Solvent Effect on Frontier Orbitals and Electronic Transitions of Manganese Carbonyl Complexes: A DFT/TDDFT Study

Elvan ÜSTÜN[a*], Ali Kemal MEHEL[a]

[a] Department of Chemistry, Faculty of Art and Science, Ordu University, 52200, Ordu, Turkey

*** Corresponding author. E-mail: elvanustun77@gmail.com**

SUPPORTING INFORMATIONS

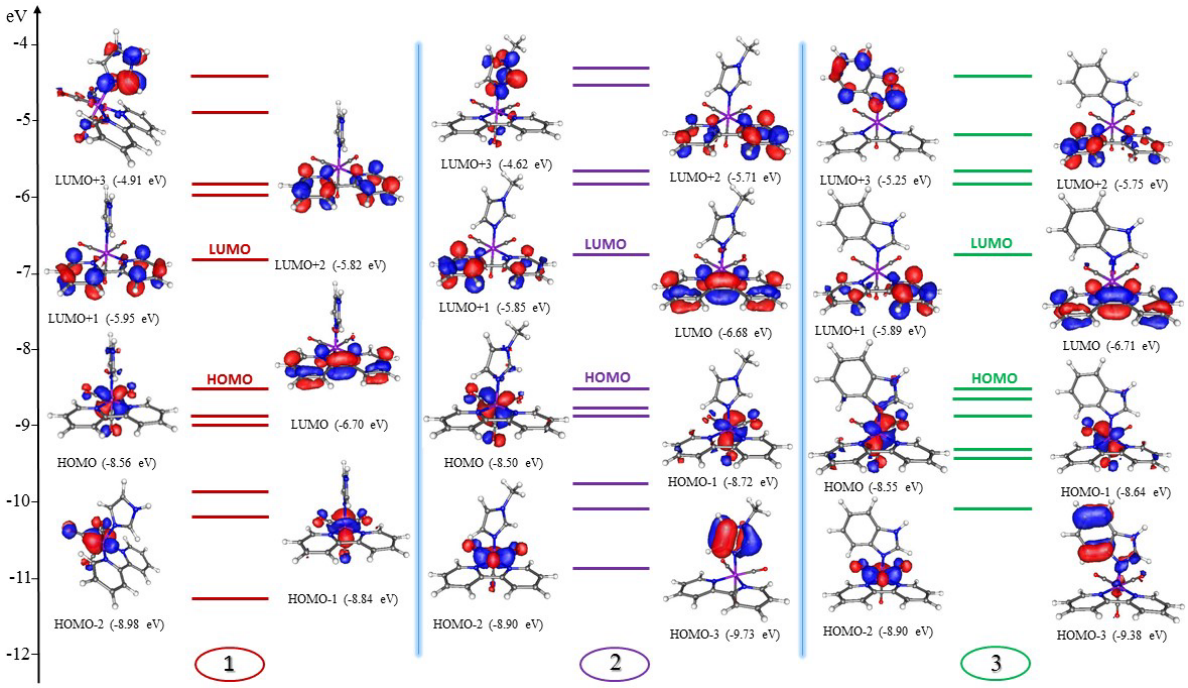

Figure S1. Molecular orbital energy diagrams of the molecules in gas phase

Table S1. Electronic transitions of **3** in gas phase

State	Composition	ΔE (eV)	λ (nm)	f_{osc}	Character*
2	HOMO-1 → LUMO, 37.9% HOMO-2 → LUMO, 35.8% HOMO → LUMO, 19.9%	2.168	572.0	0.0279	Mn/CO/bim → bpy
3	HOMO-2 → LUMO, 63.4% HOMO-1 → LUMO, 16.8% HOMO → LUMO, 11.8%	2.256	549.5	0.0253	Mn/CO → bpy
8	HOMO → LUMO+2, 47.2% HOMO-1 → LUMO+2, 38.4%	2.959	419.0	0.0198	Mn/CO/bim → bpy
11	HOMO → LUMO+2, 24.7% HOMO-1 → LUMO+2, 22.3% HOMO-1 → LUMO+1, 13.5%	3.176	390.3	0.1269	Mn/CO → bpy
14	HOMO-1 → LUMO+3, 42.3% HOMO → LUMO+3, 20.9% HOMO-4 → LUMO+1, 18.5%	3.551	349.2	0.0372	Mn/CO → bim
15	HOMO-4 → LUMO+1, 69.0%	3.611	343.3	0.0351	Mn/CO/bim → bpy
17	HOMO-2 → LUMO+3, 80.8%	3.687	336.3	0.0192	Mn/CO → bim
19	HOMO → LUMO+4, 70.7% HOMO-5 → LUMO, 14.3%	4.119	301.0	0.0427	Mn/CO → bpy

* bim: benzimidazole; bpy: 2,2'-bypyridyl

Table S2. Electronic transitions of **3** in acetone

State	Composition	ΔE (eV)	λ (nm)	f_{osc}	Character
1	HOMO → LUMO, 76.7% HOMO-4 → LUMO, 19.8%	2.093	592.4	0.0135	Mn/CO/bim → bpy
2	HOMO-1 → LUMO, 74.9% HOMO → LUMO, 15.5%	2.227	556.8	0.0259	Mn/CO/bim → bpy
8	HOMO → LUMO+2, 70.6% HOMO-1 → LUMO+2, 10.4%	3.035	408.5	0.0111	Mn/CO/bim → bpy
9	HOMO-1 → LUMO+2, 55.0% HOMO-2 → LUMO+1, 11.2%	3.246	382.0	0.0696	Mn/CO → bpy
15	HOMO-1 → LUMO+3, 38.0% HOMO-3 → LUMO+2, 30.8% HOMO → LUMO+3, 15.1%	3.762	329.6	0.0352	Mn/CO/bim → bpy/bim
16	HOMO-4 → LUMO+1, 71.7% HOMO-4 → LUMO+2, 15.2% HOMO-4 → LUMO+1, 18.5%	3.473	357.0	0.0211	Mn/CO/bim → bpy
17	HOMO-4 → LUMO+2 54.1% HOMO-4 → LUMO+1, 18.4% HOMO-5 → LUMO, 17.5%	3.687	336.3	0.0390	Mn/CO/bim → bpy

* bim: benzimidazole; bpy: 2,2'-bypyridyl

Table S3. Electronic transitions of **3** in DMSO

State	Composition	ΔE (eV)	λ (nm)	f_{osc}	Character
1	HOMO → LUMO, 79.1% HOMO-1 → LUMO, 17.2%	2.069	599.2	0.0141	Mn/CO/bim → bpy
2	HOMO-1 → LUMO, 77.7% HOMO → LUMO, 13.4%	2.201	563.2	0.0238	Mn/CO/bim → bpy
5	HOMO-4 → LUMO, 83.7%	2.683	462.1	0.0106	Mn/CO/bim → bpy
9	HOMO-1 → LUMO+2, 59.3%	3.228	384.1	0.0691	Mn/CO → bpy
15	HOMO-1 → LUMO+3, 44.1% HOMO-3 → LUMO+2, 22.3% HOMO → LUMO+3, 16.4%	3.738	331.7	0.0361	Mn/CO/bim → bpy/bim
16	HOMO-4 → LUMO+1, 63.5% HOMO-4 → LUMO+2, 21.7%	3.413	363.3	0.0202	Mn/CO/bim → bpy
17	HOMO-4 → LUMO+2, 44.9% HOMO-4 → LUMO+1, 26.8% HOMO-5 → LUMO, 17.2%	3.654	339.3	0.0441	Mn/CO/bim → bpy
19	HOMO → LUMO+4, 83.4%	4.074	304.3	0.0232	Mn/CO/bim → CO

* bim: benzimidazole; bpy: 2,2'-bypyridyl

Table S4. Electronic transitions of **3** in DCM

State	Composition	ΔE (eV)	λ (nm)	f_{osc}	Character
2	HOMO-1 → LUMO, 68.9% HOMO → LUMO, 19.7%	2.157	574.7	0.0286	Mn/CO/bim → bpy
8	HOMO → LUMO+2, 69.3% HOMO-1 → LUMO+2, 14.8%	2.966	418.1	0.0114	Mn/CO/bim → bpy
9	HOMO-2 → LUMO+1, 65.3% HOMO-1 → LUMO+2, 20.2%	3.094	400.7	0.0279	Mn/CO → bpy
10	HOMO-1 → LUMO+2, 36.5% HOMO-2 → LUMO+1, 34.4%	3.134	395.6	0.0554	Mn/CO → bpy
14	HOMO-3 → LUMO+2, 40.9% HOMO-1 → LUMO+3, 31.4% HOMO → LUMO+3, 15.9%	3.694	335.6	0.0145	Mn/CO/bim → bpy/bim
15	HOMO-3 → LUMO+2, 54.7% HOMO-1 → LUMO+3, 22.9% HOMO → LUMO+3, 10.1%	3.675	337.4	0.0281	Mn/CO/bim → bpy/bim
16	HOMO-4 → LUMO+1, 78.6%	3.378	367.0	0.0224	Mn/CO/bim → bpy
17	HOMO-4 → LUMO+2, 65.0% HOMO-5 → LUMO, 15.7% HOMO-4 → LUMO+1, 10.7%	3.607	343.8	0.0287	Mn/CO/bim → bpy
19	HOMO → LUMO+4, 79.7%	4.092	303.0	0.0359	Mn/CO/bim → CO

* bim: benzimidazole; bpy: 2,2'-bypyridyl

Table S5. Electronic transitions of **3** in hexane

State	Composition	ΔE (eV)	λ (nm)	f_{osc}	Character
3	HOMO-2 → LUMO, 81.4%	2.087	594.2	0.0133	Mn/CO → bpy
8	HOMO → LUMO+2, 57.1% HOMO-1 → LUMO+2, 29.2%	2.844	435.9	0.0149	Mn/CO/bim → bpy
10	HOMO-1 → LUMO+2, 35.0% HOMO → LUMO+2, 18.6% HOMO-1 → LUMO+1, 12.7%	3.059	405.3	0.1095	Mn/CO → bpy
14	HOMO-1 → LUMO+1, 44.2% HOMO → LUMO+3, 25.6% HOMO-4 → LUMO+1, 11.5%	3.477	356.5	0.0351	Mn/CO → bim
15	HOMO-4 → LUMO+1, 73.4%	3.341	371.1	0.0286	Mn/CO/bim → bpy
17	HOMO-4 → LUMO+2, 48.7% HOMO-2 → LUMO+3, 38.7%	3.675	337.3	0.0160	Mn/CO/bim → bpy/bim
20	HOMO → LUMO+4, 83.8%	4.131	300.2	0.0141	Mn/CO/bim → CO/bpy

* bim: benzimidazole; bpy: 2,2'-bypyridyl

Table S6. Determined bond lengths and angles of the molecules in different solvents

	1					**2**					**3**				
	gas	acetone	DMSO	DCM	hexane	gas	acetone	DMSO	DCM	hexane	gas	acetone	DMSO	DCM	hexane
$Mn\text{-}CO_{cis}$	1.716	1.711	1.712	1.713	1.717	1.720	1.711	1.711	1.712	1.717	1.718	1.711	1.711	1.712	1.715
$Mn\text{-}CO_{trans}$	1.723	1.713	1.712	1.714	1.719	1.725	1.713	1.713	1.715	1.721	1.726	1.714	1.713	1.716	1.722
$C\text{-}O_{cis}$	1.167	1.172	1.173	1.172	1.168	1.166	1.173	1.173	1.171	1.167	1.167	1.172	1.173	1.171	1.168
$C\text{-}O_{trans}$	1.166	1.170	1.171	1.169	1.165	1.163	1.171	1.171	1.170	1.165	1.163	1.170	1.171	1.170	1.165
$Mn\text{-}N_{bpy}$	1.947	1.960	1.960	1.959	1.953	1.948	1.957	1.957	1.956	1.950	1.948	1.958	1.958	1.957	1.951
$Mn\text{-}N_{imid}$	1.949	1.996	1.996	1.996	1.998	1.993	1.983	1.983	1.984	1.989	1.986	1.985	1.984	1.985	1.985
$C_{cis}\text{-}Mn\text{-}C_{cis}$	89.6	88.7	88.6	88.8	89.4	90.0	88.8	88.7	89.0	89.6	90.2	89.6	89.5	89.7	90.0
$C_{cis}\text{-}Mn\text{-}C_{trans}$	89.3	89.6	88.8	88.9	88.8	90.0	89.7	89.7	89.7	90.0	89.4	89.5	89.5	89.5	89.5
$N_{imid}\text{-}Mn\text{-}N_{bpy}$	88.3	85.5	86.7	87.0	87.8	88.8	85.9	95.7	86.1	87.8	88.7	87.6	87.5	87.7	88.3
$N_{imid}\text{-}Mn\text{-}CO_{cis}$	90.1	90.9	93.7	95.9	92.8	92.0	91.4	91.5	91.3	90.5	90.4	91.3	91.3	91.2	90.7
$N_{imid}\text{-}Mn\text{-}CO_{trans}$	178.6	177.5	177.4	177.6	178.3	179.3	178.1	177.9	178.2	179.0	179.8	178.9	178.9	179.1	179.8