SUPPLEMENTARY INFORMATION

Calculated wave numbers, molecular conformation, calculated spectra, optimized molecular structures, experimental and calculated spectra, and polarized spectra are available as supplementary data.

Table S1: Comparison of the calculated harmonic wavenumbers (ω, cm^{-1}), relative infrared intensities (A, %), relative Raman scattering activities (S, %), Raman depolarization ratios for plane (P) and unpolarized (U) incident light, reduced mass (μ, amu), and force constant (mdyn·$Å^{-1}$, f) obtained in *trans*-AZ at the B3LYP/6-31G(d,p) level. Two wavenumbers appear for each ring mode. Of these wavenumbers that with the highest IR intensity is shown in bold type, and that with the highest Raman intensity in *italic* type.

Calculated values *trans*-AZ										Scaled *trans*-AZ		Exp.[a]	Characterization[b]
B3LYP/6-31G(d,p)			B3LYP/6-311+G(2d,p)							B3LYP/6-31G(d,p)	B3LYP/6-311+G(2d,p)		
ω	A	S	ω	A	S	μ	f	P	U	ν	ν		
24	0	0	17	0	0	3.7	0.0	0.70	0.82	45	35		τ(torsion)
62	2	0	61	1	0	5.4	0.01	0.57	0.73	81	77		Butterfly
84	4	0	84	2	0	4.7	0.02	0.75	0.86	102	99	86(2)	Cogwheel
108	0	0	99	0	0	6.2	0.04	0.75	0.86	125	114		Tilting
223	0	0	223	0	0	5.6	0.17	0.53	0.69	235	233	219(0)	Shearing
260	0	0	252	0	0	6.3	0.23	0.75	0.86	270	261	251(0)	γ(N=N) + tilting
307, **531**	46	0	*306*, **529**	31	0	4.8	0.27	0.69	0.81	315, **529**	*313*, **527**	362	15, δ(C-N) + δ(N=N)
308, 492	2	0	*307*, 485	0	0	4.9	0.27	0.69	0.82	316, 492	*314*, 485		16b, γ(CCC)
419, 422	0	0	416, *421*	0	0	2.9	0.31	0.75	0.86	422, 425	419, *423*	409(0)	16a, γ(CCC)
546, *626*	11	1	549, *628*	7	1	6.5	1.51	0.62	0.77	543, *619*	547, *622*	523(13)	6b, δCCC)
561, 699	13	0	558, *693*	19	0	2.2	0.61	0.75	0.86	557, *689*	555, *685*	544(18)	4, γ(CCC)
632, *684*	2	0	634, *686*	0	0	6.6	1.83	0.55	0.71	625, *675*	628, *678*	617(1)	6a, δ(CCC)
706, 781	100	0	700, *772*	100	0	1.6	0.55	0.75	0.86	696, 767	692, *761*	690(100)	11, γ(CH)
800	100	0	794	81	0	1.9	0.72	0.14	0.24	786	782	774(79)	10b, γ(C-N, C-H) + δ(N=N)
839	2	0	836	0	0	6.1	2.50	0.34	0.51	823	822		1, δ(CCC) + δ(N=N)
864, *865*	0	0	851, *852*	0	0	1.2	0.53	0.75	0.86	847, *848*	837, *838*	834(1)	10a, γ(C-H)
940	0	0	937	0	0	6.9	3.55	0.65	0.78	919	920	913(1)	δ(N=N) + 18b, δ(C-N)
950, 955	15	0	*941*, 948	11	0	1.4	0.73	0.75	0.86	*929*, 933	*923*, 930	926(5)	17b, γ(C-H)
989, 989	0	0	985, 985	0	0	1.4	0.78	0.75	0.86	966, 966	966, 966	967(1)	17a, γ(C-H)
1008, 1008	2	0	1000, 1000	0	0	1.3	0.76	0.75	0.86	984, 984	980, 980	983(1)	5, γ(C-H)
1016, *1017*	6	8	1019, 1019	2	16	6.2	3.81	0.23	0.38	992, *993*	998, 998	1003(14)	12, δ(CCC)
1045, 1045	19	1	1039, 1039	18	0	2.1	1.32	0.03	0.07	1019, 1019	1018, 1018	1021(6)	18a, δ(C-H)
1100, 1104	20	1	*1096*, 1100	14	1	1.5	1.08	0.20	0.33	*1072*, 1076	*1073*, 1076	1070(8)	18b, δ(C-H)
1167, 1178	63	74	*1158*, 1176	38	100	2.2	1.74	0.30	0.46	*1136*, 1146	*1132*, 1149	1146(85)	9a, δ(C-H)
1185, *1186*	0	2	1182, 1182	0	2	1.1	0.94	0.65	0.79	1153, *1154*	1155, 1155	1155(10)	9b, δ(C-H)
1213, 1261	44	31	*1205*, 1248	21	21	1.6	1.40	0.33	0.49	*1180*, 1225	*1177*, 1219	1184(32)	7a, ν(C-N, C-H)
1336, *1343*	4	9	1333, *1341*	7	10	3.6	3.78	0.36	0.53	1297, *1304*	1300, *1308*	1307(3)	3, δ(C-H)
1367, *1369*	15	3	*1347*, 1348	5	5	1.7	1.87	0.38	0.55	1327, *1329*	*1314*, 1315	1315(11)	14, ν(C=C)
1487, 1494	22	61	*1476*, 1488	13	92	2.7	3.45	0.36	0.53	*1441*, 1448	*1438*, 1449	1454(17)	19b, ν(C-H, C=C)
1515, 1527	19	35	*1506*, 1520	13	39	2.2	3.00	0.36	0.53	*1468*, 1479	*1467*, 1480	1473(50)	19a, ν(C-H, C=C)
1559	0	100	1542	0	80	4.4	6.20	0.36	0.53	1510	1501	1443(100)	ν(N=N)+ 19a, ν(C-H, C=C)
1636, *1642*	9	0	1618, *1624*	5	0	6.0	9.28	0.18	0.30	1583, *1589*	1574, *1580*	1586(5)	8b, ν(C=C)
1654, *1657*	6	20	1634, *1638*	4	21	5.9	9.30	0.44	0.61	1601, *1603*	1590, *1594*	1595(31)	8a, ν(C=C) + ν(N=N)
3182, 3182	6	3	3163, 3163	2	3	1.1	6.40	0.58	0.73	3059, 3059	3060, 3060	3044(36)	13, ν(C-H)
3192, 3192	28	7	3173, 3173	18	8	1.1	6.46	0.73	0.84	3068, 3068	3070, 3070	3060(36)	7b?, ν(C-H)
3203, 3203	100	15	3184, 3184	41	13	1.1	6.52	0.32	0.49	3079, 3079	3080, 3080	3066(36)	20a, ν(C-H)
3213, *3214*	63	14	3193, 3193	34	16	1.1	6.58	0.12	0.21	3088, *3089*	3089, 3089	3073(36)	2, ν(C-H)
3229, 3229	15	4	3207, 3207	9	4	1.1	6.62	0.15	0.26	3104, 3104	3102, 3102	3085(36)	20b?, ν(C-H)

[a]Experimental values from ref. [35b,36b-d]. In parentheses appear the intensity. [b]ν-stretching, δ-in-plane bending, γ-out-of-plane bending, τ-torsion, Γ-rocking.

(Table S1). Continued.

Calculated AZ+PMMA			Scaled AZ+PMMA	
B3LYP/6-31G(d,p)			B3LYP/6-31G(d,p)	
ω	A	S	ν	$\Delta\nu^c$
24	0	0	45	0
56	0	0	76	5
84	3	0	102	0
142	0	0	158	-33
210	0	0	222	12
274	3	1	284	-14
342, 537	17	0	*348*, 535	-33, -6
294, 482	4	0	*303*, 482	13, 10
421, *424*	1	0	424, *427*	-2, -2
549, *626*	0	1	*546*, *619*	-3, 0
562, 701	3	0	*558*, 691	-1, -2
632, *683*	1	0	625, *674*	0, 1
709, *783*	35	0	699, *769*	-3, -2
801	31	0	786	0
838	1	0	822	1
862, 869	3	1	*845*, 851	2, -3
930	4	1	910	9
948, *958*	7	0	927, *936*	2, -3
984, 1001	1	0	*961*, 977	5, -11
1005, *1021*	3	0	981, *996*	3, -12
1013, *1015*	3	5	989, *991*	3, 2
1042, 1047	2	2	*1016*, 1021	2, -2
1104, 1108	14	0	*1076*, 1079	-4, -3
1169, 1182	27	63	*1138*, 1150	-2, -4
1186, 1186	100	2	1154, 1154	-1, 0
1213, 1261	13	21	*1180*, 1225	0, 0
1335, *1343*	2	8	1296, *1304*	1, 0
1365, *1370*	9	4	1325, *1329*	2, 0
1487, 1491	8	56	*1441*, 1445	0, 3
1513, 1527	7	38	*1466*, 1479	2, 0
1553	7	100	1504	6
1633, 1639	4	0	1580, 1586	2, 3
1651, *1655*	4	19	1598, *1601*	3, 1
3184, *3186*	3	4	3061, *3062*	-2, -3
3193, *3202*	5	10	3069, *3078*	-1, -10
3204, 3210	15	10	*3080*, 3085	-1, -6
3214, *3216*	11	24	3089, *3091*	-1, -2
3227, *3257*	4	9	3102, *3130*	2, -26

[c] $\Delta\nu$ = ν(scaled in AZ) - ν(scaled in AZ+PMMA).

Table S2: Comparison of the calculated harmonic wavenumbers (ω, cm^{-1}), relative infrared intensities (A, %), relative Raman scattering activities (S, %), Raman depolarization ratios for plane (P) and unpolarized (U) incident light, reduced mass (μ, amu), and force constant (mdyn·$Å^{-1}$, f) obtained in *cis*-AZ at the B3LYP/6-31G(d,p) level.

Calculated values										scaled		Characterization[a]
B3LYP/6-31G(d,p)			B3LYP/6-311+G(2d,p)							B3LYP/ 6-31G(d,p)	B3LYP/6-311+G(2d,p)	
ω	A	S	ω	A	S	μ	f	P	U	ν	ν	
46, *48*	2	7	*47*, **48**	1	3	4.1	0.01	0.56	0.72	66, 68	64, 65	τ(ring)
71, ***159***	5	1	*65*, **156**	4	2	4.4	0.01	0.65	0.79	90, 174	81, 169	τ(ring)
274	0	1	272	0	2	4.4	0.19	0.11	0.19	284	280	Γ(ring)
174, **286**	10	3	*173*, **293**	6	5	5.2	0.09	0.44	0.61	188, 295	185, 300	15, δ(C-N) + γ(N=N)
413, 416	5	10	**412**, *414*	4	3	3.0	0.30	0.30	0.46	416, 419	415, 417	16a, γ(CCC)
434, ***455***	6	17	***435***, 452	5	2	5.0	0.56	0.53	0.69	436, 456	437, 453	16b, γ(CCC)
509, *550*	5	1	**509**, *550*	6	0	4.7	0.84	0.52	0.68	508, 547	508, 547	6a, δ,γ(CCC)
609	6	4	612	6	10	5.3	1.16	0.28	0.44	603	607	γ(N=N) + 4, γ(CCC)
630, *633*	0	8	633, *636*	0	2	6.4	1.52	0.25	0.40	623, 626	627, 630	6b, δCCC)
699	5	0	702	23	0	2.8	0.82	0.75	0.86	689	694	4, γ(CCC)
708, **718**	100	2	706, ***712***	100	1	1.7	0.52	0.75	0.86	698, 707	697, 703	11, γ(CH)
765	0	14	763	0	2	4.4	1.52	0.21	0.35	752	752	1, δ(CCC) + δ(N=N)
780, 791	65	45	**777**, *789*	47	1	2.3	0.86	0.53	0.69	766, 777	766, 777	10b, γ(C-N, C-H) + δ(N=N)
853, *854*	6	20	**845**, *847*	2	2	1.3	0.53	0.37	0.54	836, 837	831, 833	10a, γ(C-H)
866	8	4	866	4	5	3.2	1.40	0.75	0.86	849	851	δ(N=N) + 10b, γ(C-N)
930, ***935***	36	2	929, ***936***	27	1	1.8	0.93	0.75	0.86	910, 914	912, 919	17b, γ(C-H)
973, 973	0	21	976, *978*	0	0	1.4	0.78	0.44	0.61	951, 951	957, 958	17a, γ(C-H)
997, 997	2	28	***996***, 997	1	0	1.3	0.77	0.55	0.71	974, 974	976, 977	5, γ(C-H)
1015, 1015	2	1	1018, 1018	1	27	6.1	3.74	0.05	0.09	991, 991	997, 997	12, δ(CCC)
1050, *1051*	6	1	1045, 1045	6	5	2.2	1.41	0.02	0.03	1024, 1025	1023, 1023	18a, δ(C-H)
1106, *1107*	17	7	***1100***, 1102	14	1	1.6	1.12	0.75	0.86	1078, 1078	1076, 1078	18b, δ(C-H)
1152, **1174**	3	4	*1146*, **1167**	1	52	3.4	2.63	0.17	0.28	1121, 1142	1121, 1141	7a, ν(C-N, C-H)
1187, 1187	0	8	1182, *1183*	0	2	1.1	0.94	0.68	0.81	1155, 1155	1155, 1156	9b, δ(C-H)
1206, 1206	2	10	*1200*, 1201	0	1	1.3	1.10	0.71	0.83	1173, 1173	1173, 1174	9a, δ(C-H)
1331, *1339*	2	5	**1315**, *1325*	2	2	4.5	4.65	0.34	0.50	1292, 1300	1283, 1293	3, δ(C-H)
1357, 1361	2	1	1352, *1354*	0	1	1.5	1.62	0.74	0.85	1317, 1321	1319, 1321	14, ν(C=C)
1486, 1492	10	1	**1480**, *1487*	7	1	2.2	2.89	0.72	0.84	1440, 1446	1442, 1449	19b, ν(C-H, C=C)
1520, **1523**	11	8	*1514*, **1517**	8	13	2.1	2.83	0.37	0.54	1473, 1475	1474, 1477	19a, ν(C-H, C=C)
1609	52	17	1587	33	100	9.0	13.32	0.30	0.46	1558	1545	ν(N=N)
1629, 1636	8	5	***1613***, 1620	6	4	5.2	7.96	0.75	0.86	1577, 1583	1570, 1576	8b, ν(C=C)
1648, ***1657***	14	8	*1630*, **1638**	9	19	5.4	8.41	0.75	0.86	1595, 1603	1586, 1594	8a, ν(C=C) + ν(N=N)
3183, 3183	2	54	3164, *3165*	1	6	1.1	6.41	0.63	0.77	3060, 3060	3061, 3062	13, ν(C-H)
3192, 3192	22	100	3171, *3172*	6	24	1.1	6.45	0.74	0.85	3068, 3068	3068, 3069	7b, ν(C-H)
3203, 3203	33	1	3182, 3182	13	15	1.1	6.51	0.75	0.86	3079, 3079	3078, 3078	20b, ν(C-H)
3210, *3211*	65	69	3190, 3190	38	70	1.1	6.57	0.06	0.12	3085, 3086	3086, 3086	20a, ν(C-H)
3218, 3218	8	6	*3196*, **3197**	4	34	1.1	6.59	0.08	0.14	3093, 3093	3092, 3093	2, ν(C-H)

[a]ν-stretching, δ-in-plane bending, γ-out-of-plane bending, τ-torsion, Γ-rocking.

Table S3: Comparison of the calculated harmonic wavenumbers (ω, cm^{-1}), scaled values and experimental ones obtained in the complex with Ni at three DFT levels and using the 6-31G(d,p) basis set.

Calculated ω			Scaled ν			Exp	Characterization
B3LYP	M052X	M062X	B3LYP	M052X	M062X		
727	755	753	716	732	732	721 w	δ(CC,CO) in ring
1204	1221	1209	1171	1168	1161	1144 w	δ(CC, CH) in ring
1260	1265	1256	1225	1209	1205	1211 w	δ(C-H) in ring
1330	1370	1352[b]	1291	1308	1296	1304 w	δ(C-H) in CH
1413[a]	1438	1436	1371	1371	1375	1377 m	δ(O-H) + δ(C-H) in CH_2
1492	1548	1539	1446	1474	1472	1462 s	ν(C-O) + ν(CC) in ring
1684	1740	1734	1629	1654	1656	1629 w	ν(C-N)
3006	3067	3048	2891	2897	2893	2853 s	ν_s(C-H) in CH_2
3048	3117	3096	2931	2944	2938	2925 s	ν_{as}(C-H) in CH_2

[a]Characterized as: δ(C-H) in CH [b]+δ(C-H) in ring.

Table S4: Comparison of the calculated harmonic wavenumbers (ω, cm^{-1}), scaled values and experimental ones obtained in the complex with Cu at three DFT levels and using the 6-31G(d,p) basis set.

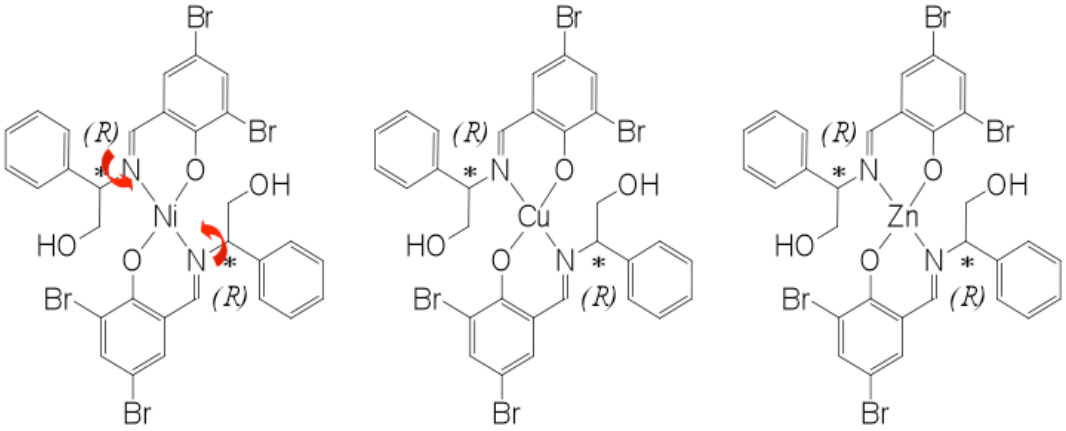
Calculated ω			Scaled ν			Exp	Characterization
B3LYP	M052X	M062X	B3LYP	M052X	M062X		
732	734	735	721	712	715	721 w	δ(CC,CO) in ring
1171	1201	1193	1140	1149	1146	1151 w	δ(CC) in ring
1429[a]	1441	1430	1386	1374	1369	1376 m	δ(O-H) + δ(C-H) in CH_2
1493	1549	1548	1447	1475	1480	1462 s	ν(C-O) + ν(CC) in ring
1676	1743	1741	1622	1657	1662	1628 w	ν(C-N)
3006	3055	3036	2891	2886	2882	2854 s	ν_s(C-H) in CH_2
3047	3101	3064	2930	2929	2908	2925 s	ν_{as}(C-H) in CH_2

[a]+ δ(C-H) in CH and in ring.

Table S5: Comparison of the calculated harmonic wavenumbers (ω, cm^{-1}), scaled values and experimental ones obtained in the complex with Zn at three DFT levels and using the 6-31G(d,p) basis set.

Calculated ω			Scaled ν			Exp	Characterization
B3LYP	M052X	M062X	B3LYP	M052X	M062X		
712	732	736	702	710	716	702 w	δ(CC,CO) in ring
1052[a]	1079	1078	1026	1035	1038	1028 w	δ(C-C, C-H) in ring
1086	1091	1082	1058	1046	1042	1052 w	δ(OH, CO) + δ(CH)
1182	1203	1195	1150	1151	1148	1146 w	δ(CC) in ring
1251	1262	1253	1216	1206	1203	1212 w	δ(C-H) in ring
1325	1377[b]	1345	1287	1314	1289	1301 w	δ(C-H) in CH
1428	1434	1431	1385	1368	1370	1377 m	δ(O-H) + δ(C-H) in CH_2
1496	1537[c]	1537	1450	1464	1470	1461 m	ν(C-O) + ν(CC) in ring
1667	1736	1730	1613	1650	1652	1610 w	ν(C-N)
3017	3066	3027	2901	2896	2873	2854 s	ν_s(C-H) in CH_2
3073	3116	3095	2955	2943	2937	2923 s	ν_{as}(C-H) in CH_2

[a]+δ(C-C, C-H) in –CH-CH_2 [b]Characterized as: δ(CC) in ring. [c]+δ(C-H) in CH_2.



Scheme S1: Complexes of **Ni**, **Cu** and **Zn**. Two different conformers can be obtained in these complexes by rotation around the bond length shown in red colour.

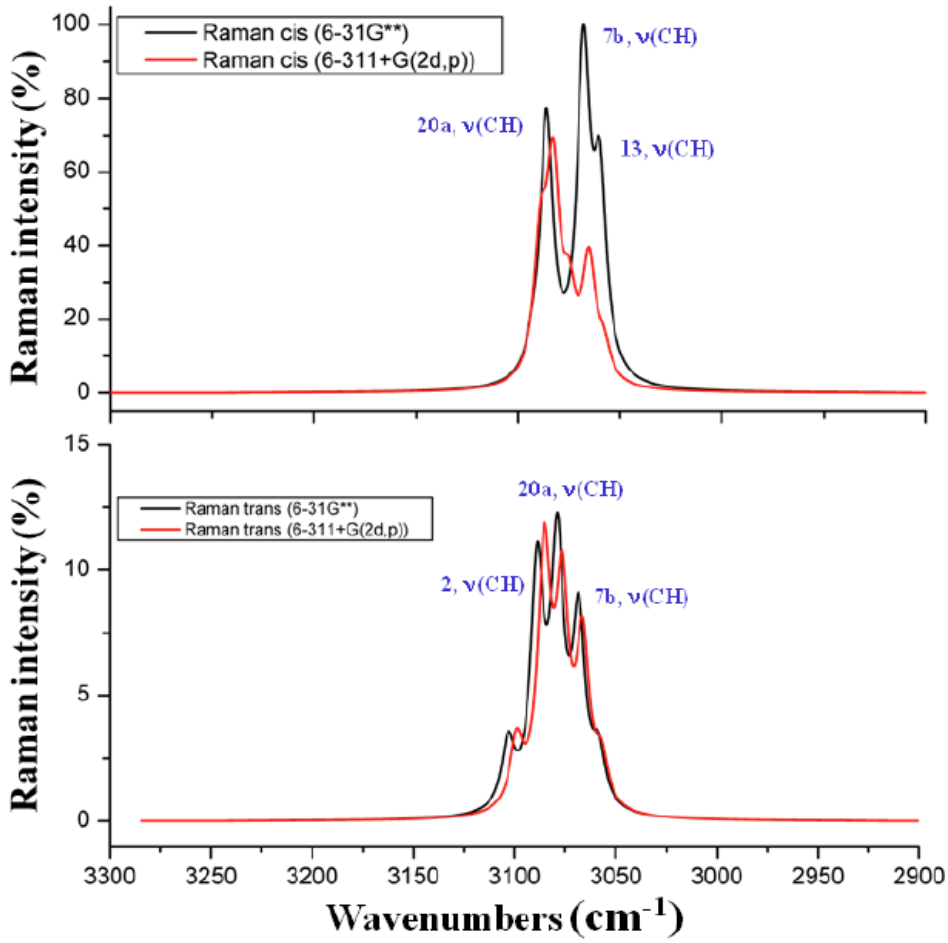


Figure S1: Theoretical scaled Raman spectrum in the 3300-2900 cm^{-1} range using the scale equation procedure from the benzene molecule.

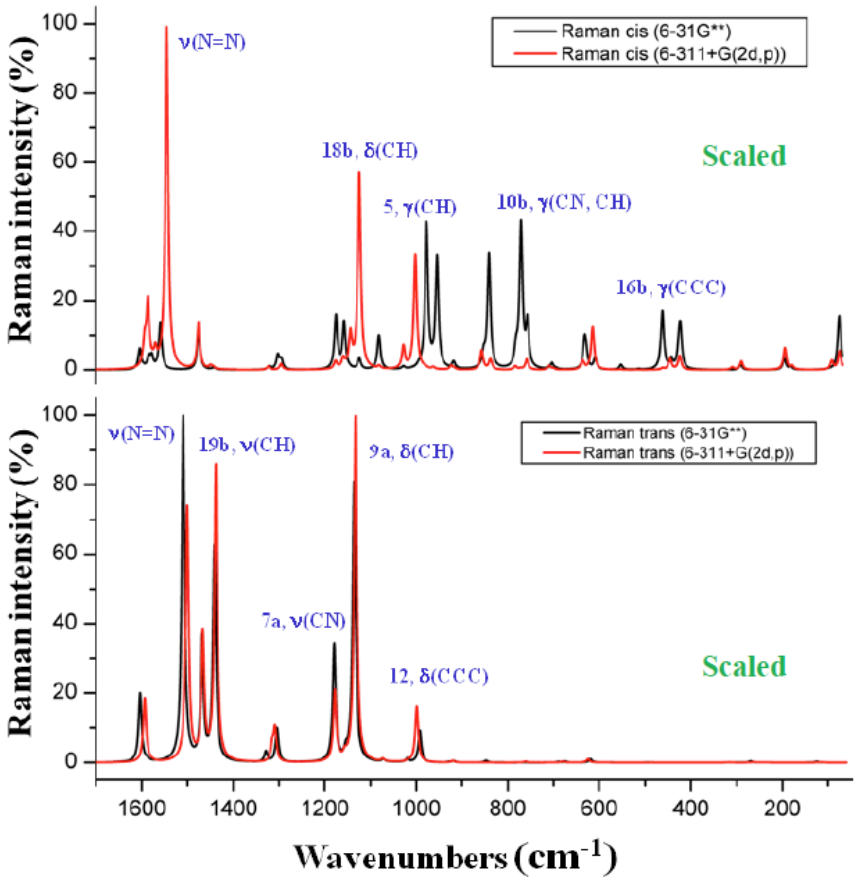


Figure S2: Theoretical scaled Raman spectrum in the 1700-50 cm^{-1} range using the scale equation procedure from the benzene molecule.

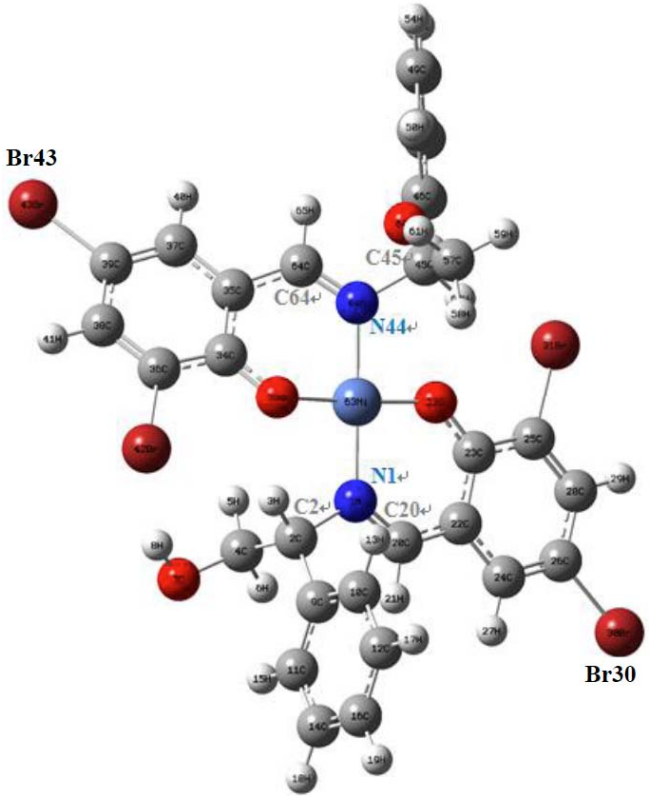


Figure S3: Optimized molecular structure of the complex with **Ni** with the notation of their atoms.

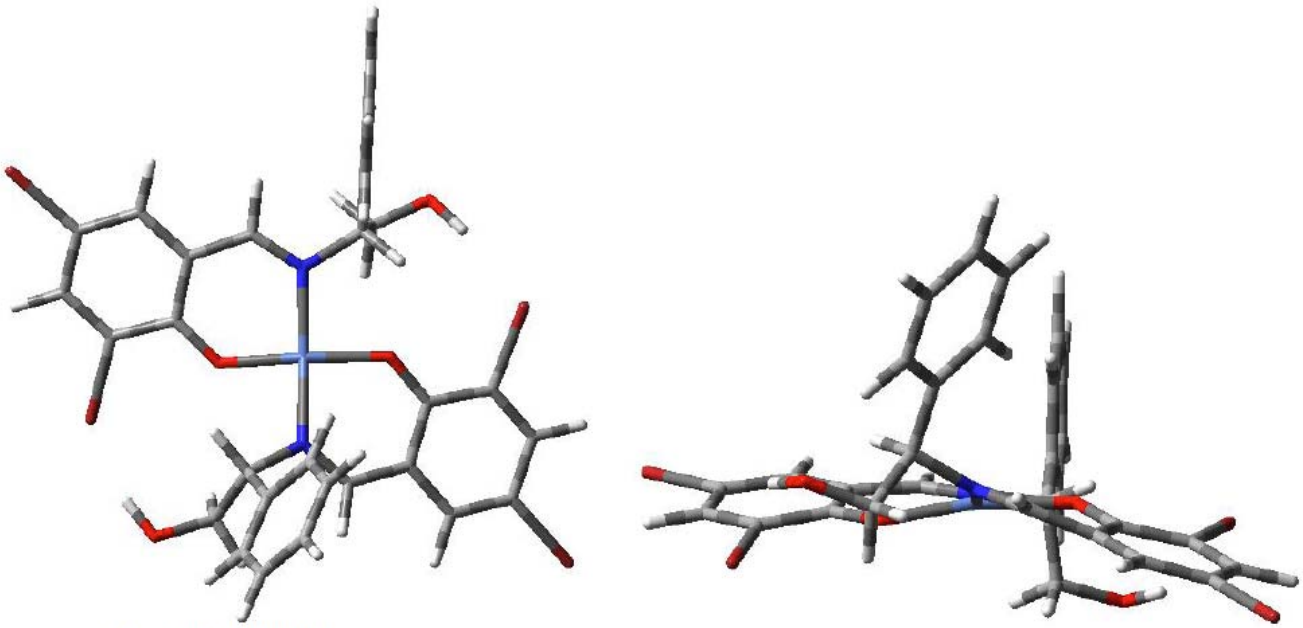


Figure S4: Two views of the optimized molecular structure at the B3LYP/6-31G(d,p) level in conformer 2 of azobenzene complex with **Ni**.

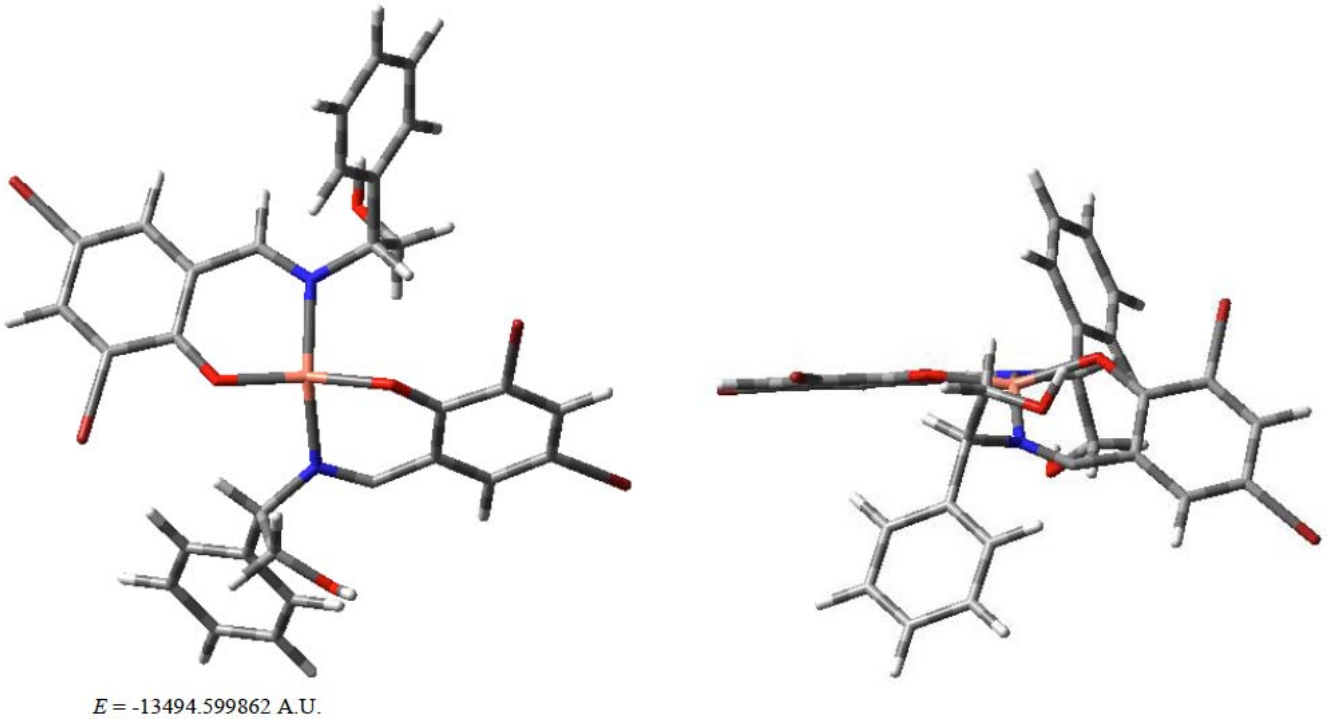


Figure S5: Two views of the optimized molecular structure at the B3LYP/6-31G(d,p) level in conformer 2 of azobenzene complex with **Cu**.

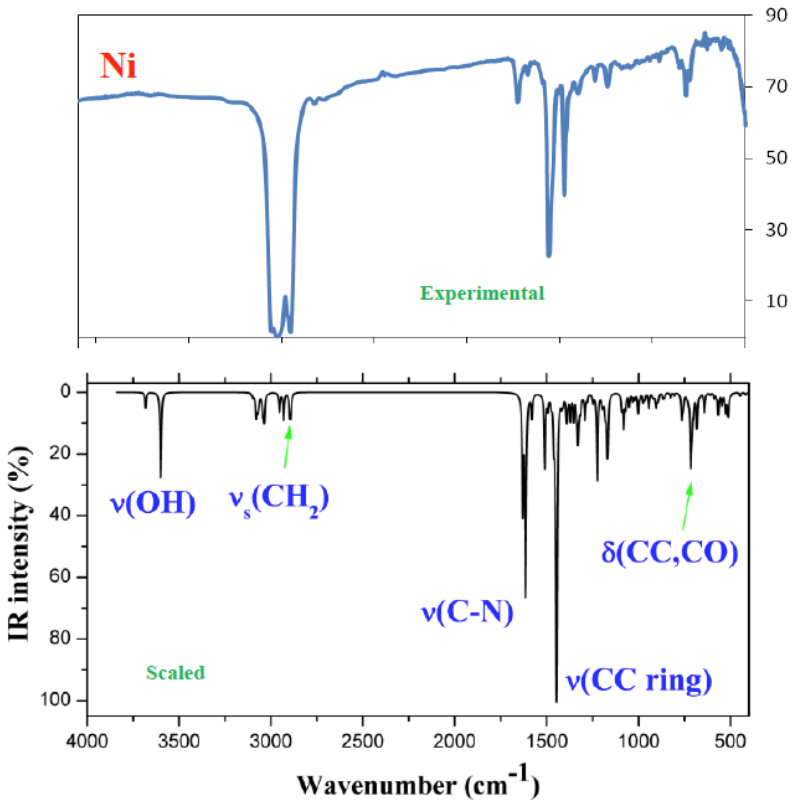


Figure S6: Experimental IR spectrum of the complex with **Ni**, and theoretical scaled one at the B3LYP/6-31G(d,p) level with the assignment of the stronger bands.

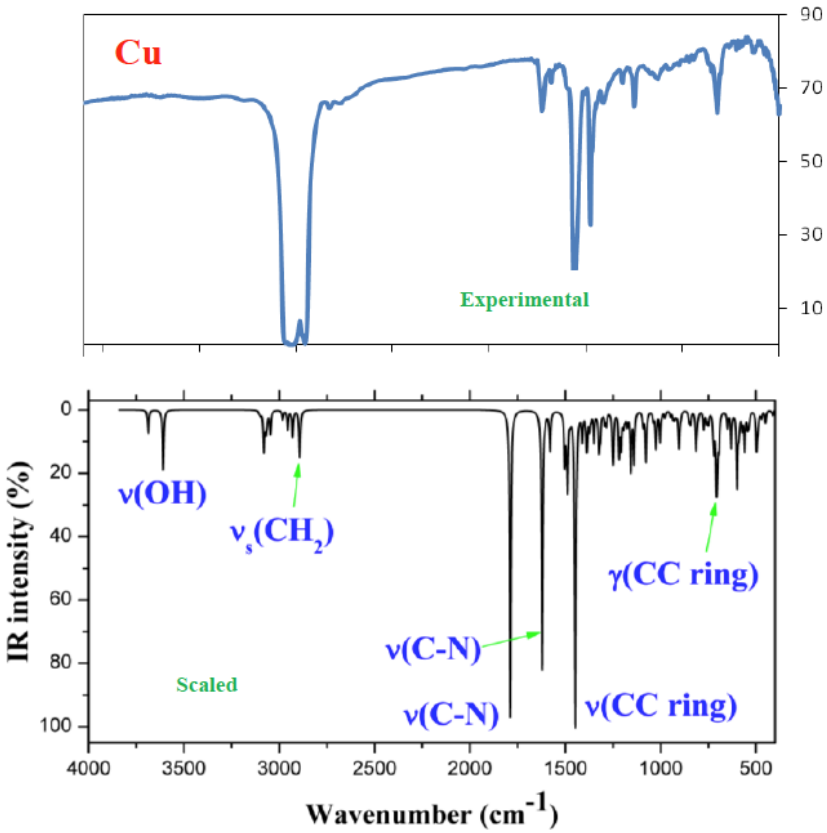


Figure S7: Experimental IR spectrum of the complex with **Cu**, and theoretical scaled one at the B3LYP/6-31G(d,p) level with the assignment of the stronger bands.

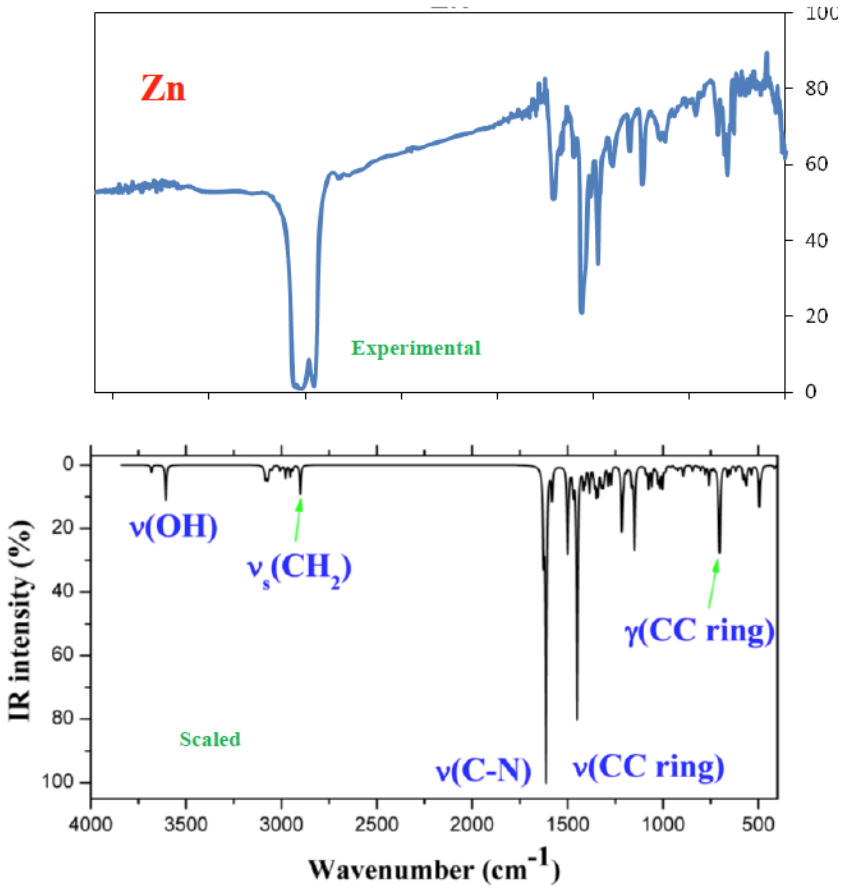


Figure S8: Experimental IR spectrum of the complex with **Zn**, and theoretical scaled one at the B3LYP/6-31G(d,p) level with the assignment of the stronger bands.

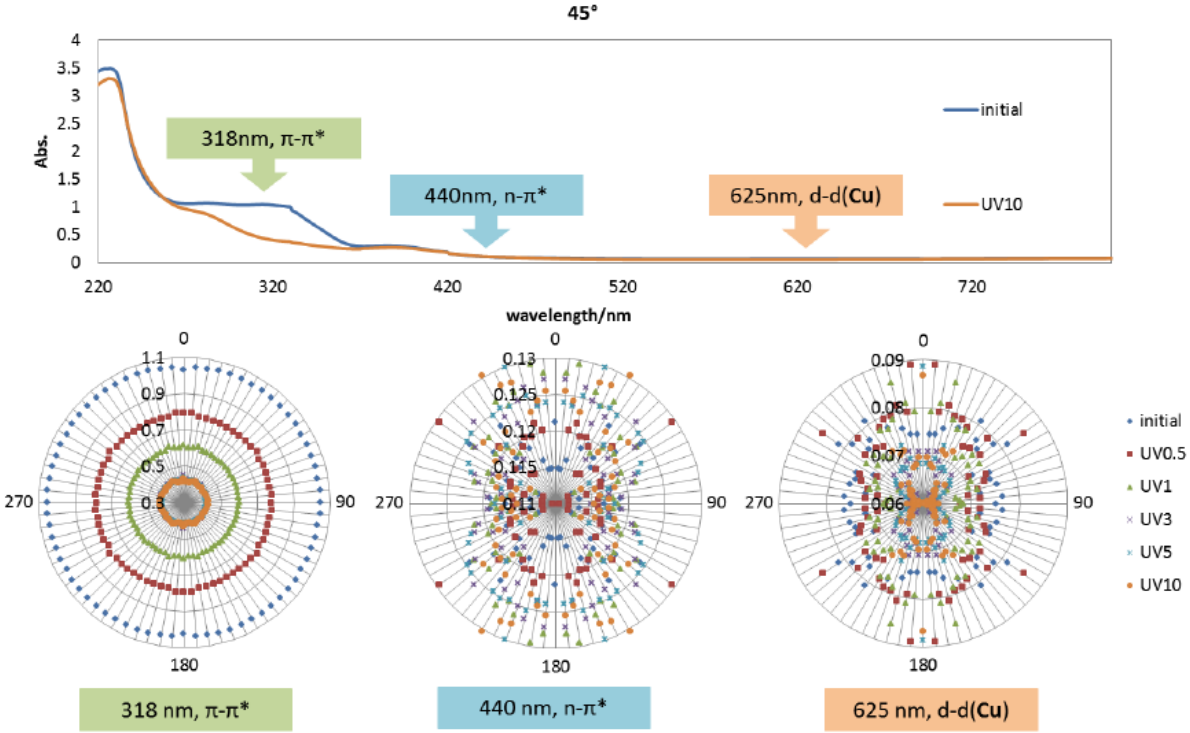


Figure S9: Polarized absorption spectra at 45° and angular dependence at 318, 440 and 625 nm for **Cu+AZ+PMMA** after UV light irradiation for 0-10 min.

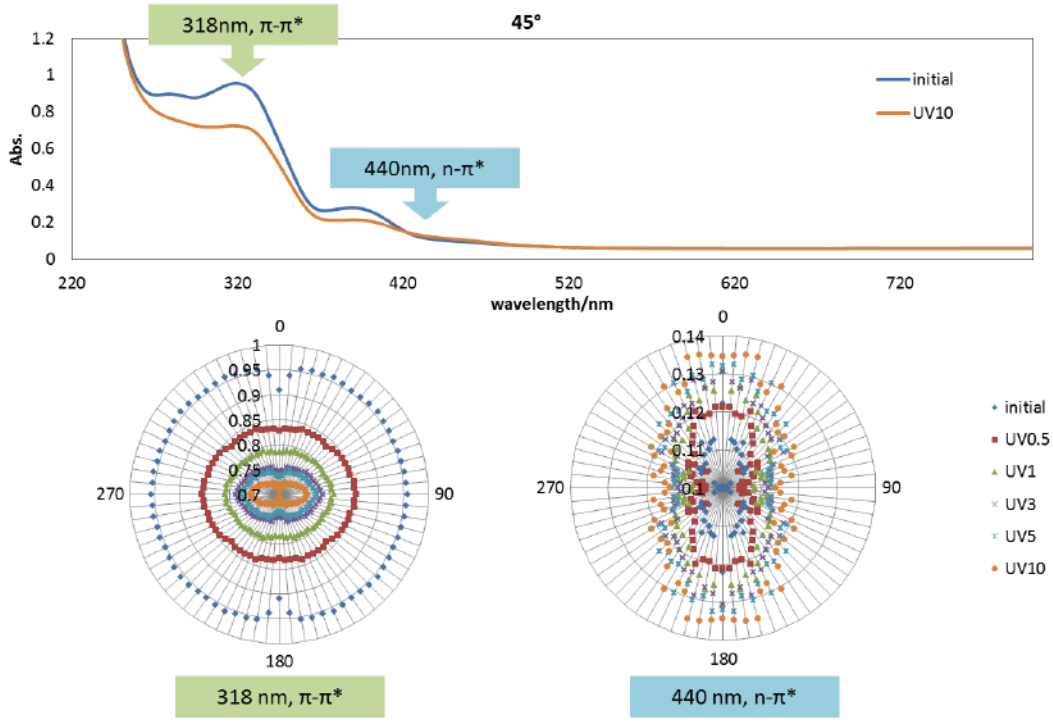


Figure S10: Polarized absorption spectra at 45° and angular dependence at 318 and 440 nm for **Zn+AZ+PMMA** after UV light irradiation for 0-10 min.

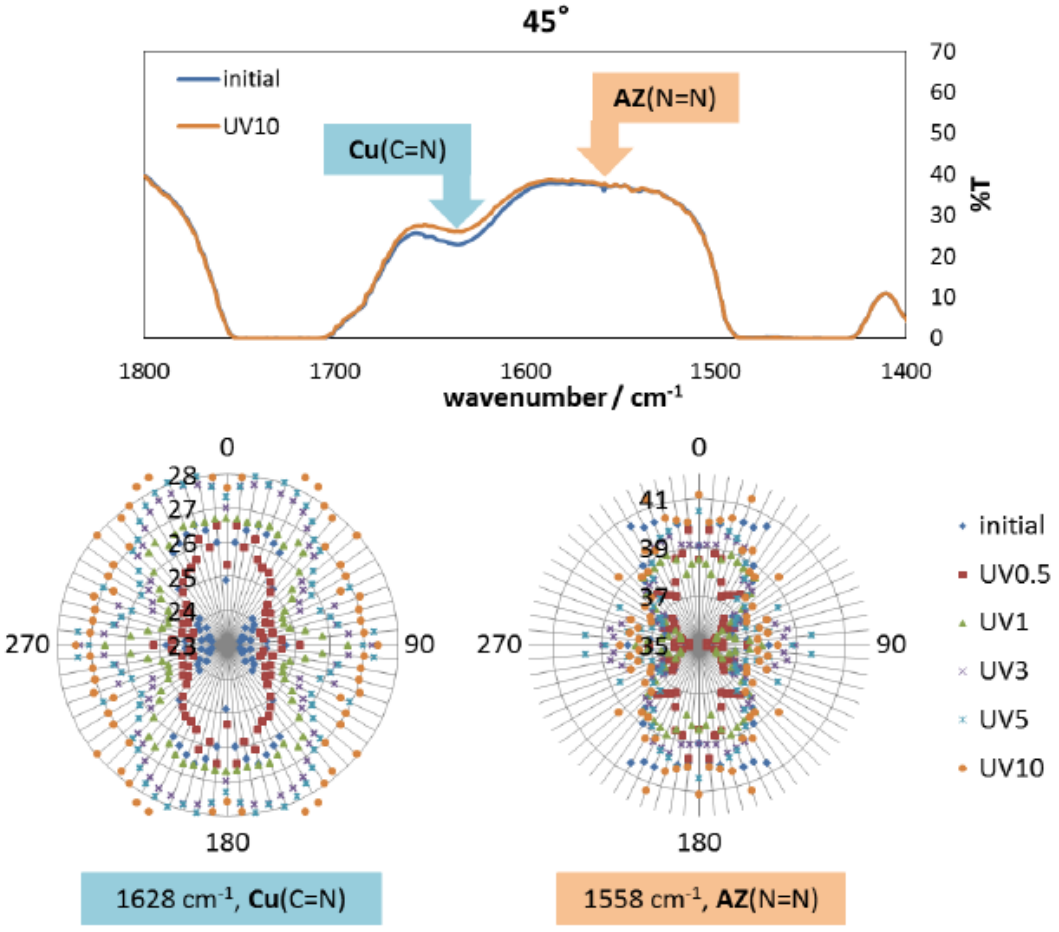


Figure S11: Polarized IR spectra at 45° and angular dependence of a polarizer in transmittance at 1628(C=N) and 1558 cm^{-1} (N=N) for **Cu+AZ+PMMA** after UV light irradiation for 0-10 min.

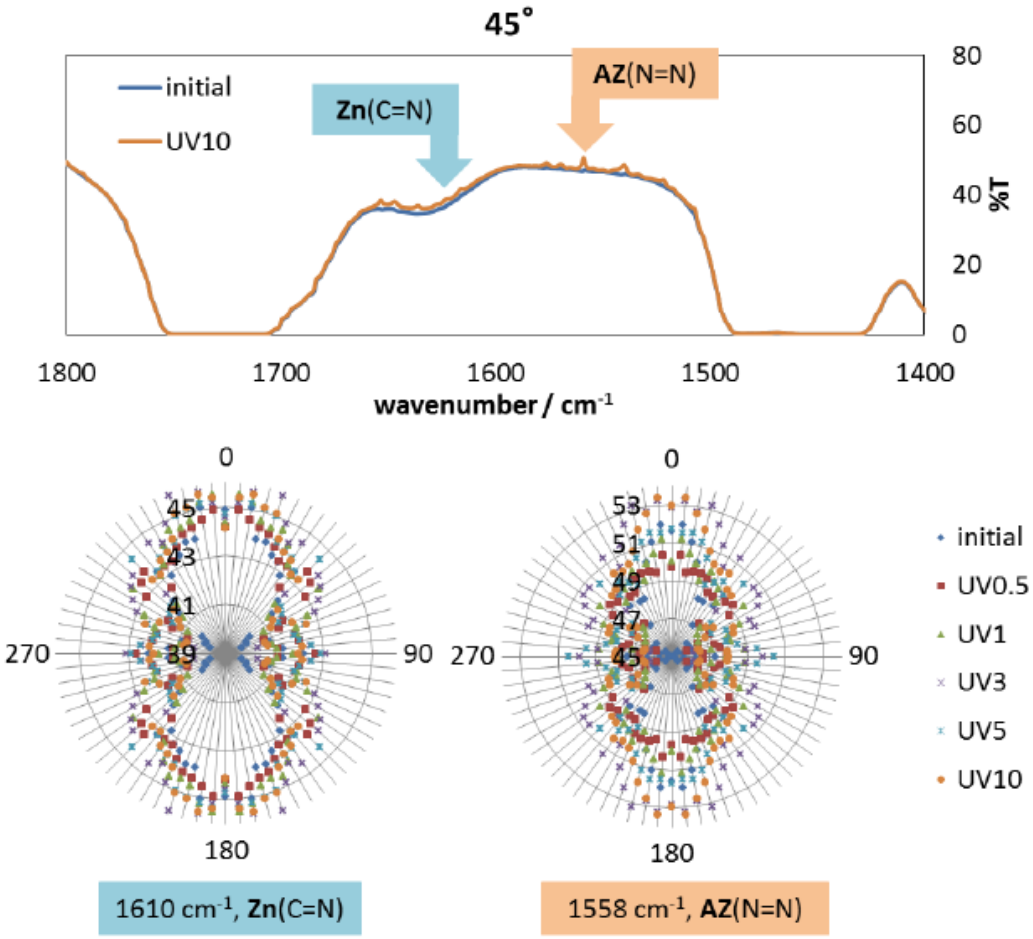


Figure S12: Polarized IR spectra at 45° and angular dependence of a polarizer in transmittance at 1610(C=N) and 1558 cm^{-1} (N=N) for **Zn+AZ+PMMA** after UV light irradiation for 0-10 min.