C	-0.17511	1.11845	-0.01376	C	0.91078	1.17157	0.19500	C	-2.31264	0.33397	0.03475
N	0.62405	0.00000	-0.03927	N	1.58536	-0.00264	0.02488	C	-1.36233	1.34895	-0.00976
H	0.25820	-2.10602	-0.02221	H	1.26292	-2.04780	0.52775	C	0.00014	1.05941	-0.04847
H	-2.35231	-1.35971	0.02217	H	-0.92165	-1.07008	1.80341	N	1.78806	-0.60877	-0.13584
H	-2.35231	1.35971	0.02217	H	-0.89160	1.64412	1.35668	H	-0.20135	-2.33278	-0.01073
H	0.25820	2.10602	-0.02221	H	1.33726	2.11110	-0.11714	H	-2.60105	-1.80078	0.074712
C	2.07411	0.00000	0.02609	Cu	-1.57809	-0.07778	-0.45261	H	-3.36995	0.56779	0.06755
H	2.46340	0.88404	-0.48093	C	2.87059	-0.13185	-0.67259	H	-1.67869	2.38669	-0.00984
H	2.43258	-0.00004	1.06034	H	3.40216	-0.99718	-0.28101	H	0.71532	1.87138	-0.07776
H	2.46341	-0.88400	-0.48099	H	2.71228	-0.25469	-1.74534	H	2.00146	-1.54344	0.17484
				H	3.46512	0.76198	-0.49165	C	2.83872	0.36378	0.09350
								H	2.83485	1.13009	-0.68725
								H	2.76057	0.87039	1.06715
								H	3.80234	-0.14517	0.045501

Table S3. B3LYP/6-311G(d,p) Optimized Geometries of the Ground State Neutral π-Ligands and Cu^+(π-ligand) Complexes[a]

	$Cu^+(C_6H_5NHCH_3)$ π4				$C_6H_5N(CH_3)_2$				$Cu^+(C_6H_5N(CH_3)_2)$ π4		
	x, y, z				x, y, z				x, y, z		
C	0.32299	-0.87316	1.03768	C	0.18152	-0.00005	-0.06581	C	-0.74098	1.22740	0.80982
C	-0.96787	-0.87122	0.56500	C	-0.55251	-1.20576	-0.02883	C	0.56330	1.22722	0.38977
C	-1.53822	0.32151	0.03850	C	-1.94187	-1.19605	0.01525	C	1.27206	0.00100	0.18085
C	-0.73095	1.49921	-0.01744	C	-2.65473	0.00005	0.03507	C	0.55954	-1.22174	0.39606
C	0.55378	1.49311	0.44988	C	-1.94180	1.19608	0.01568	C	-0.74490	-1.21540	0.81617
C	1.15399	0.29714	0.97821	C	-0.55240	1.20570	-0.02840	C	-1.47117	0.00777	1.01905
H	0.70835	-1.76357	1.52143	N	1.56965	-0.00007	-0.14819	H	-1.22559	2.17168	1.03013
H	-1.56248	-1.77206	0.62956	H	-0.04006	-2.15760	-0.03460	H	1.06614	2.17282	0.25115
N	-2.80669	0.36494	-0.40114	H	-2.47087	-2.14299	0.03945	N	2.56589	-0.00197	-0.19598
H	-1.16201	2.41410	-0.40909	H	-3.73745	0.00006	0.07148	H	1.05926	-2.16966	0.26226
H	1.12609	2.41346	0.45420	H	-2.47069	2.14308	0.04023	H	-1.23200	-2.15688	1.04296
H	1.94596	0.40648	1.71962	H	-0.03989	2.15750	-0.03386	H	-2.28081	0.01121	1.74961
H	-3.15127	1.25463	-0.72880	C	2.29477	1.24193	0.05687	Cu	-2.50219	-0.00364	-0.61388
Cu	2.19191	-0.31720	-0.53225	H	3.35993	1.05760	-0.07997	C	3.30121	1.25639	-0.36751
C	-3.75735	-0.74132	-0.36243	H	1.99734	1.99599	-0.67738	H	4.30966	1.03146	-0.70316
H	-4.69583	-0.40237	-0.79640	H	2.14480	1.66759	1.06084	H	2.82705	1.88966	-1.12146
H	-3.39701	-1.59129	-0.94766	C	2.29483	-1.24186	0.05764	H	3.36814	1.81013	0.57342
H	-3.94865	-1.06678	0.66386	H	2.14473	-1.66713	1.06179	C	3.29752	-1.26355	-0.35930
				H	1.99778	-1.99633	-0.67636	H	3.35932	-1.81308	0.58441
				H	3.36003	-1.05749	-0.07908	H	2.82378	-1.89878	-1.11192
								H	4.30791	-1.04366	-0.69236

[a]Obtained from structures optimized at the B3LYP/6-311G(d,p) level of theory.

Table S4. Enthalpies and Free Energies of Binding of Cu^+ to π-Ligands at 0 and 298K in kJ/mol[a]

System	ΔH_0	ΔH_0[b]	$\Delta H_{298}-\Delta H_0$[b]	ΔH_{298}	ΔH_{298}[b]	$T\Delta S_{298}$[b]	ΔG_{298}	ΔG_{298}[b]
$Cu^+(C_6H_5F)$	183.3 (4.8)	186.0	1.0 (0.2)	184.3 (4.8)	187.0	31.8 (0.7)	152.5 (4.9)	155.2
$Cu^+(C_6H_5Br)$	201.7 (12.5)	186.8	0.9 (0.2)	202.6 (12.5)	187.7	31.8 (0.7)	170.8 (12.5)	162.7
$Cu^+(C_6H_5Cl)$	194.9 (7.7)	189.4	0.9 (0.2)	195.8 (7.7)	190.3	31.5 (0.7)	164.3 (7.7)	155.8
$Cu^+(C_6H_6)$	217.1 (5.8)	204.6	0.5 (0.2)	217.6 (5.8)	205.1	31.6 (0.8)	186.0 (5.9)	173.5
$Cu^+(C_6H_5I)$	221.0 (7.7)	192.3	-0.3 (0.1)	220.7 (7.7)	193.2	25.0 (0.8)	195.7 (7.7)	161.5
$Cu^+(C_6H_5OH)$	210.3 (11.6)	212.6	1.2 (0.2)	211.5 (11.6)	213.8	31.7 (0.7)	179.8 (11.6)	182.1
$Cu^+(C_6H_5CH_3)$	219.0 (9.6)	216.9	0.8 (0.3)	219.8 (9.6)	217.7	34.9 (0.8)	184.9 (9.6)	182.8
$Cu^+(C_{10}H_8)$	231.6 (8.7)	222.3	0.8 (0.2)	232.4 (8.7)	223.1	32.1 (0.7)	200.3 (8.7)	191.0
$Cu^+(C_6H_5OCH_3)$	236.4 (8.7)	223.9	0.8 (0.2)	237.2 (8.7)	224.7	31.5 (0.7)	205.7 (8.7)	193.2
$Cu^+(C_4H_5N)$	239.3 (12.5)	236.5	1.8 (0.2)	241.1 (12.5)	238.3	32.2 (0.6)	208.8 (12.5)	206.7
$Cu^+(C_8H_7N)$	253.8 (8.7)	245.5	1.3 (0.2)	255.1 (8.7)	246.8	32.7 (0.7)	217.5 (8.7)	222.4
$Cu^+(C_6H_5NH_2)$	251.8 (10.6)	246.2	0.9 (0.2)	252.7 (10.6)	247.1	29.8 (0.7)	222.9 (10.6)	217.3
$Cu^+(C_4H_4NCH_3)$	267.3 (7.7)	252.1	1.4 (0.2)	268.7 (7.7)	253.5	31.6 (0.7)	237.1 (7.7)	221.9
$Cu^+(C_6H_5NHCH_3)$	241.2 (6.8)	256.2	1.1 (0.2)	242.3 (6.8)	257.3	31.5 (0.7)	210.8 (6.8)	225.8
$Cu^+(C_6H_5N(CH_3)_2)$[c]	232.5 (11.6)	262.2	1.0 (0.1)	233.5 (11.6)	263.2	30.4 (0.7)	203.1 (11.6)	232.8

[a]Uncertainties are listed in the parentheses. [b]Values from theoretical calculations at the B3LYP/6-311+G(3df,2p) level of theory using the B3LYP/6-311G(d,p) optimized ground state geometries with frequencies scaled by 0.9804. Uncertainties in the enthalpic and entropic corrections are determined by 10% variation in the molecular constants. [c]value estimated for dissociation via simple CID accompanied by charge transfer to the π-ligand, eqn (8).

Figure S1. Cross sections for the collision-induced dissociation of the Cu^+(π-ligand) complexes, where π-ligand = C_6H_5F, C_6H_5Cl, C_6H_5I, C_6H_5OH, $C_6H_5CH_3$, $C_{10}H_8$, $C_6H_5OCH_3$, C_4H_5N, $C_6H_5NH_2$, $C_4H_4NCH_3$, $C_6H_5NHCH_3$, and $C_6H_5N(CH_3)_2$, parts a through l, respectively, with Xe as a function of collision energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). Data are shown for a Xe pressure of 0.2 mTorr.

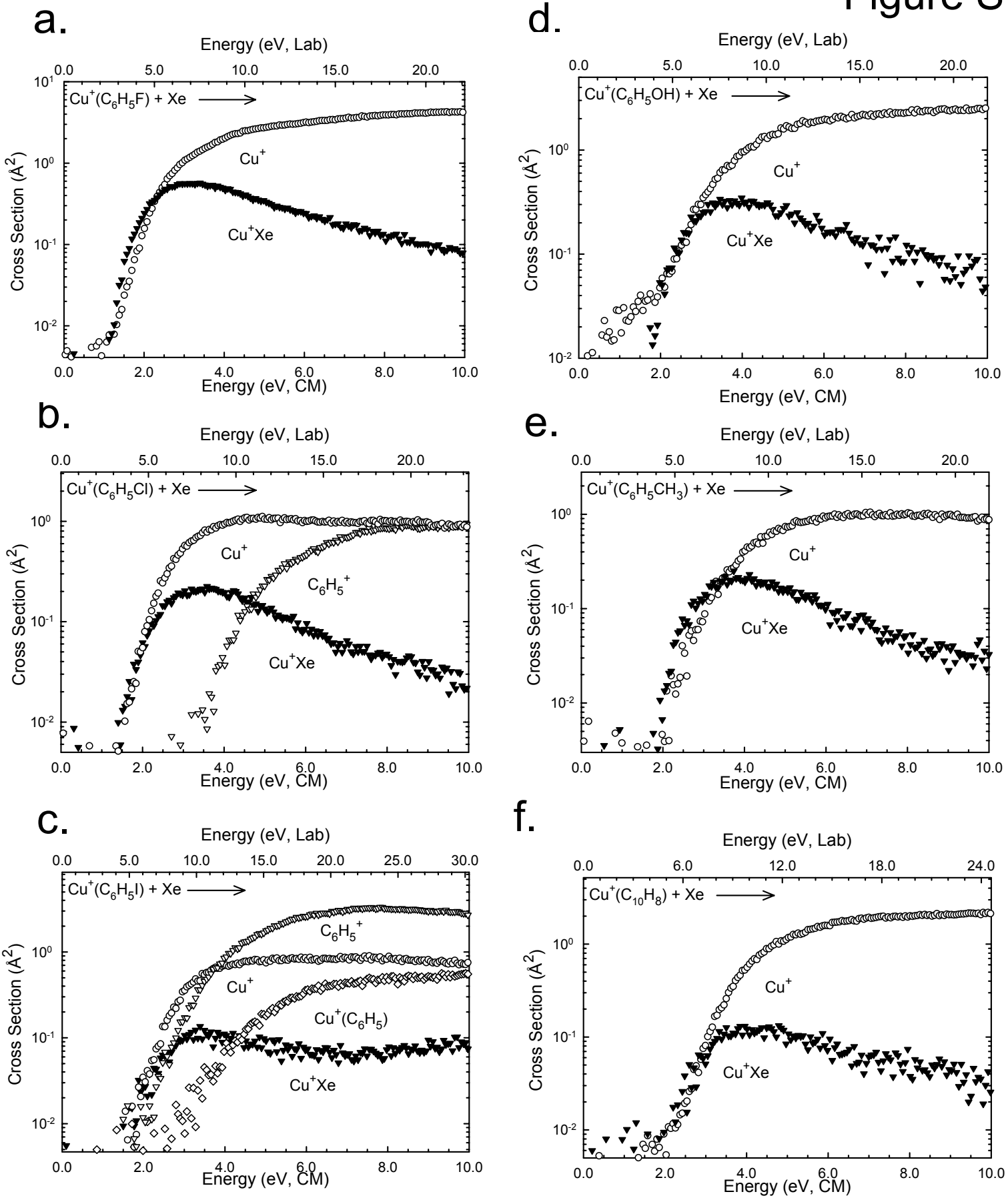
Figure S2. Zero-pressure-extrapolated cross sections for independent analysis of the collision-induced dissociation product cross sections of Cu^+(π-ligand) complexes with Xe in the threshold region as a function of kinetic energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). Data are shown for fits to the Cu^+ product cross sections for π-ligand = C_6H_5F, C_6H_5Cl, C_6H_5Br, C_6H_5I, C_6H_5OH, $C_6H_5CH_3$, $C_{10}H_8$, $C_6H_5OCH_3$, C_4H_5N, C_8H_7N, $C_6H_5NH_2$, $C_4H_4NCH_3$, and $C_6H_5NHCH_3$, parts a through m, respectively, to the π-ligand$^+$ product cross sections for π-ligand = $C_6H_5N(CH_3)_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$, C_8H_7N, $C_4H_4NCH_3$, parts n through r, respectively, and to the fragmentation product cross sections, π-ligand = C_6H_5Cl, C_6H_5Br, C_6H_5I, parts s to v. The solid line shows the best fit to the data using eq. (1) convoluted over the neutral and ion kinetic and internal energy distributions. The dotted line shows the model cross sections in the absence of experimental kinetic energy broadening for reactants with an internal energy corresponding to 0 K.

Figure S3. Zero-pressure-extrapolated cross sections for competitive analyses of the collision-induced dissociation product cross sections of Cu^+(π-ligand) complexes with Xe in the threshold region as a function of kinetic energy in the center-of-mass frame (lower *x*-axis) and laboratory frame (upper *x*-axis). Data are shown for π-ligand = $C_4H_4NCH_3$, C_6H_5Cl, C_6H_5I, $C_6H_5NH_2$, $C_6H_5NHCH_3$, parts a through e. The solid line shows the best fit to the data using eq. (2) convoluted over the neutral and ion kinetic and internal energy distributions. The dotted line shows the model cross sections in the absence of experimental kinetic energy broadening for reactants with an internal energy corresponding to 0 K.

Figure S4. B3LYP/6-311G(d,p) optimized geometries and B3LYP/6-311+G(3df,2p) relative stabilities of Cu^+(π-ligand) complexes. Two views of each structure are shown.

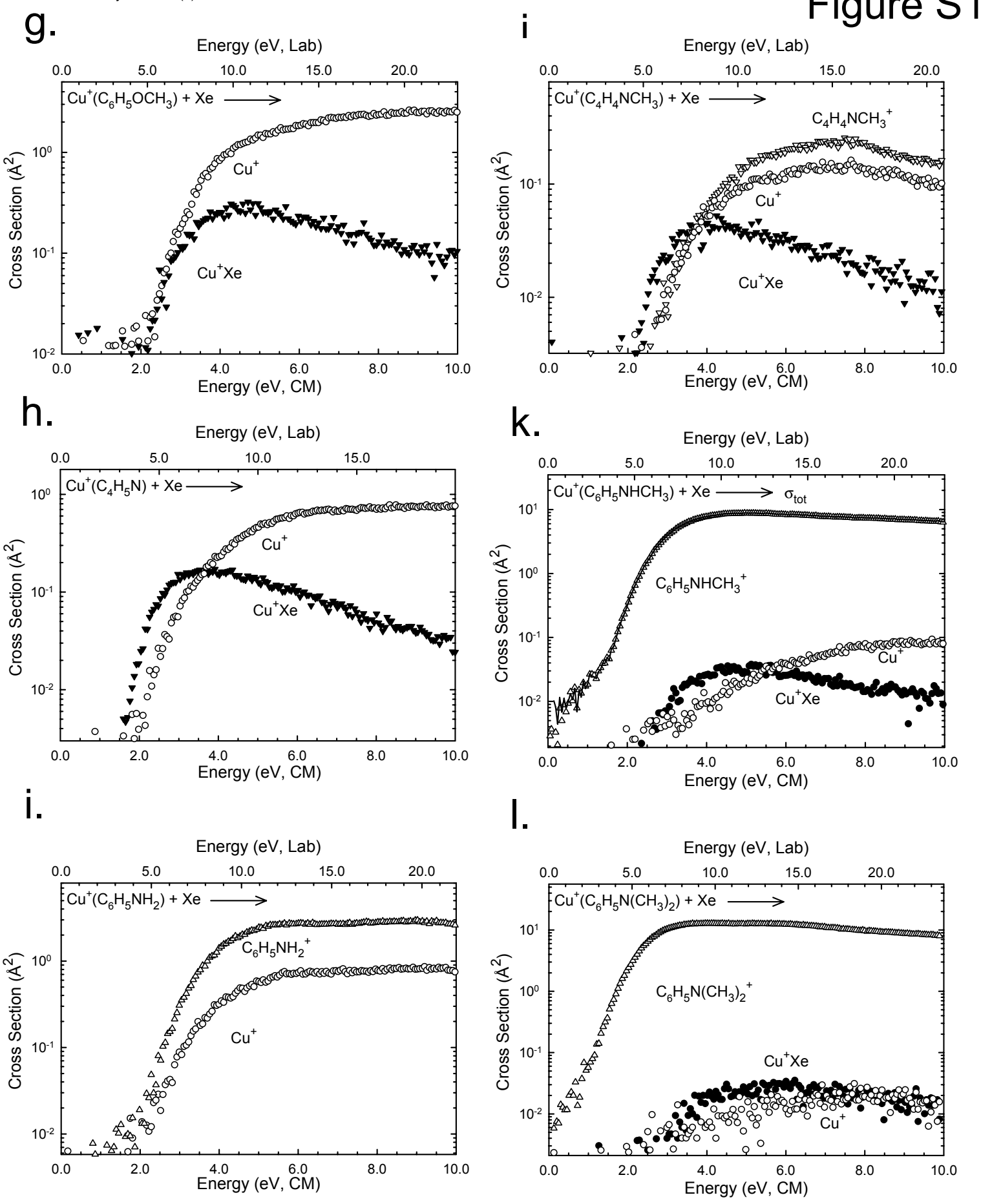
Electronic Supplementary Material for PCCP

Figure S1.



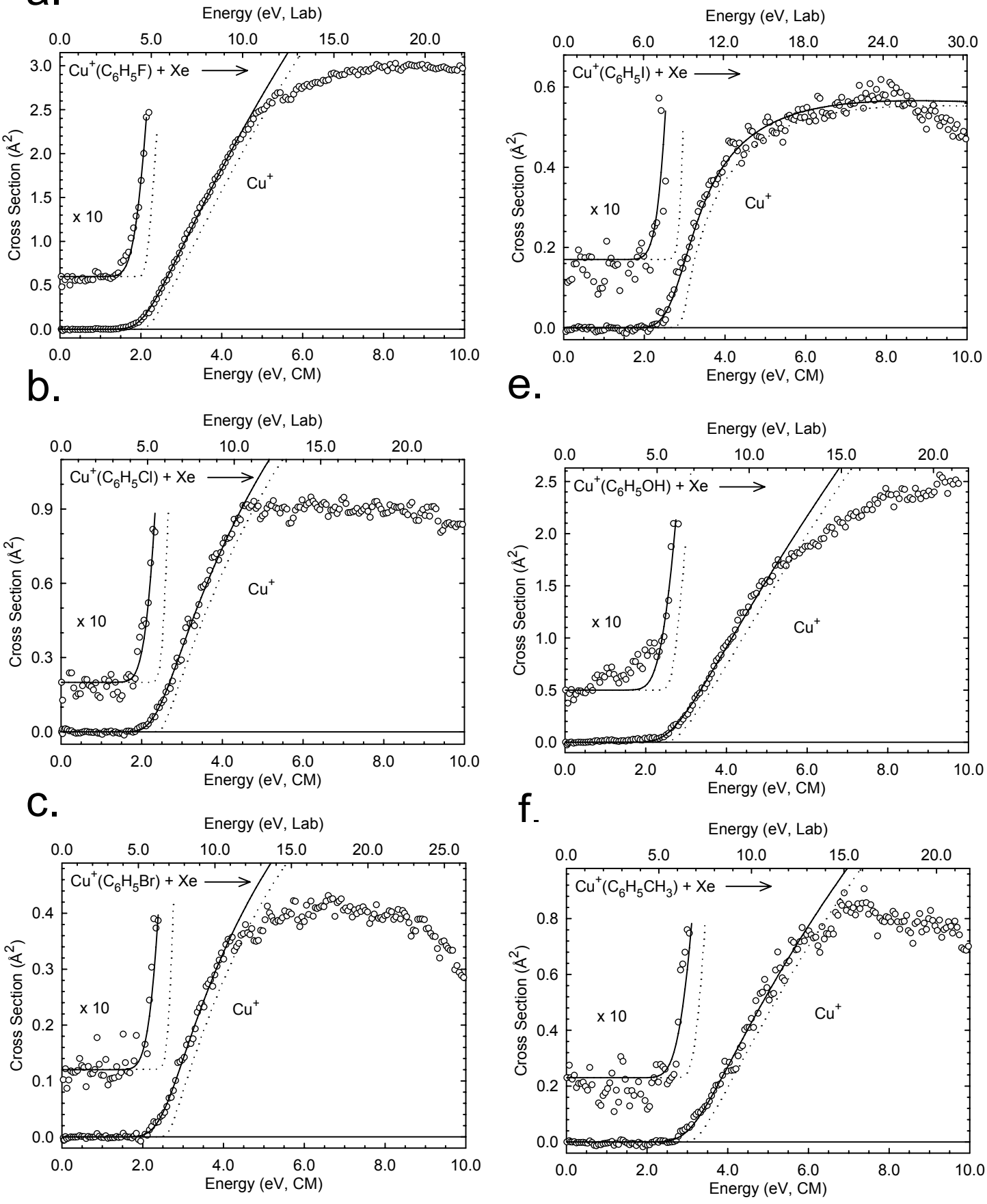
Electronic Supplementary Material for PCCP

Figure S1.



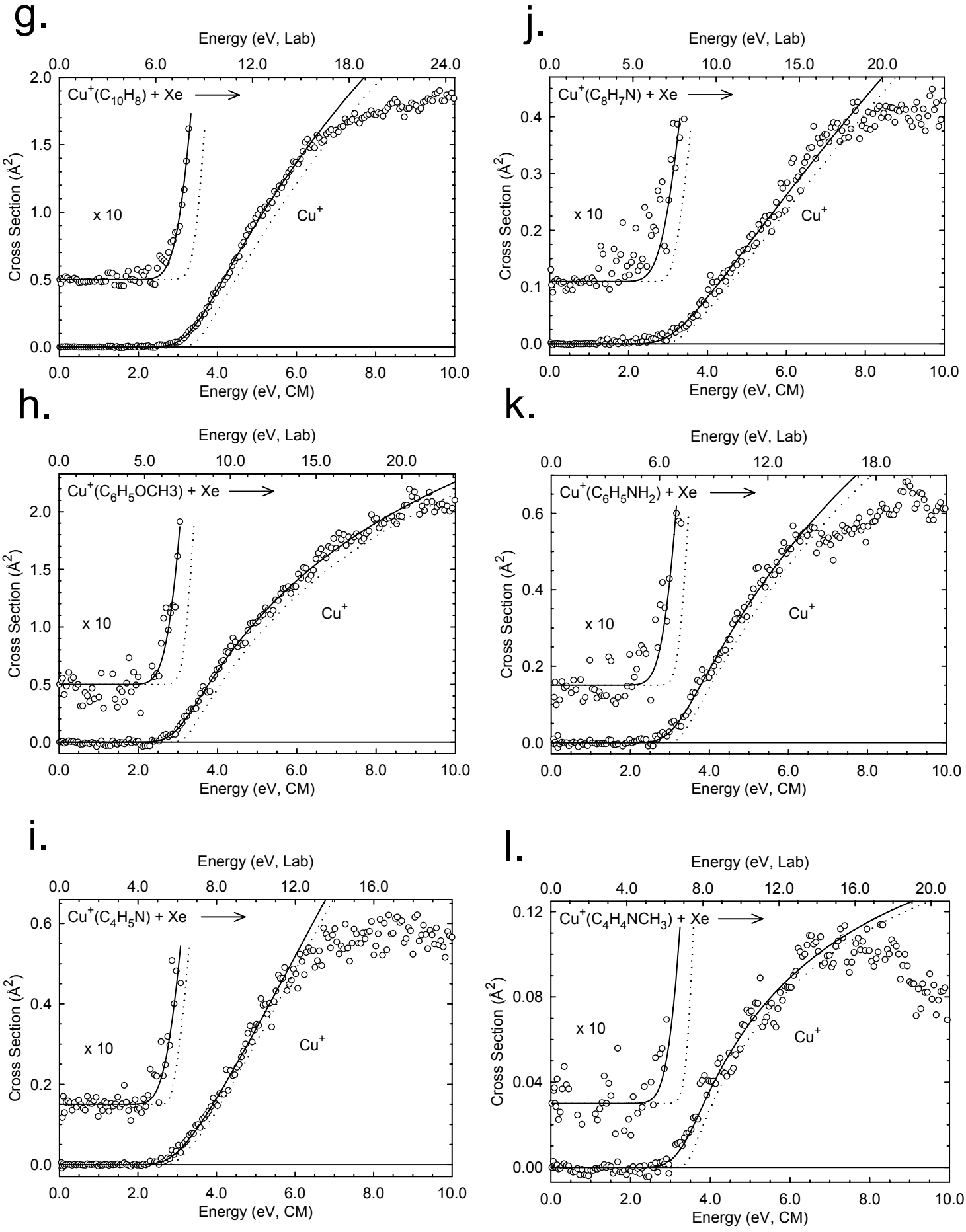
Electronic Supplementary Material for PCCP

Figure S2.



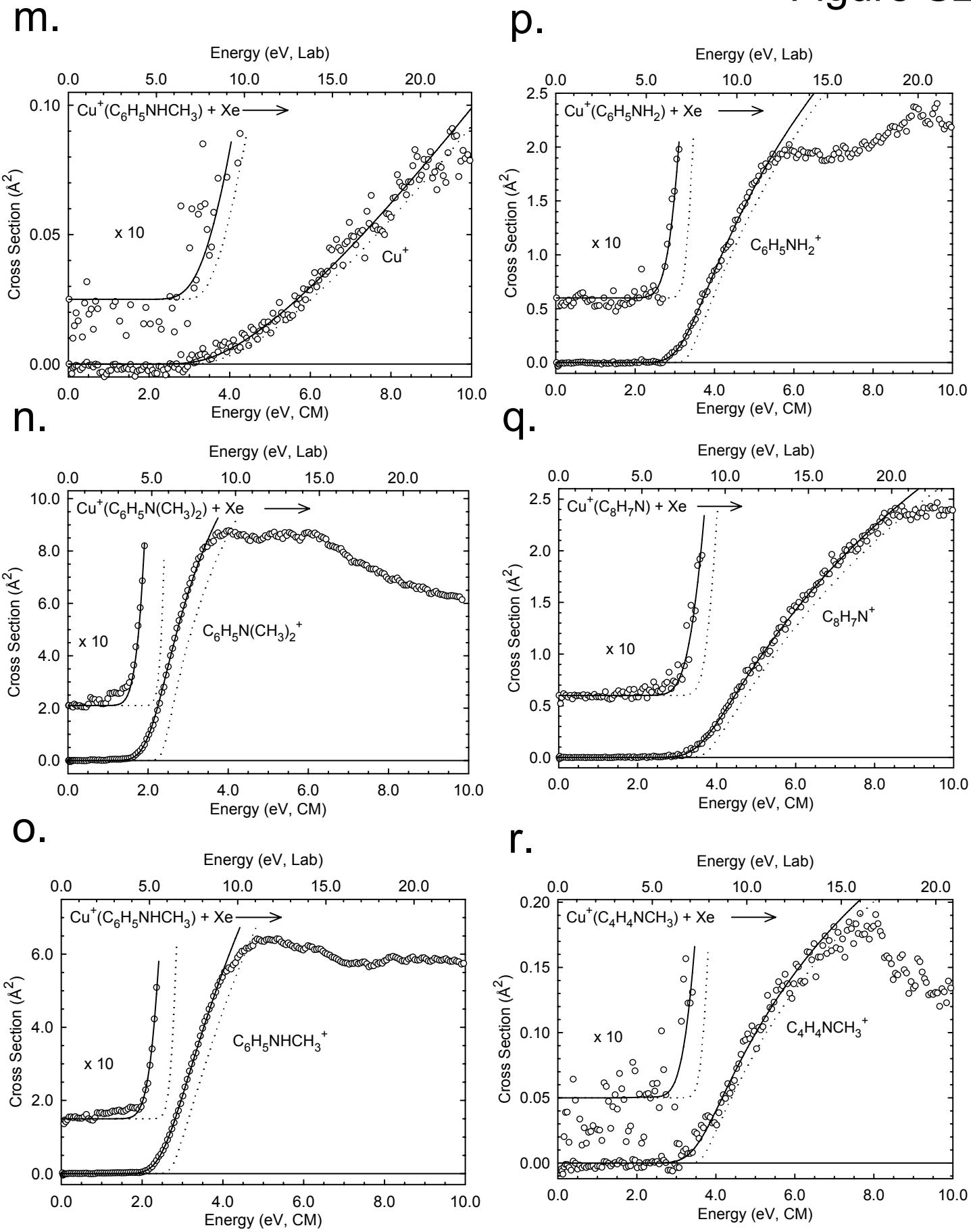
Electronic Supplementary Material for PCCP

Figure S2.



Electronic Supplementary Material for PCCP

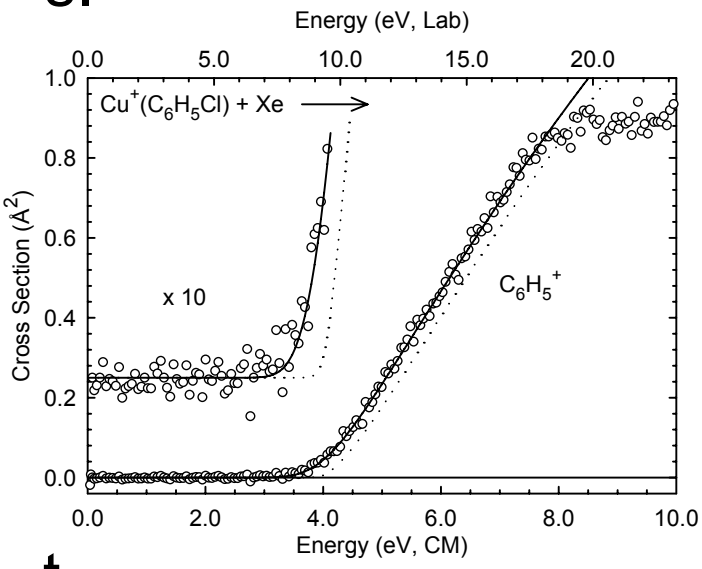
Figure S2.



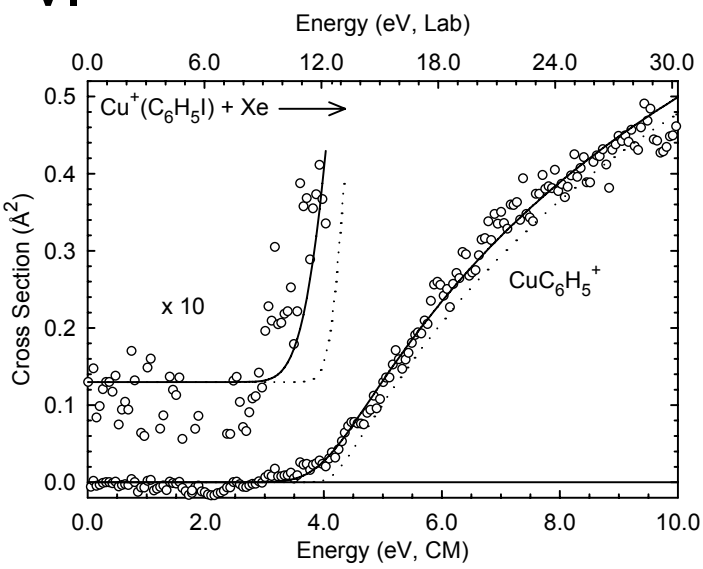
Electronic Supplementary Material for PCCP

Figure S2.

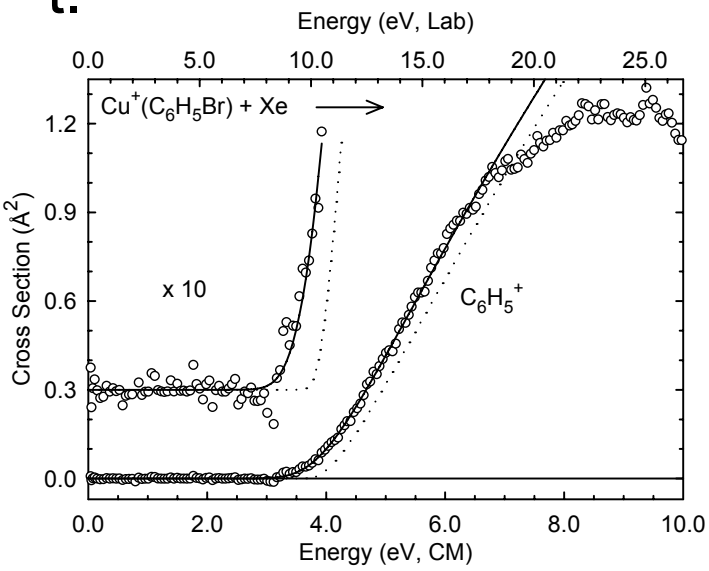
s.



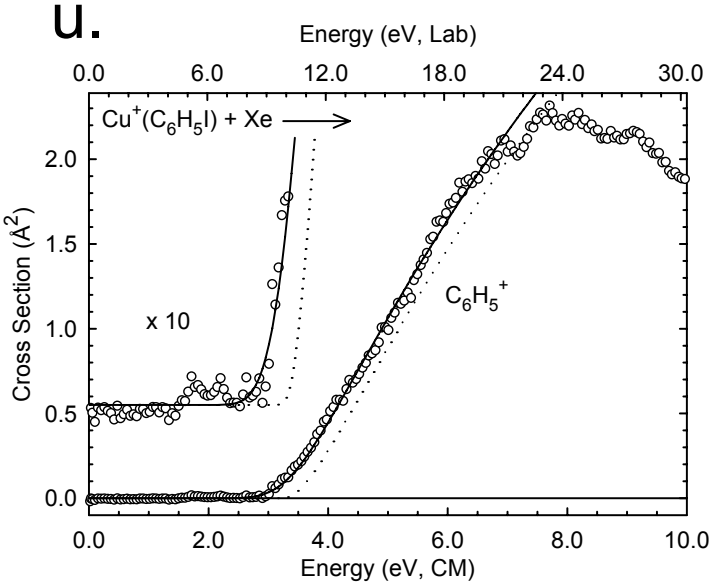
v.



t.

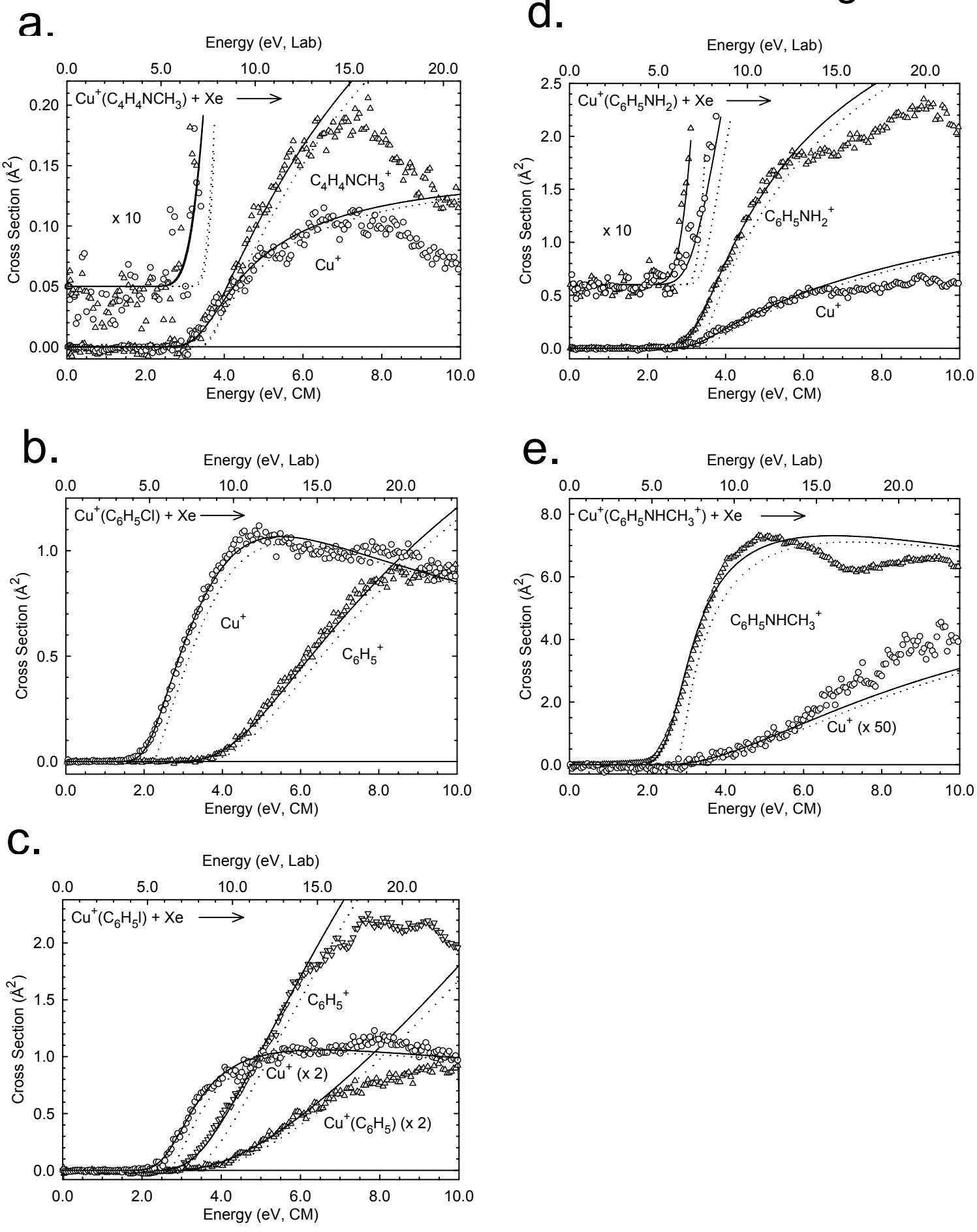


u.



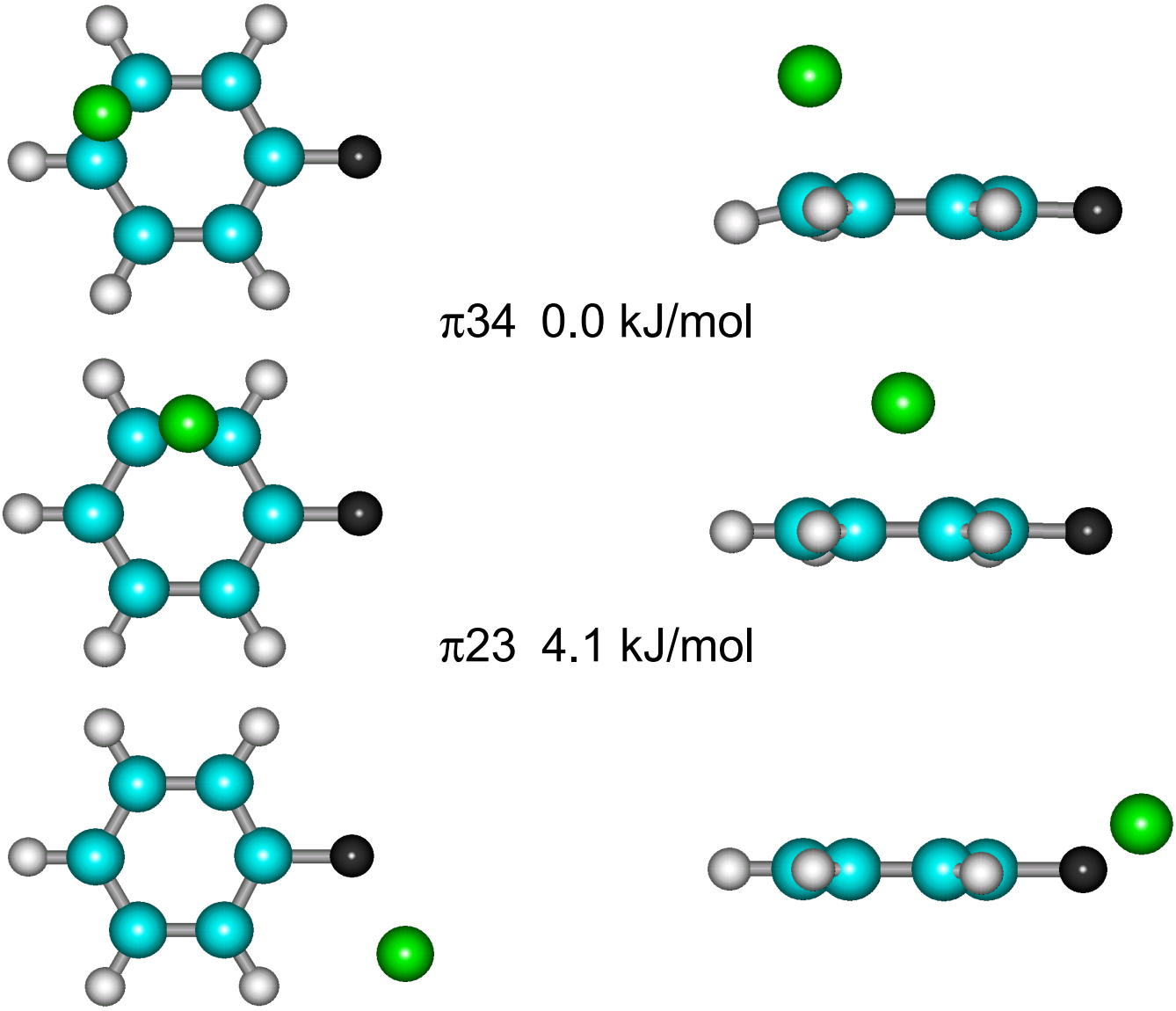
Electronic Supplementary Material for PCCP

Figure S3.



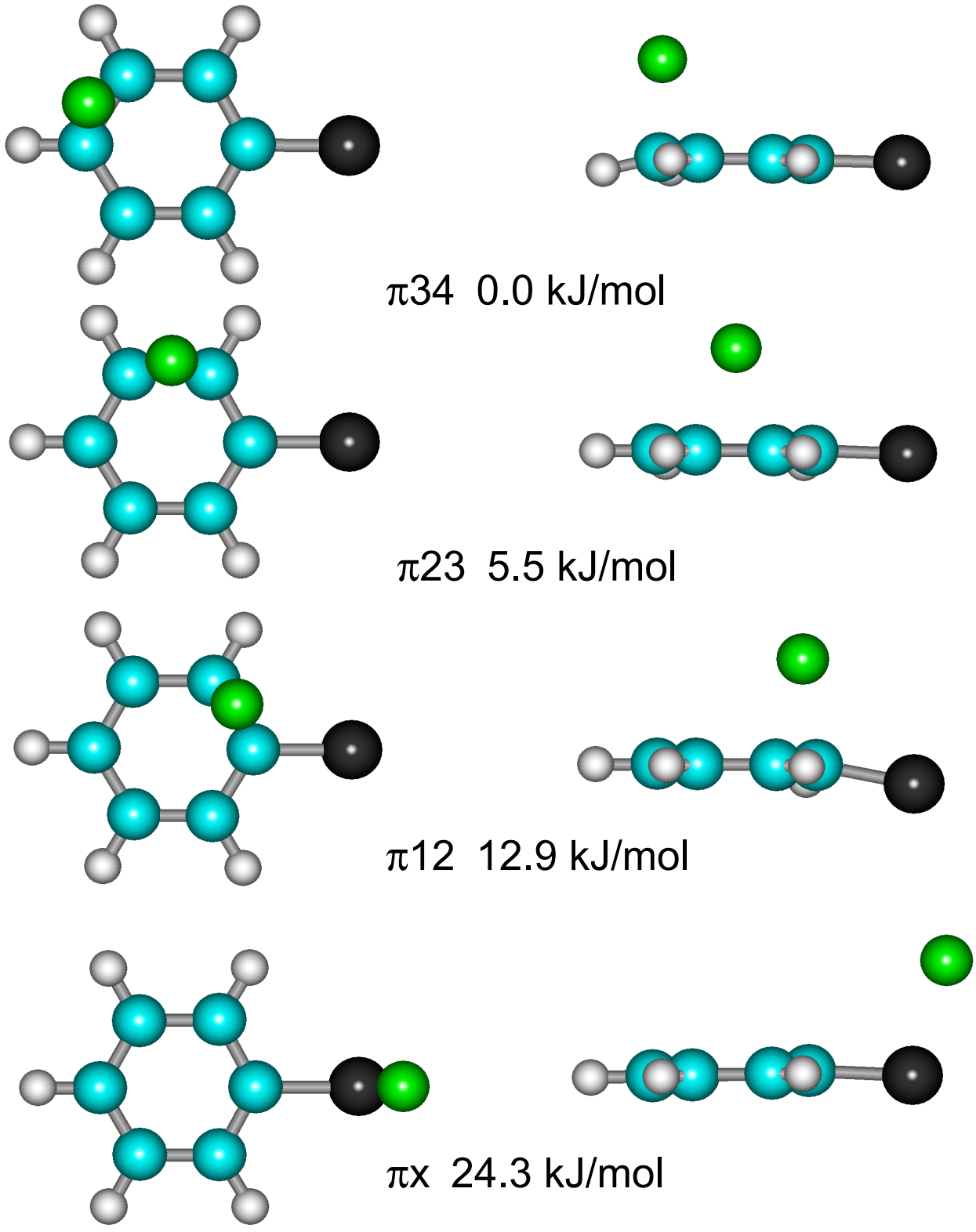
Electronic Supplementary Material for PCCP

Figure S4.



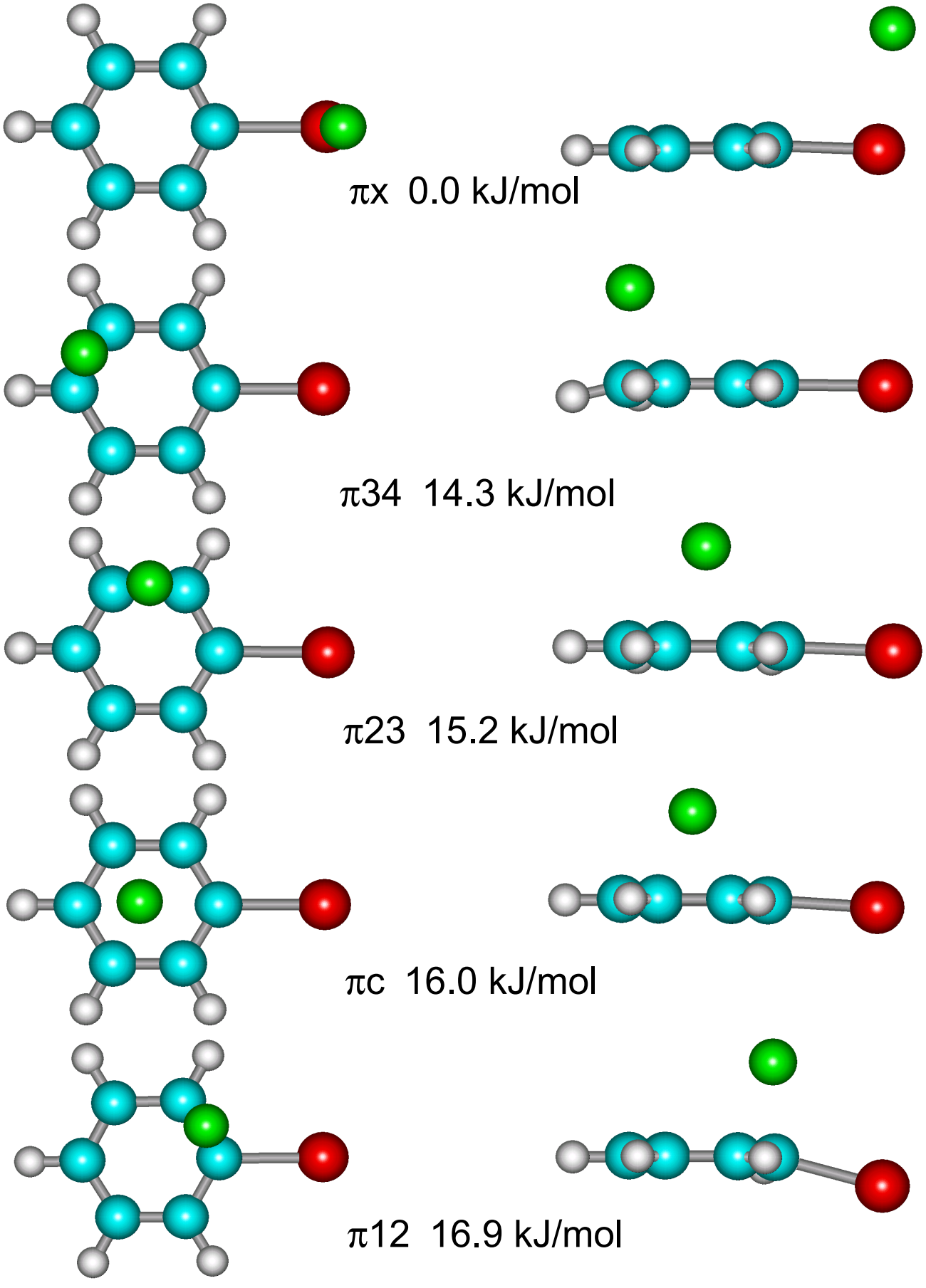
Electronic Supplementary Material for PCCP

Figure S4.



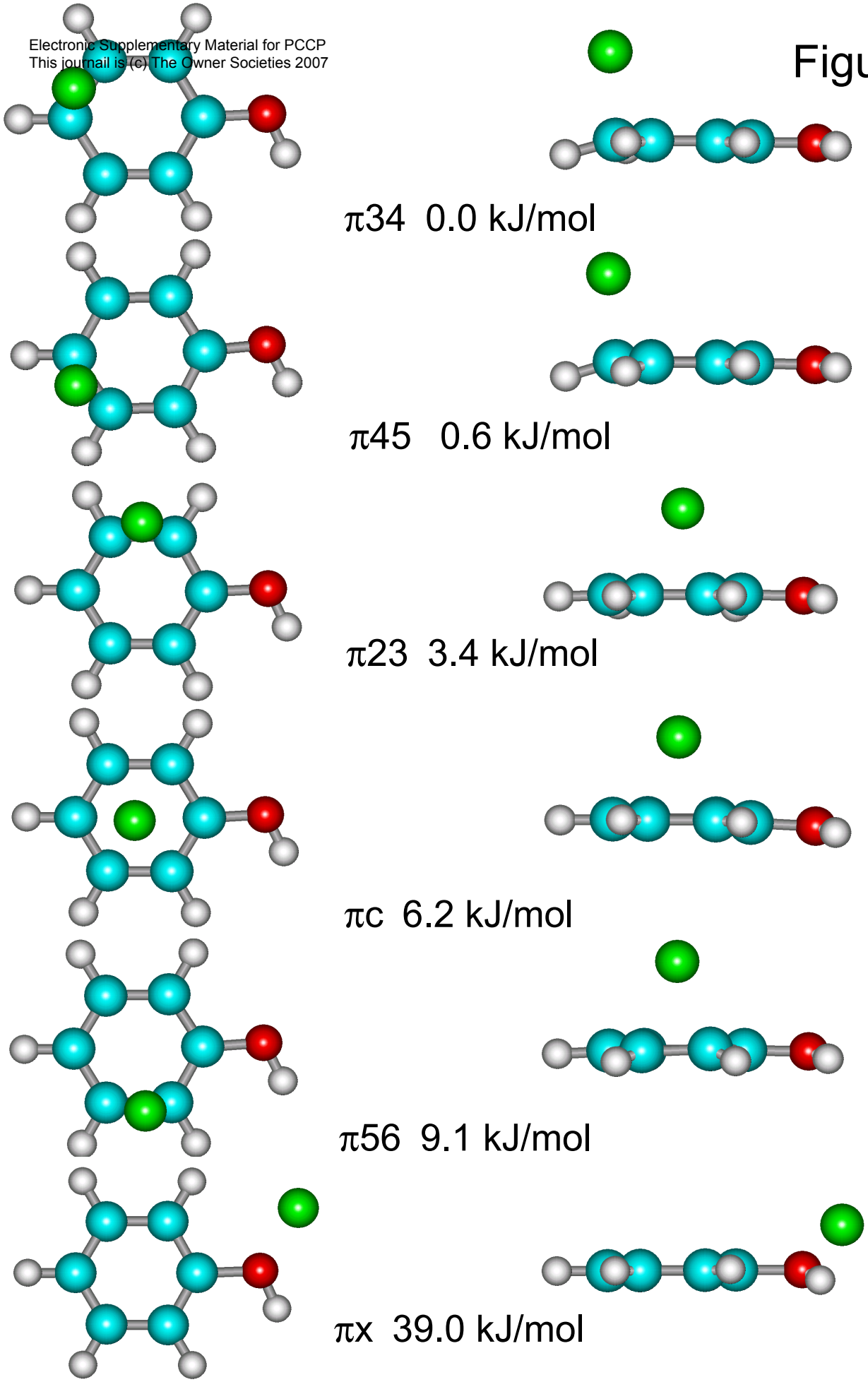
Electronic Supplementary Material for PCCP

Figure S4.



$Cu^{+}(C_6H_5I)$

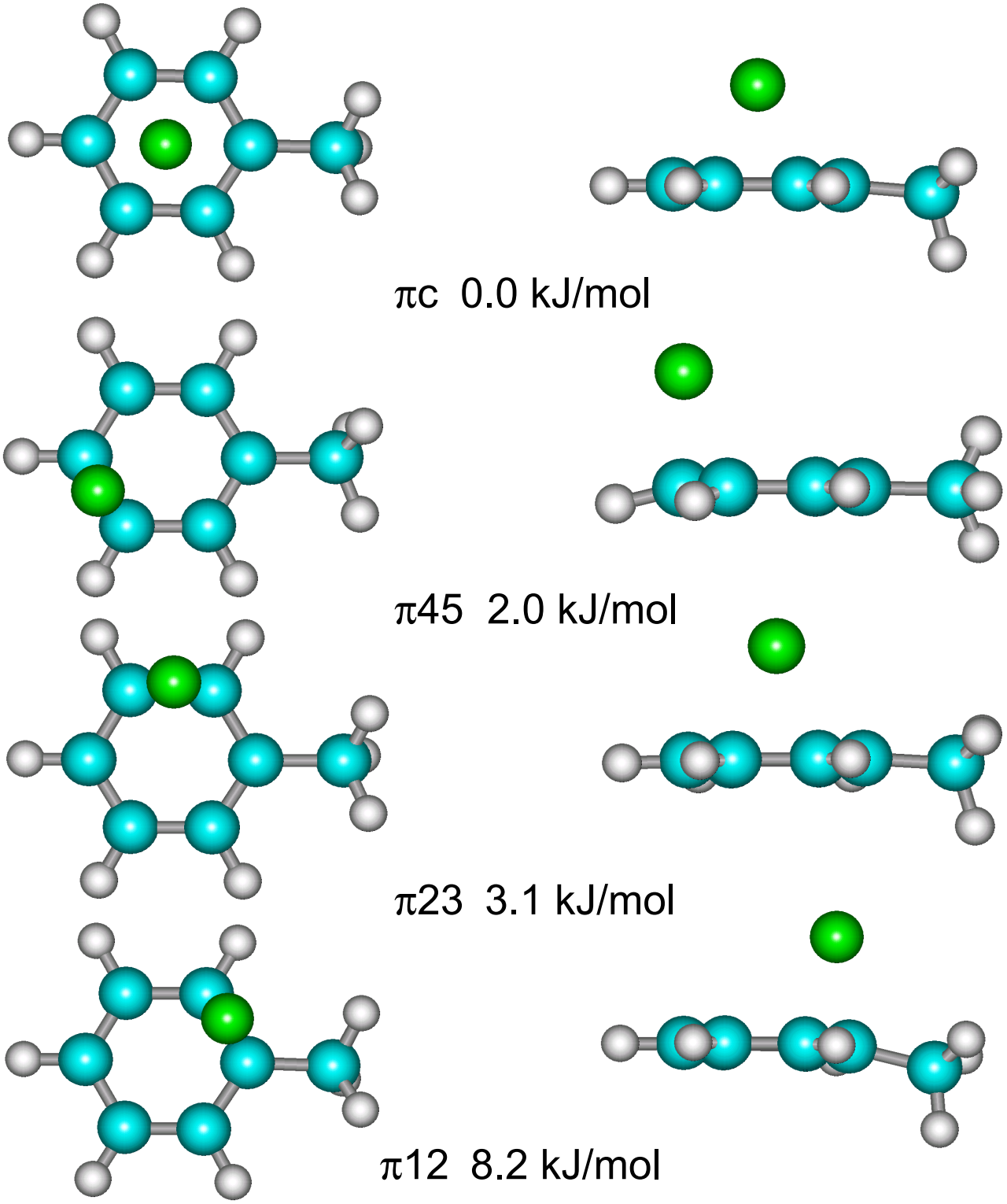
Figure S4.



$Cu^+(C_6H_5OH)$

Electronic Supplementary Material for PCCP

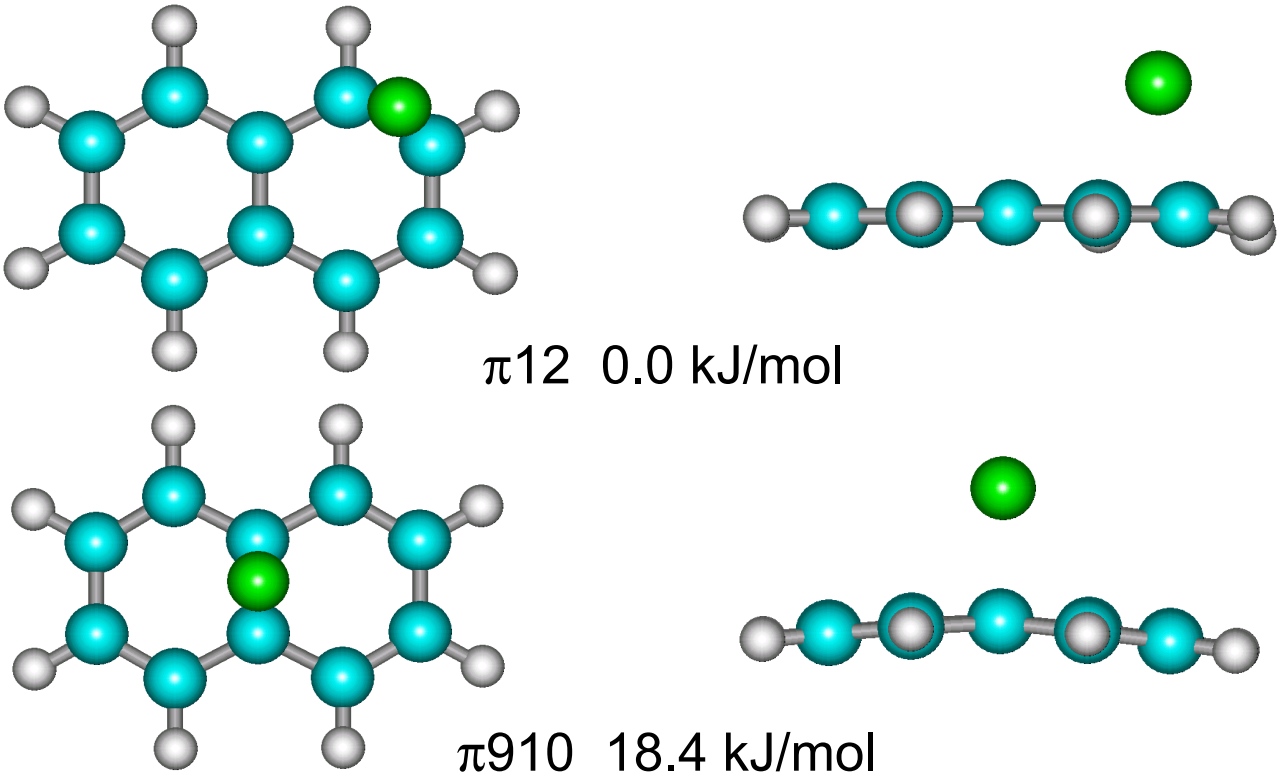
Figure S4.



$Cu^+(C_6H_5CH_3)$

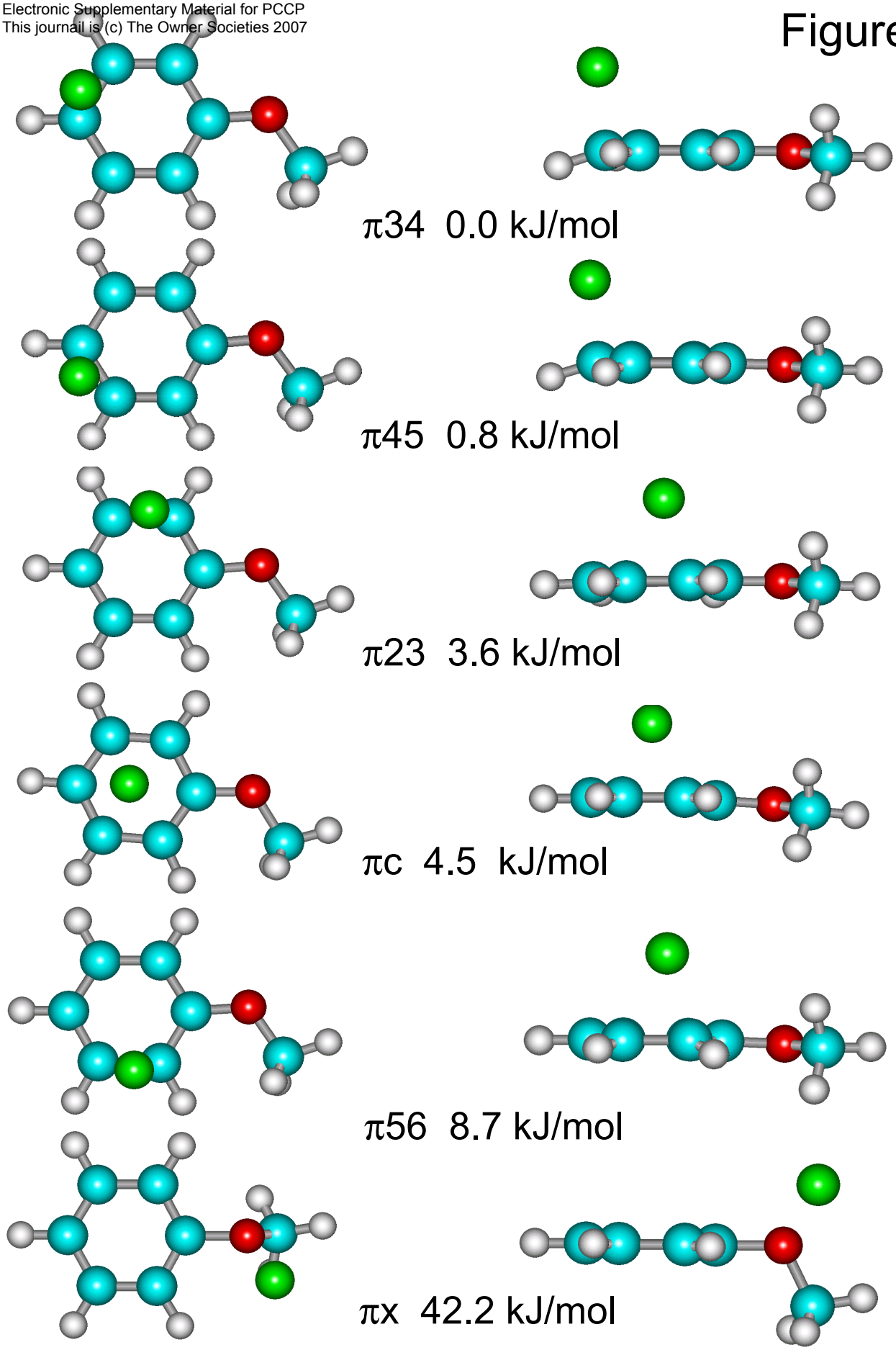
Electronic Supplementary Material for PCCP

Figure S4.



$Cu^{+}(C_{10}H_{8})$

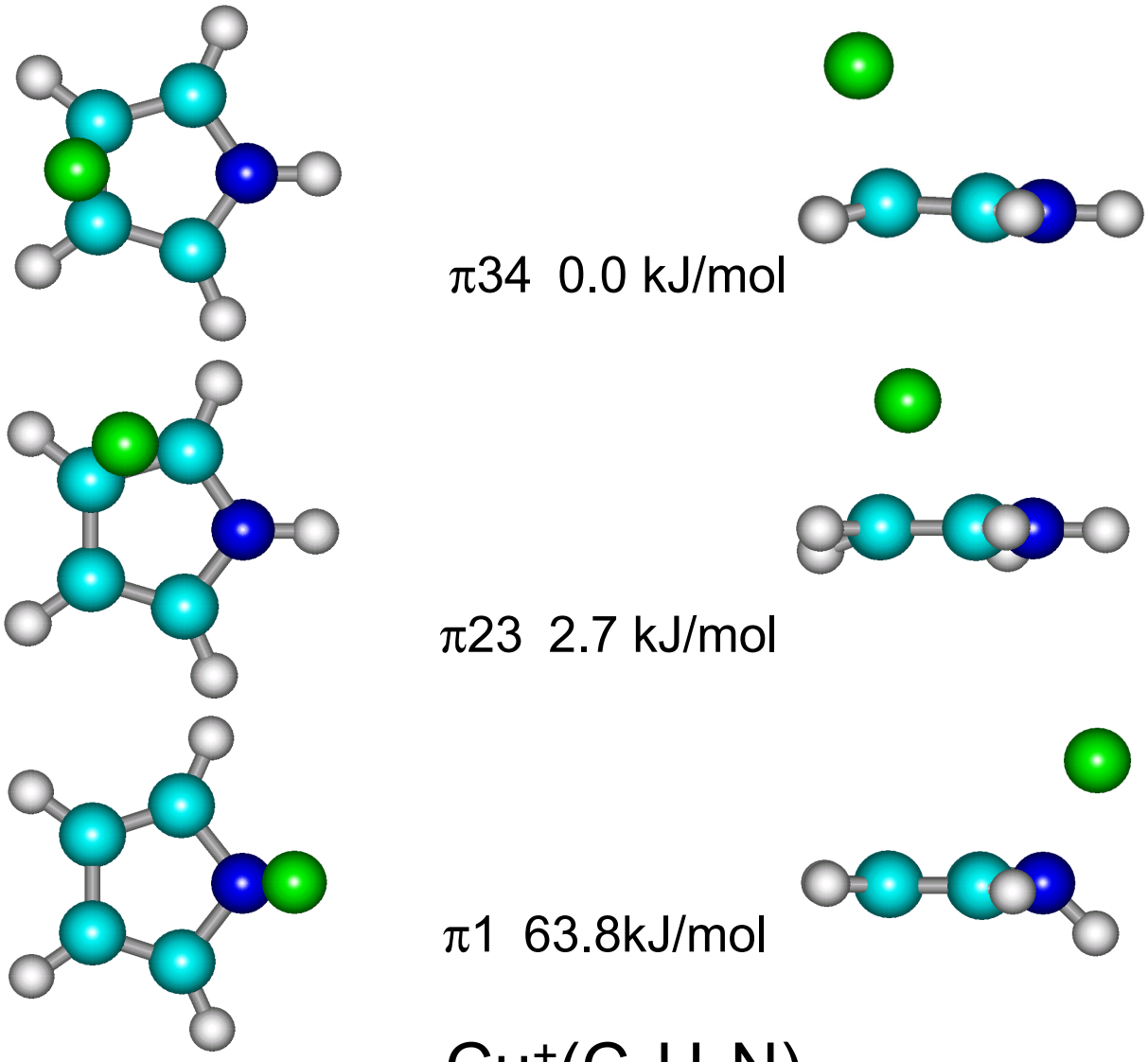
Figure S4.



$Cu^+(C_6H_5OCH_3)$

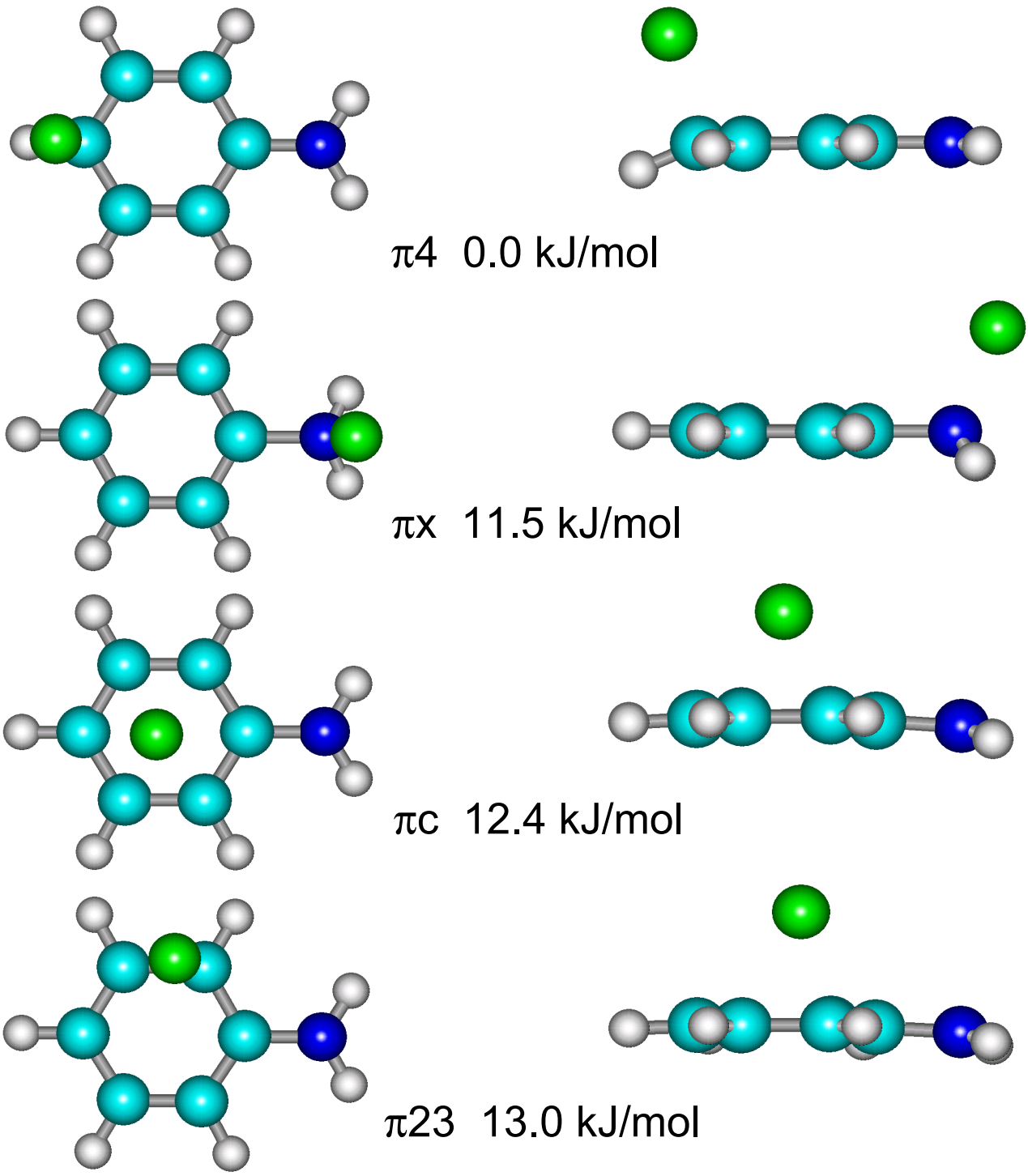
Electronic Supplementary Material for PCCP

Figure S4.



Electronic Supplementary Material for PCCP

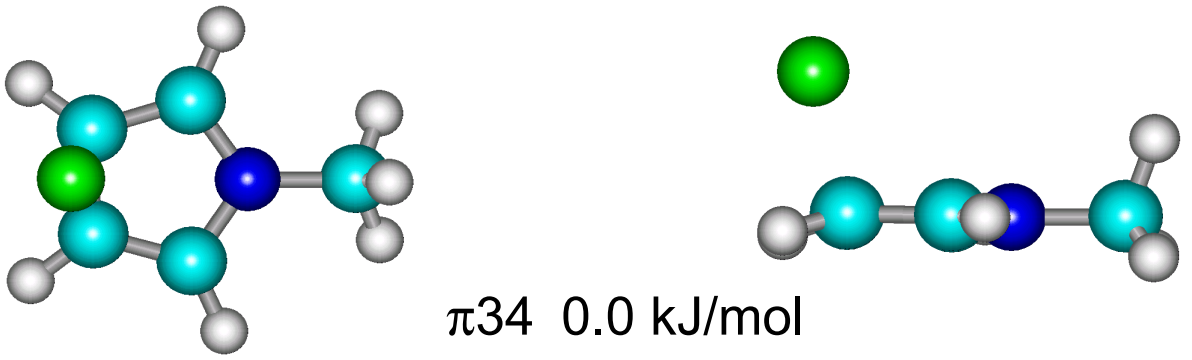
Figure S4.



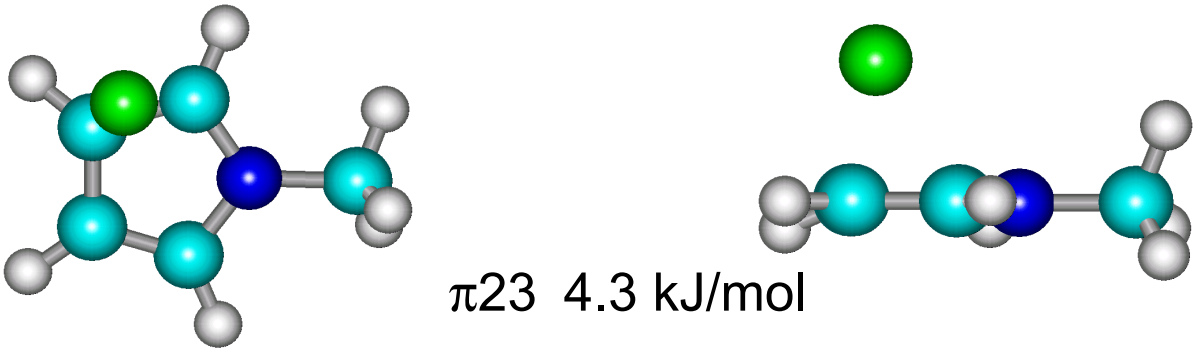
$Cu^+(C_6H_5NH_2)$

Electronic Supplementary Material for PCCP

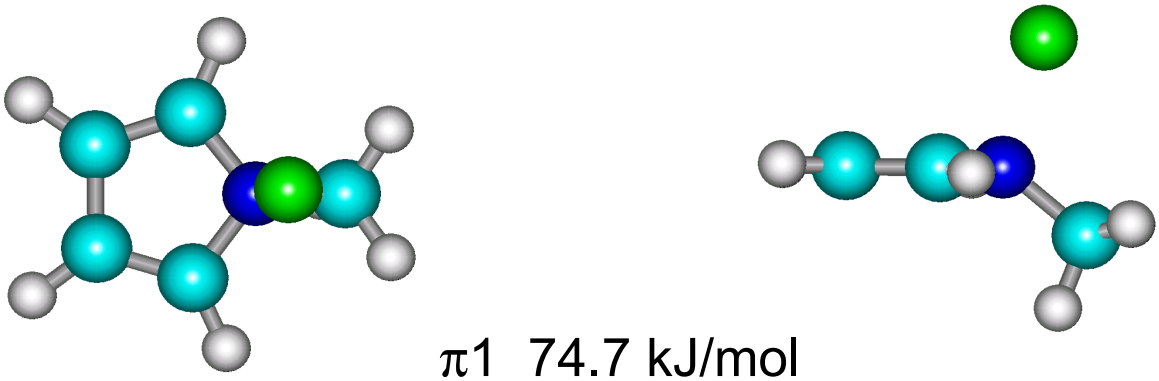
Figure S4.



π34 0.0 kJ/mol



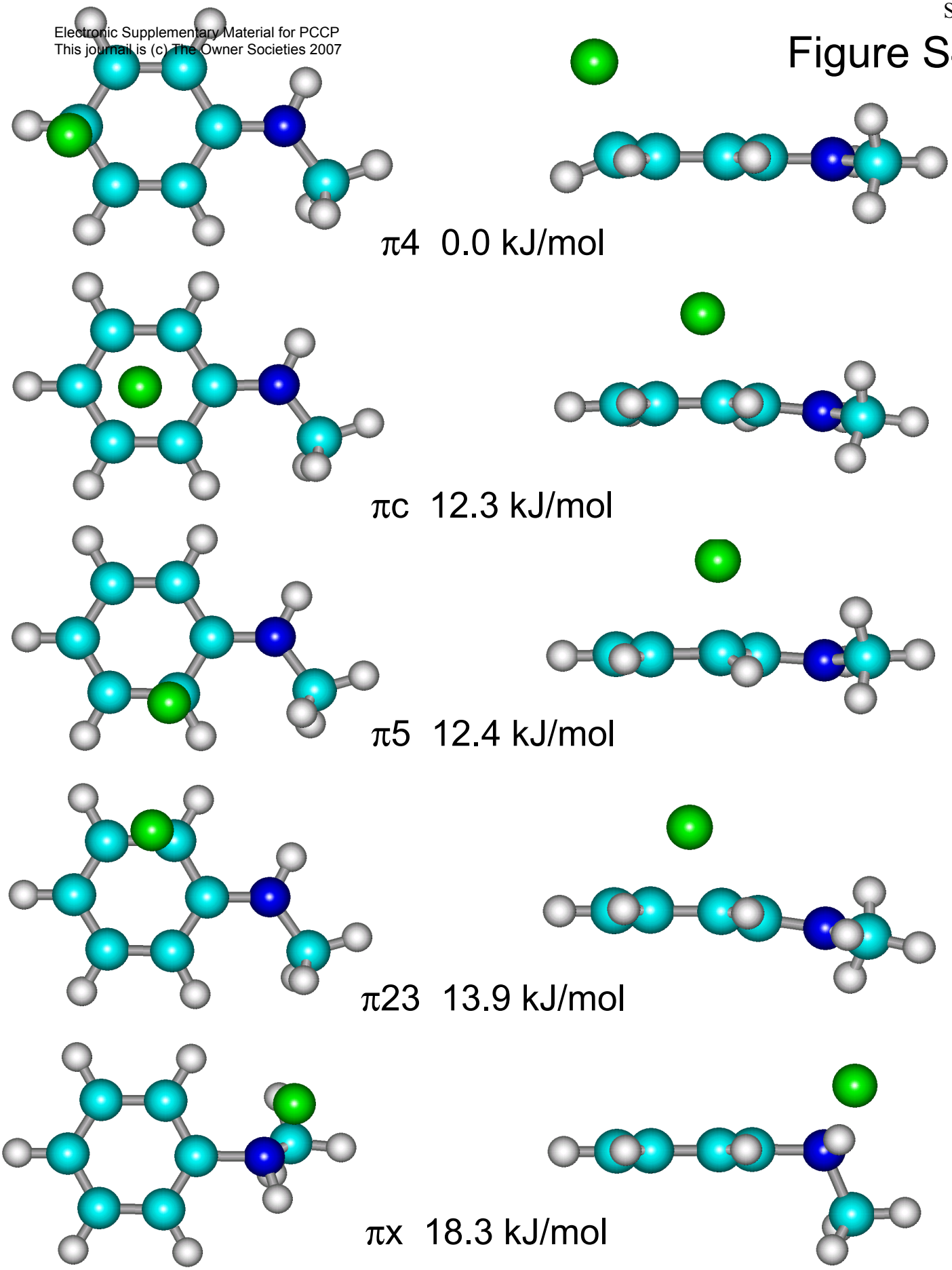
π23 4.3 kJ/mol



π1 74.7 kJ/mol

$Cu^{+}(C_4H_4NCH_3)$

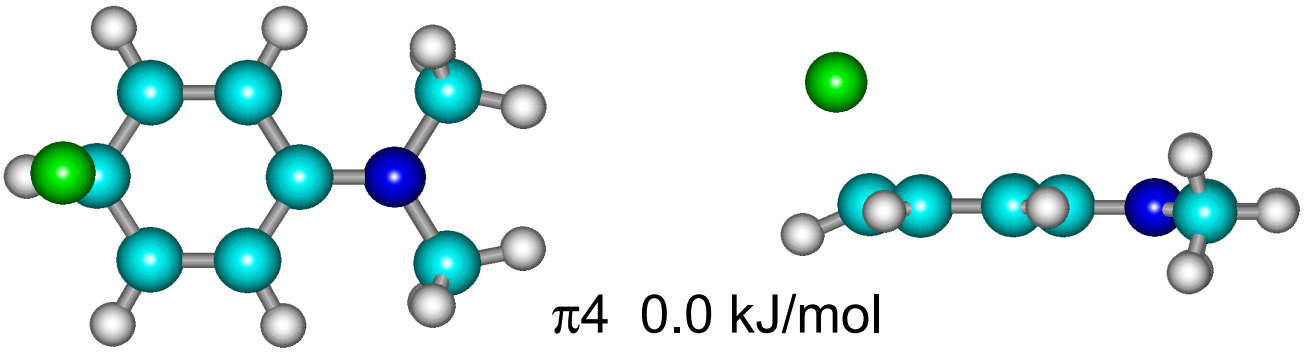
Figure S4.



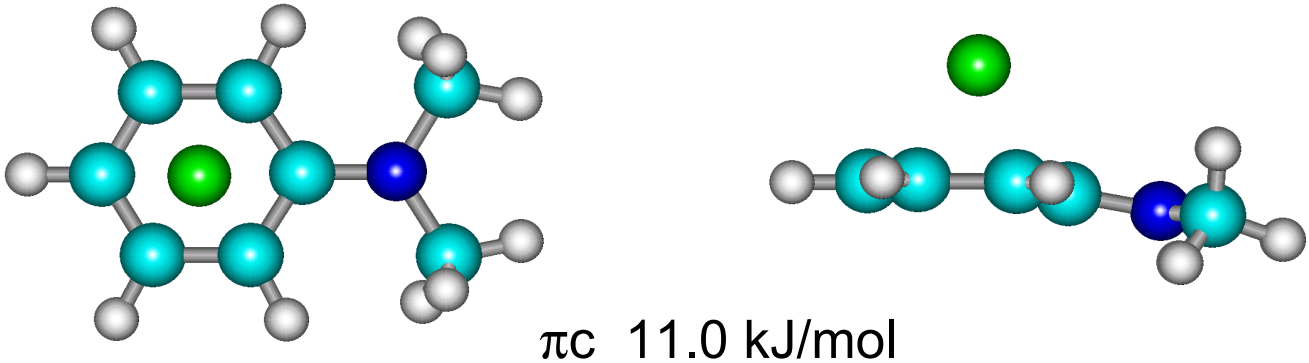
$Cu^+(C_6H_5NHCH_3)$

Electronic Supplementary Material for PCCP

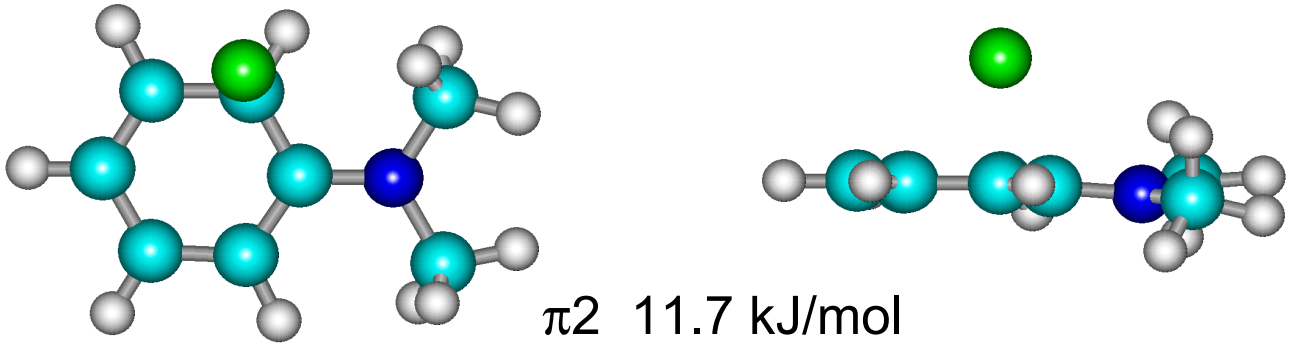
Figure S4.



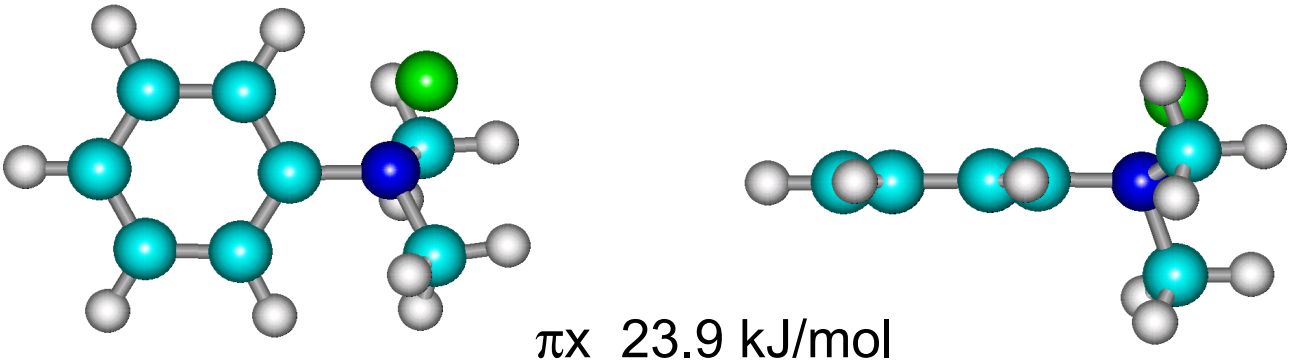
π4 0.0 kJ/mol



πc 11.0 kJ/mol



π2 11.7 kJ/mol



πx 23.9 kJ/mol

$Cu^{+}(C_6H_5N(CH_3)_2$