Supplementary Material (ESI) for Physical Chemistry Chemical Physics

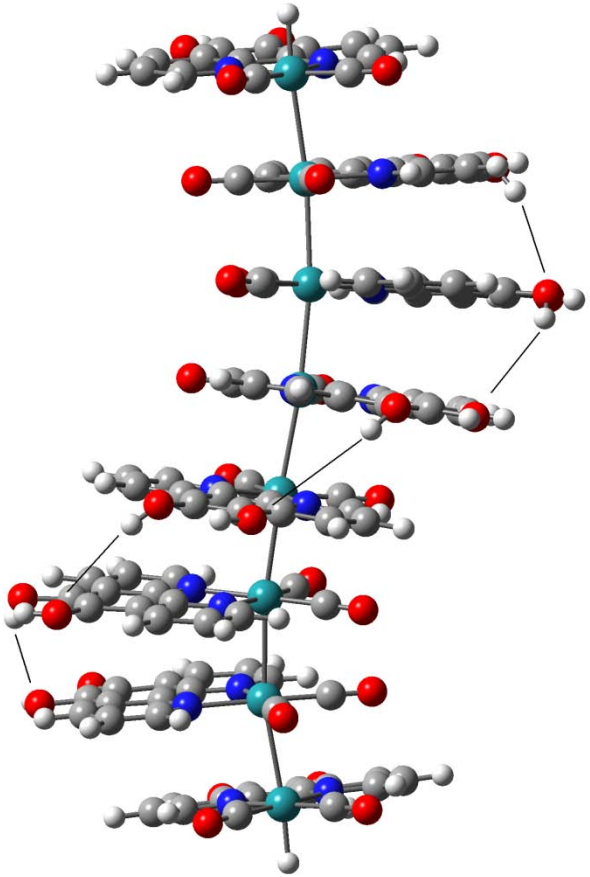
The effect of N-ligands on the geometry, bonding, and electronic absorption properties of ruthenium carbonyl chains

Supplementary data

3.2. Torsional Behaviour of the Ligands

Weak OH-O interactions in $[Ru(phen(OH)_2(CO)_2]_8H_2$ (distance ~4.1 – 4.2 Å)

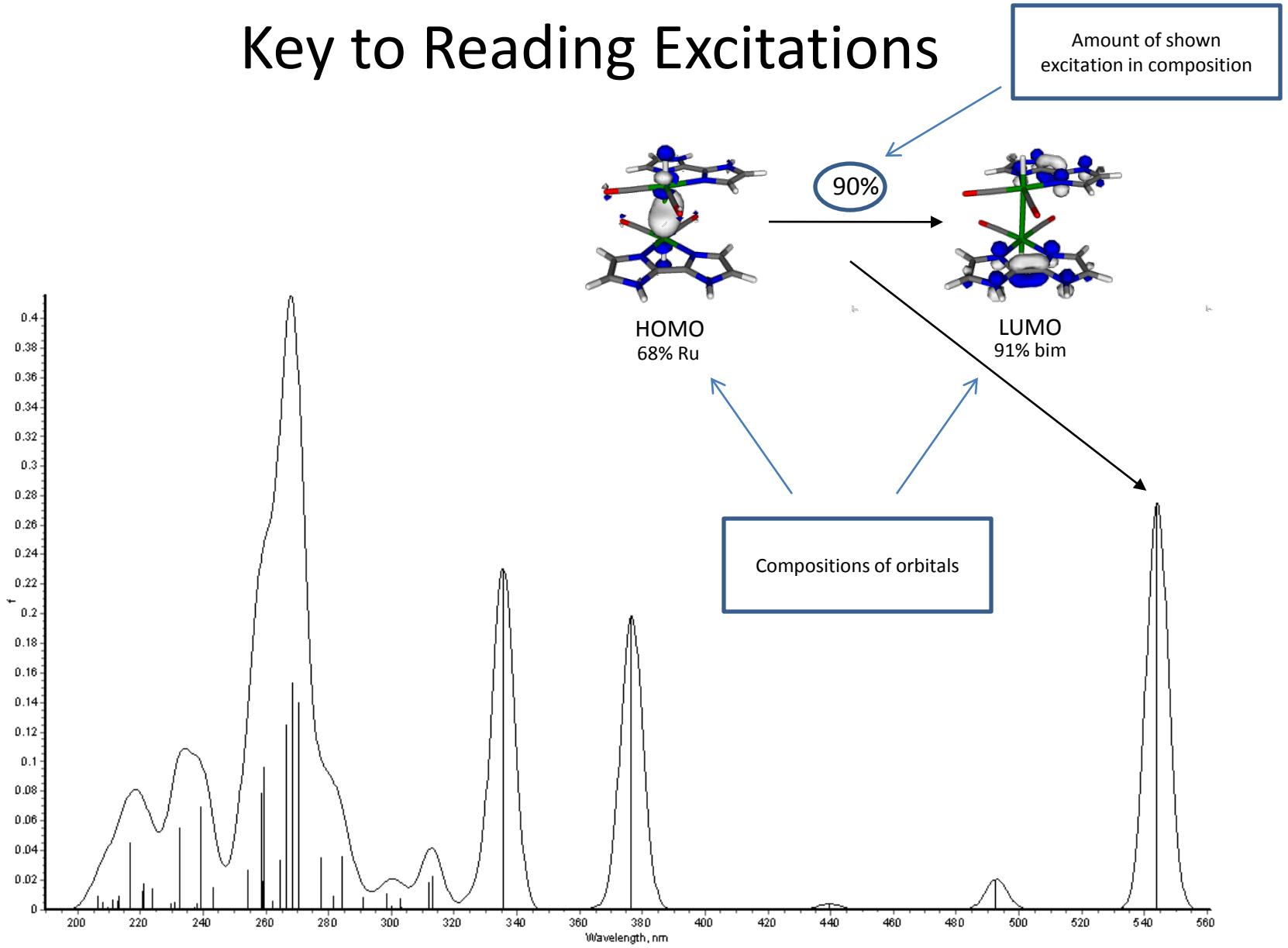
While the effect is small in this case, perhaps more far reaching substituent would make the effect stronger



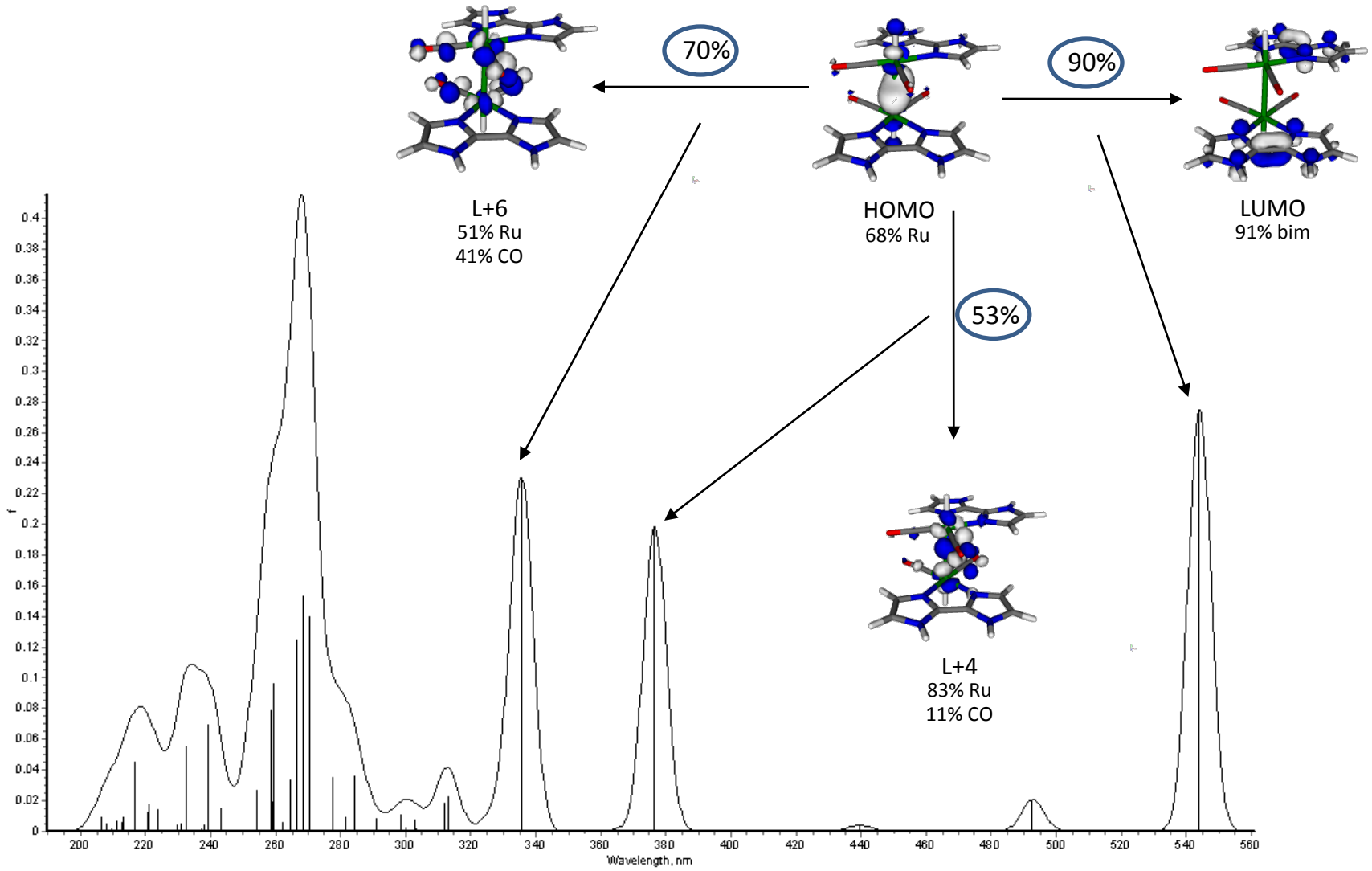
3.6. TD-DFT Calculations

- Spectra for studied dimeric complexes using ~135 degree dihedral angles
- Sample spectra for dimeric complexes (bim, bpy ligands) using ~45 degree dihedral angles
- Sample spectra for n=4 chains (bim, bpy ligands) using ~135 degree dihedral angles
- Summaries of similar low-energy excitations in n=2 and n=4 case

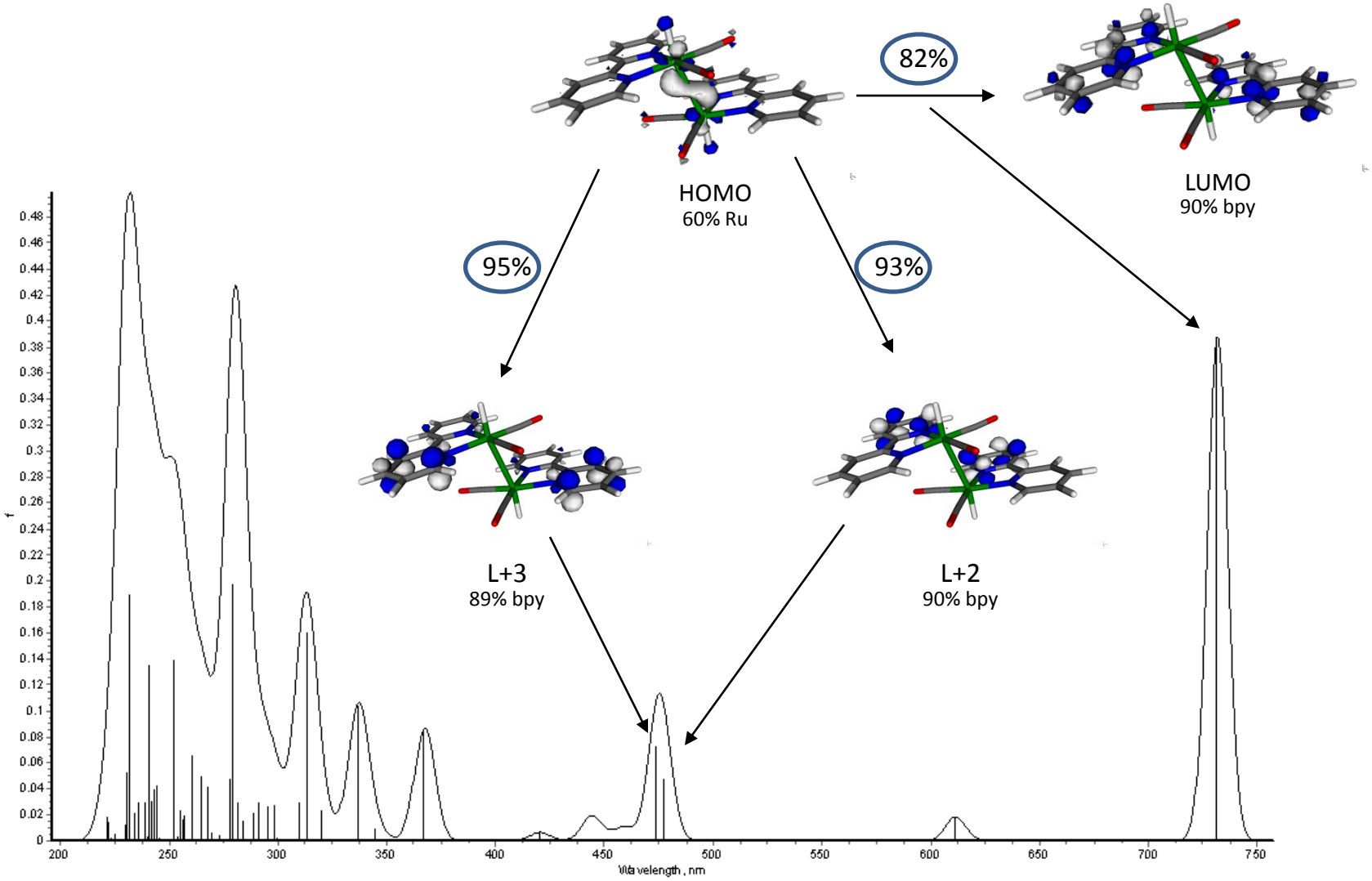
Key to Reading Excitations



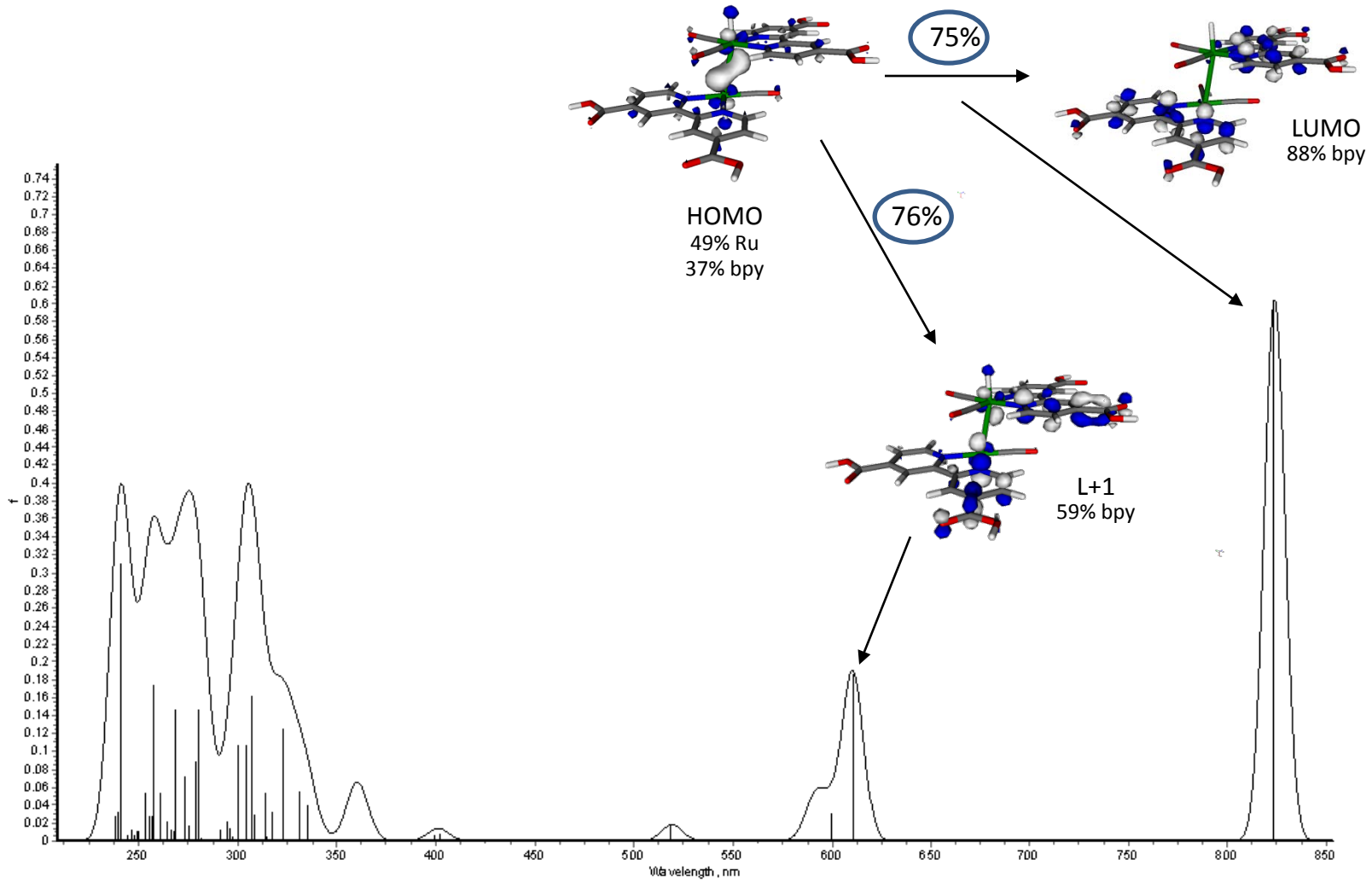
$[Ru(bim)(CO)_2]_2H_2$, ~135 dihedral angle



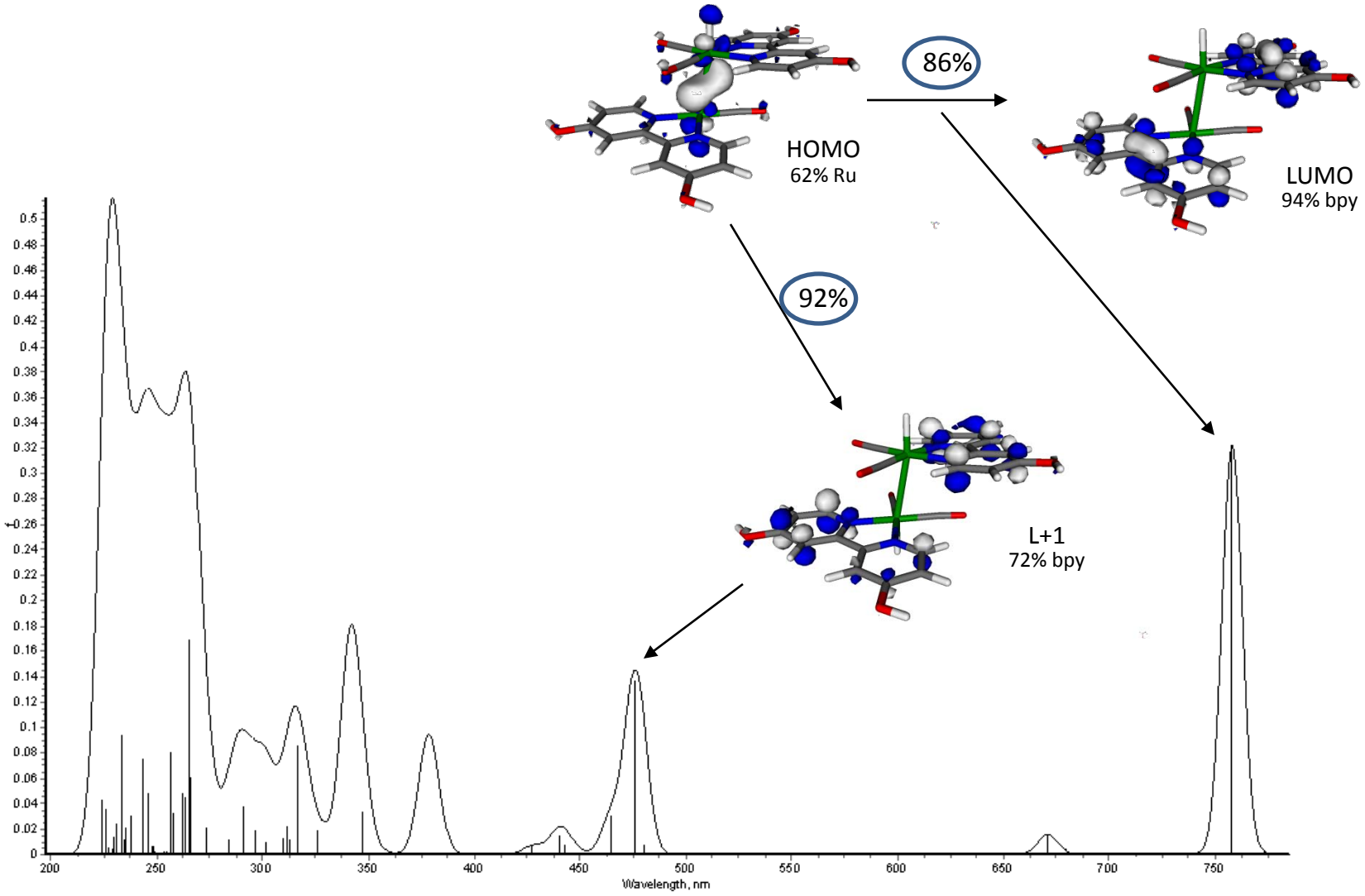
$[Ru(bpy)(CO)_2]_2H_2$, ~135 dihedral angle



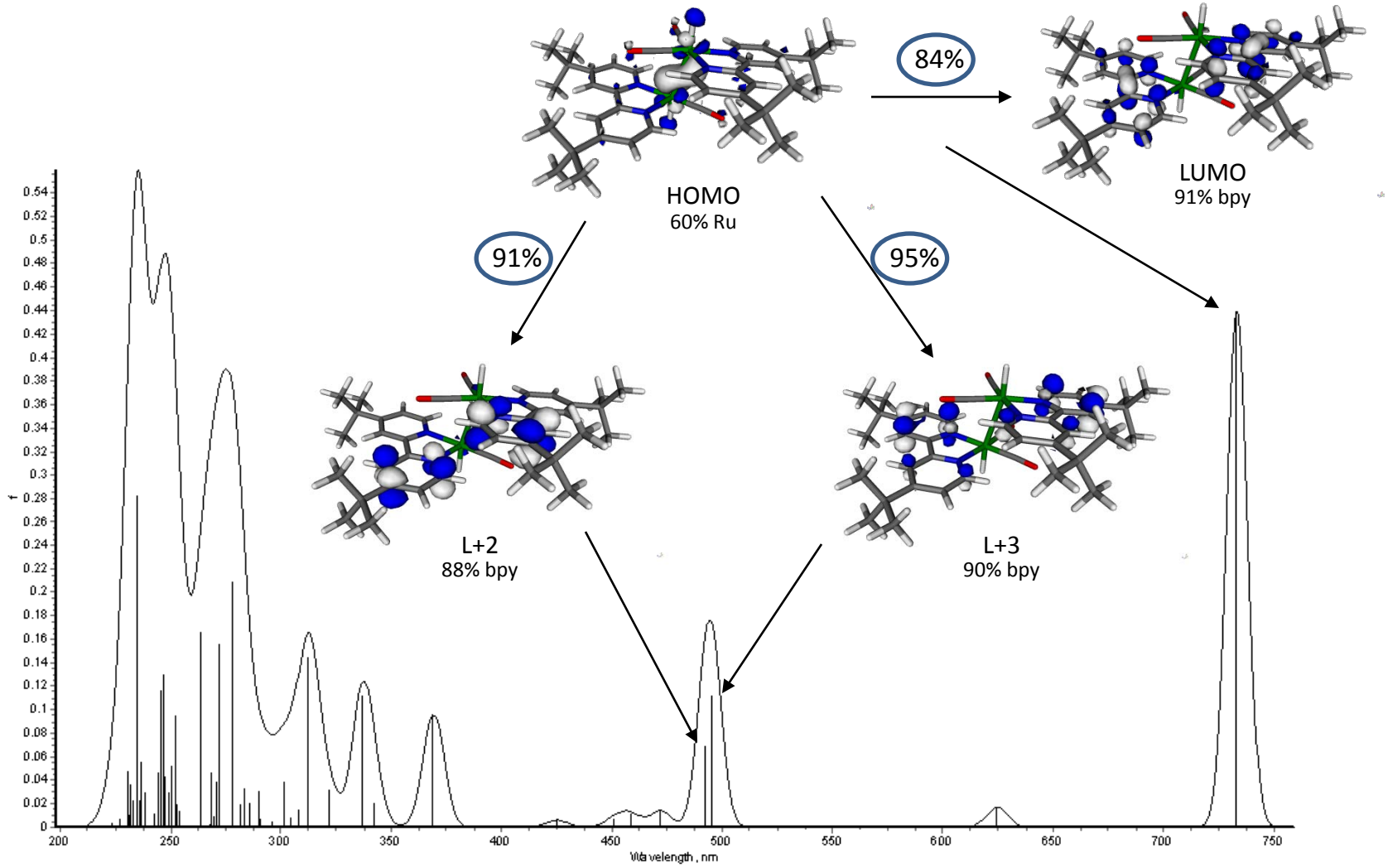
$[Ru(bpy(COOH)_2)(CO)_2]_2H_2$, ~135 dihedral angle



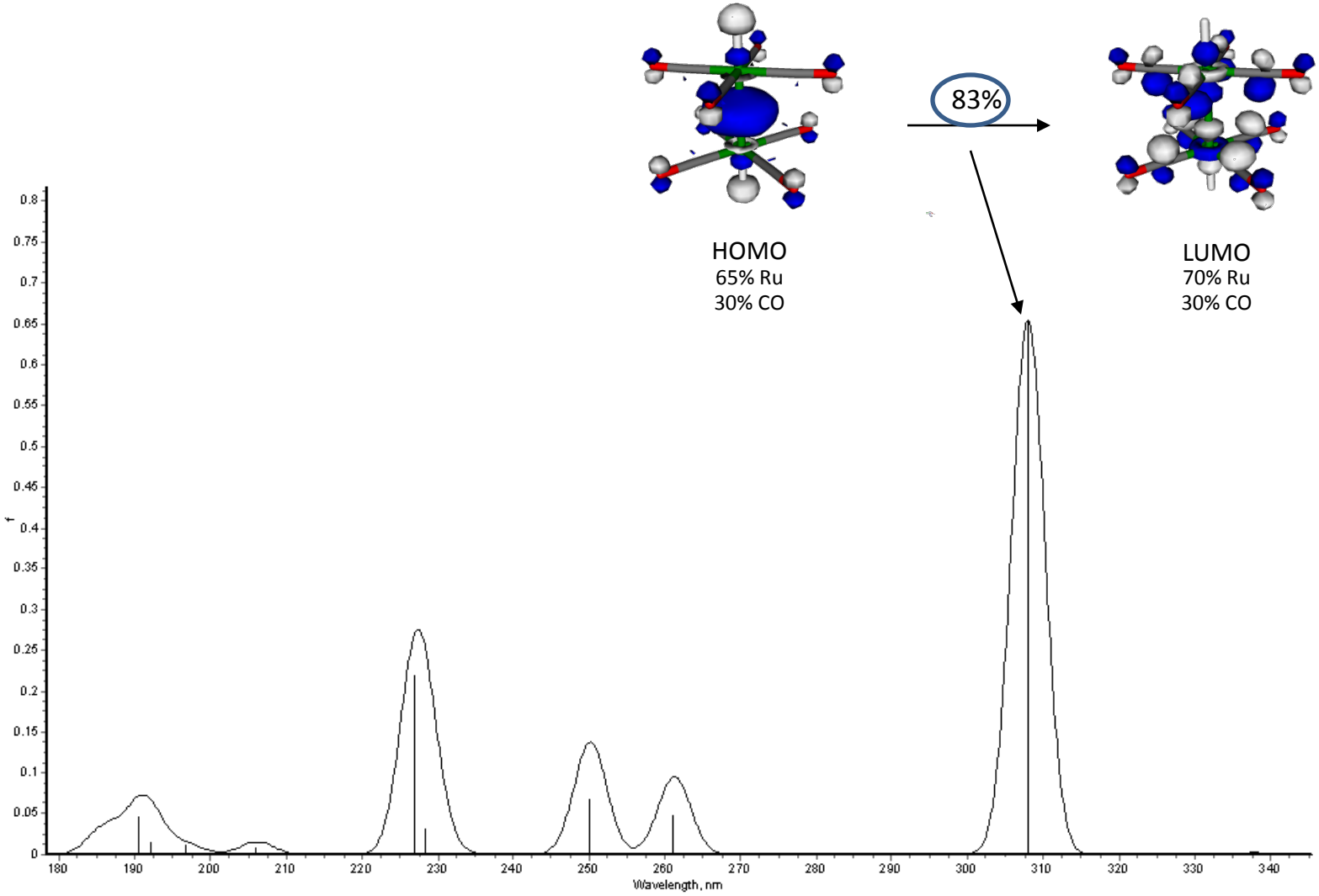
$[Ru(bpy(OH)_2)(CO)_2]_2H_2$, ~135 dihedral angle



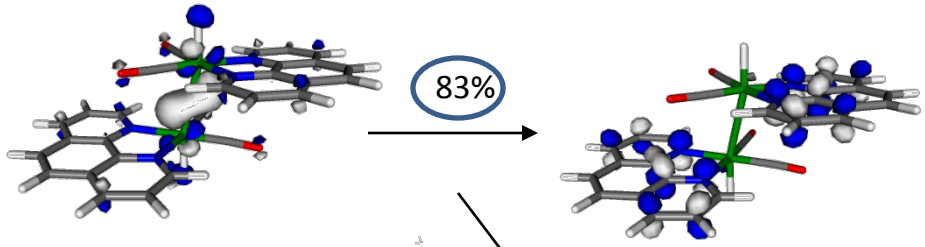
$[Ru(bpy(t\text{-}but)_2)(CO)_2]_2H_2$, ~135 dihedral angle



$[Ru(CO)_4]_2H_2$, ~135 dihedral angle

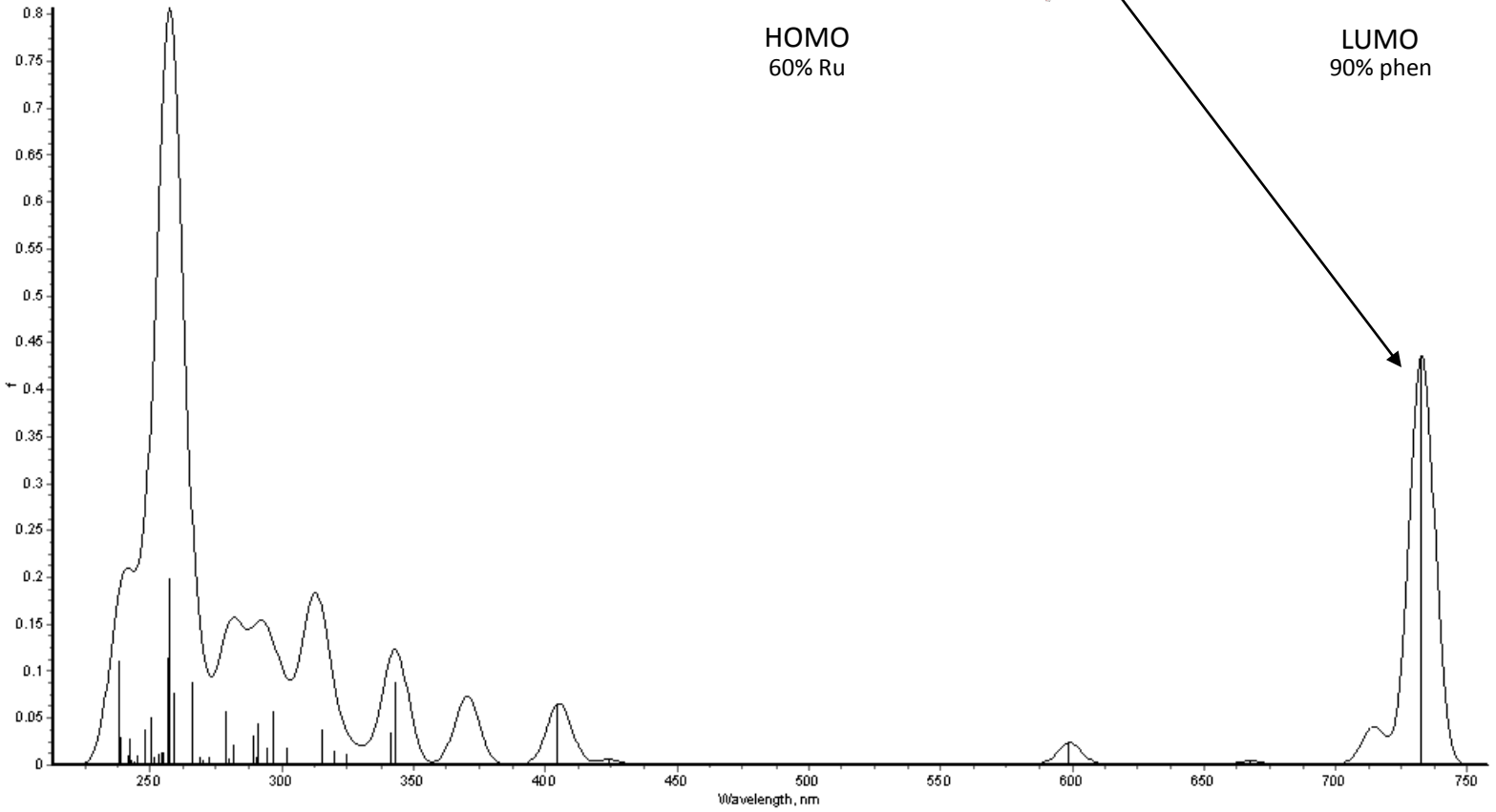


$[Ru(phen)(CO)_2]_2H_2$, ~135 dihedral angle

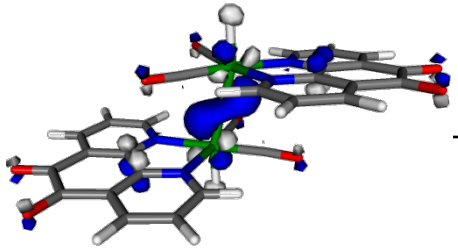


HOMO
60% Ru

LUMO
90% phen

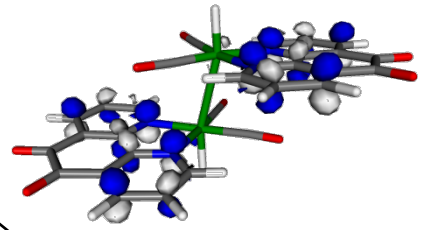


$[Ru(phen(O)_2)(CO)_2]_2H_2$, ~135 dihedral angle

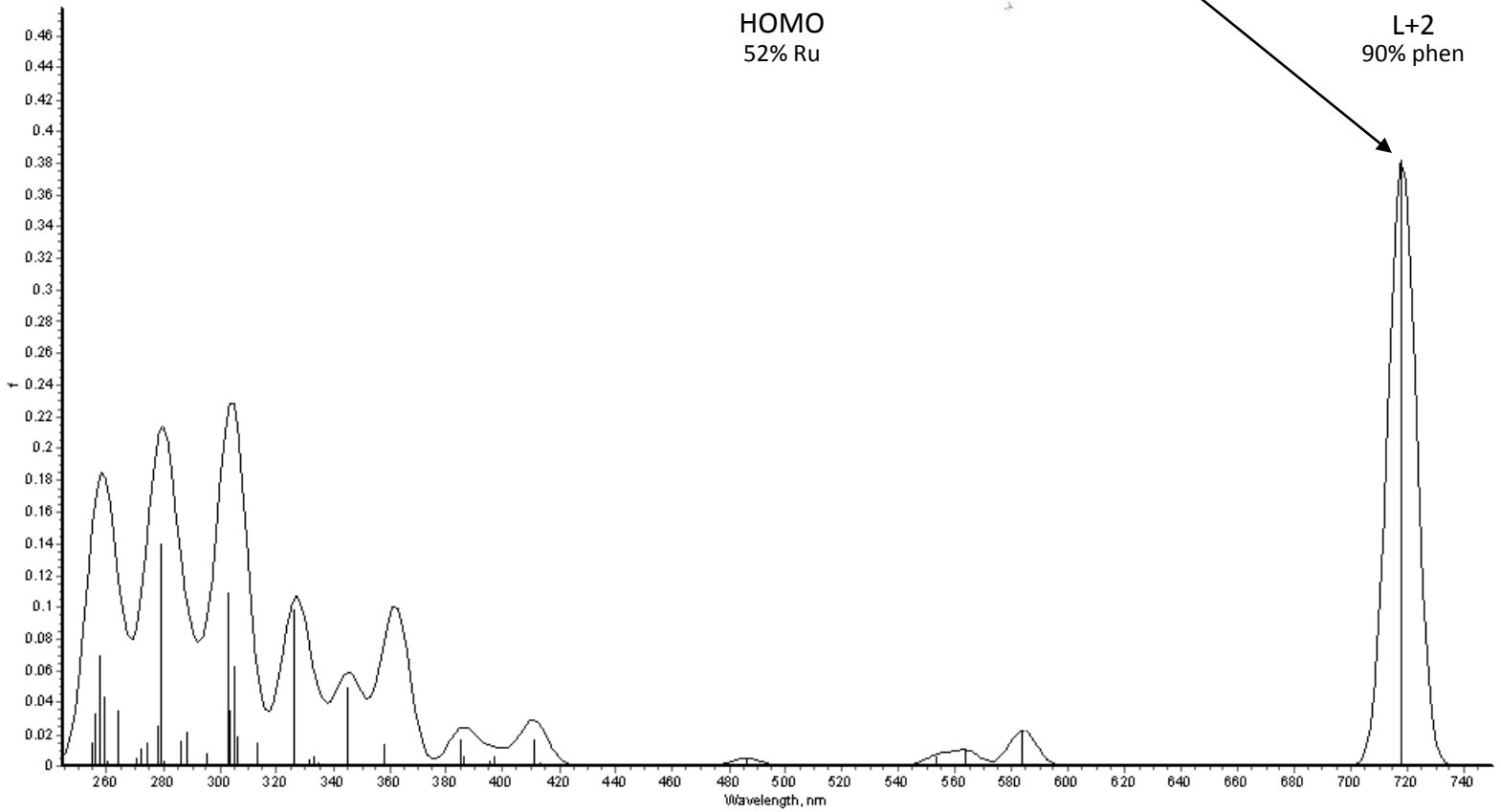


HOMO
52% Ru

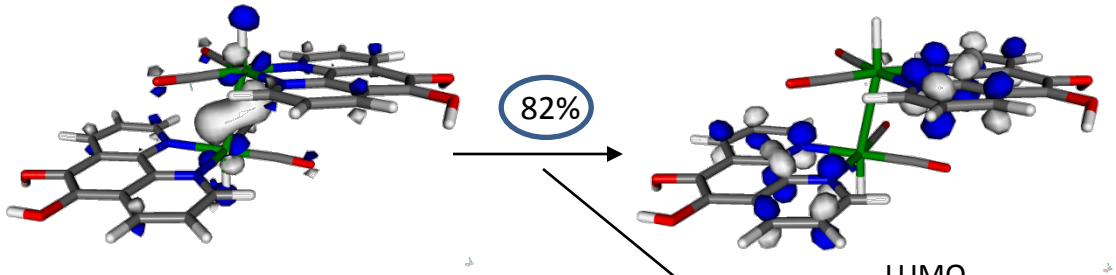
82%



L+2
90% phen

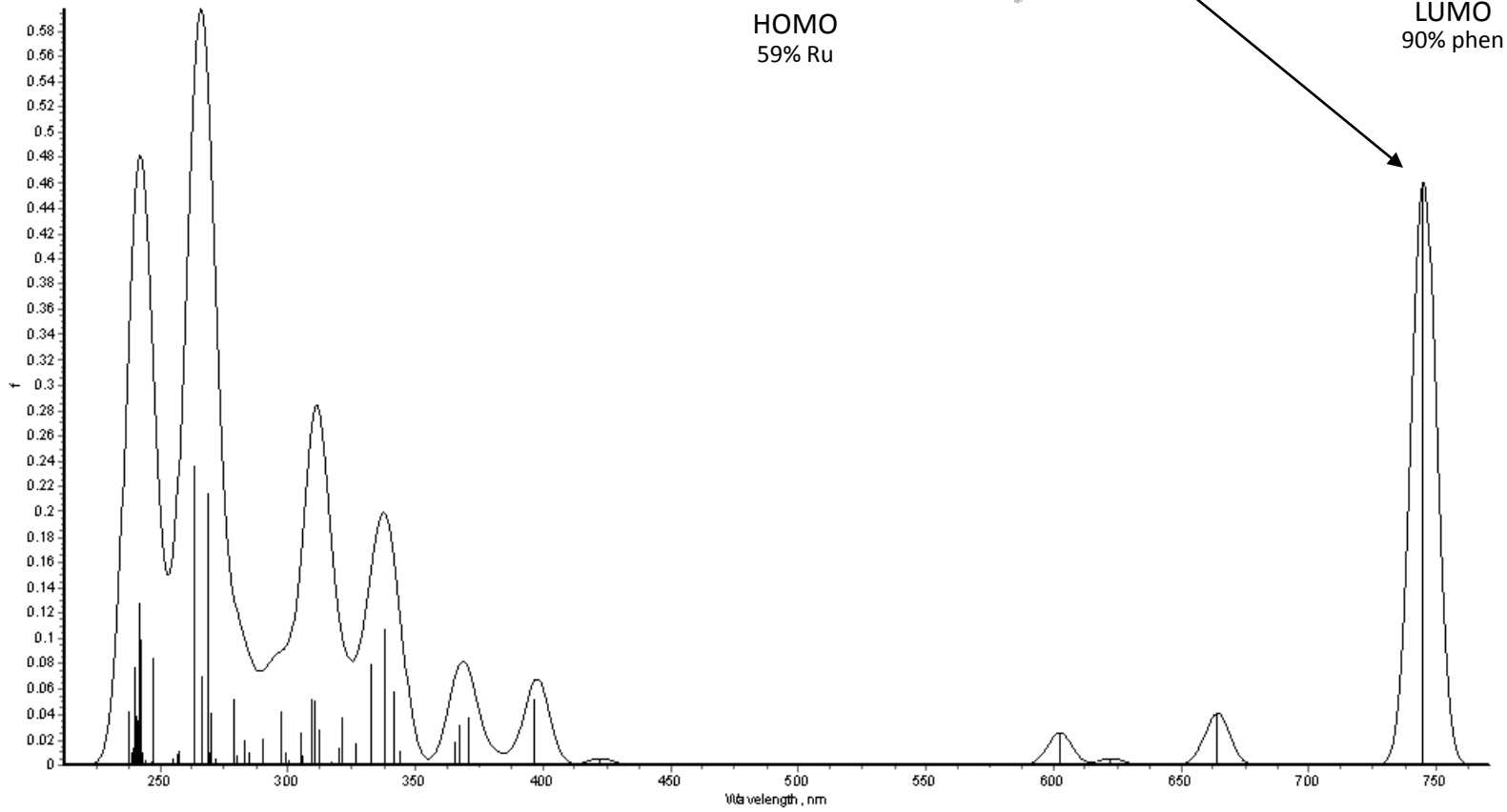


$[Ru(phen(OH)_2)(CO)_2]_2H_2$, ~135 dihedral angle

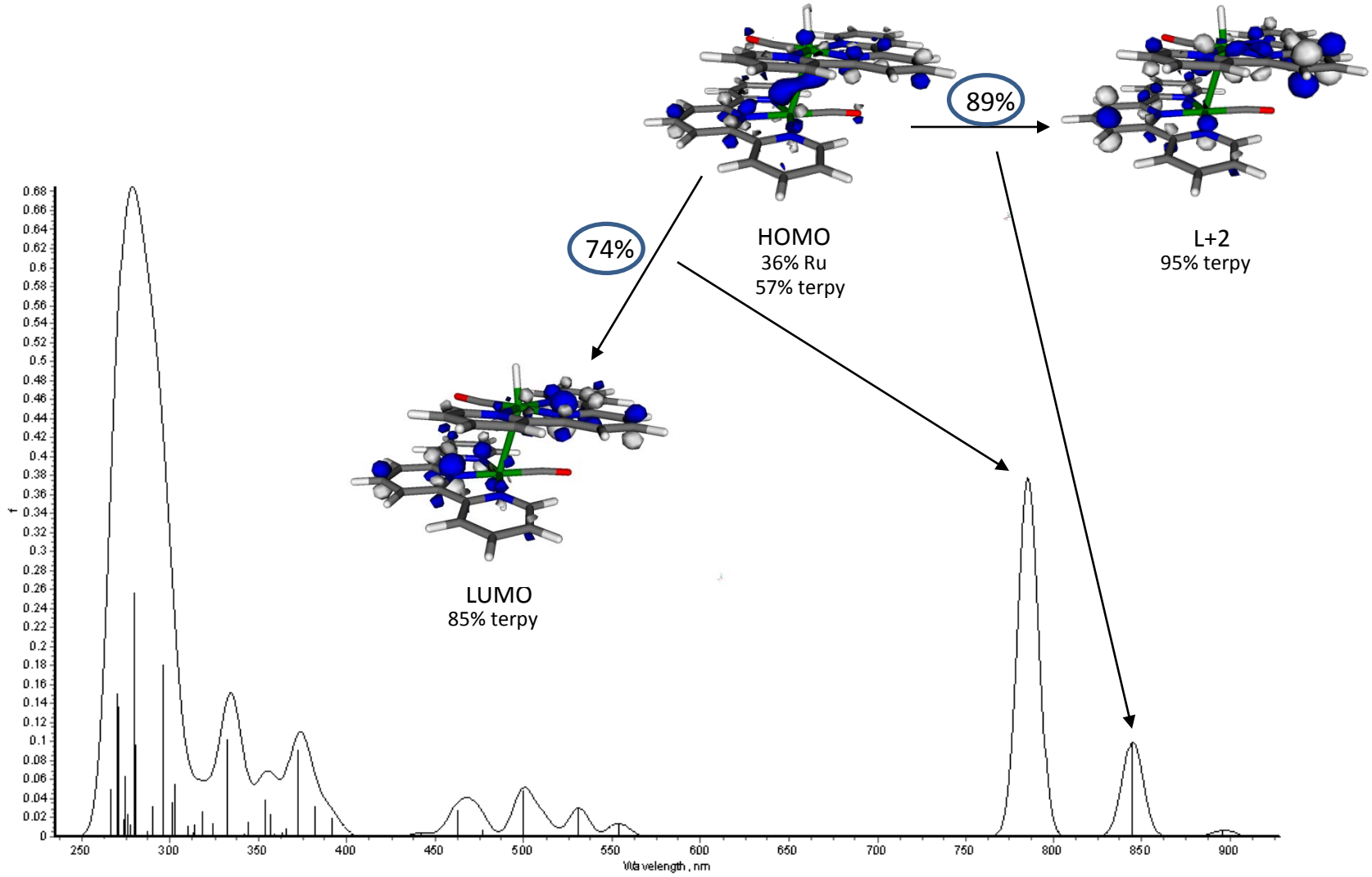


HOMO
59% Ru

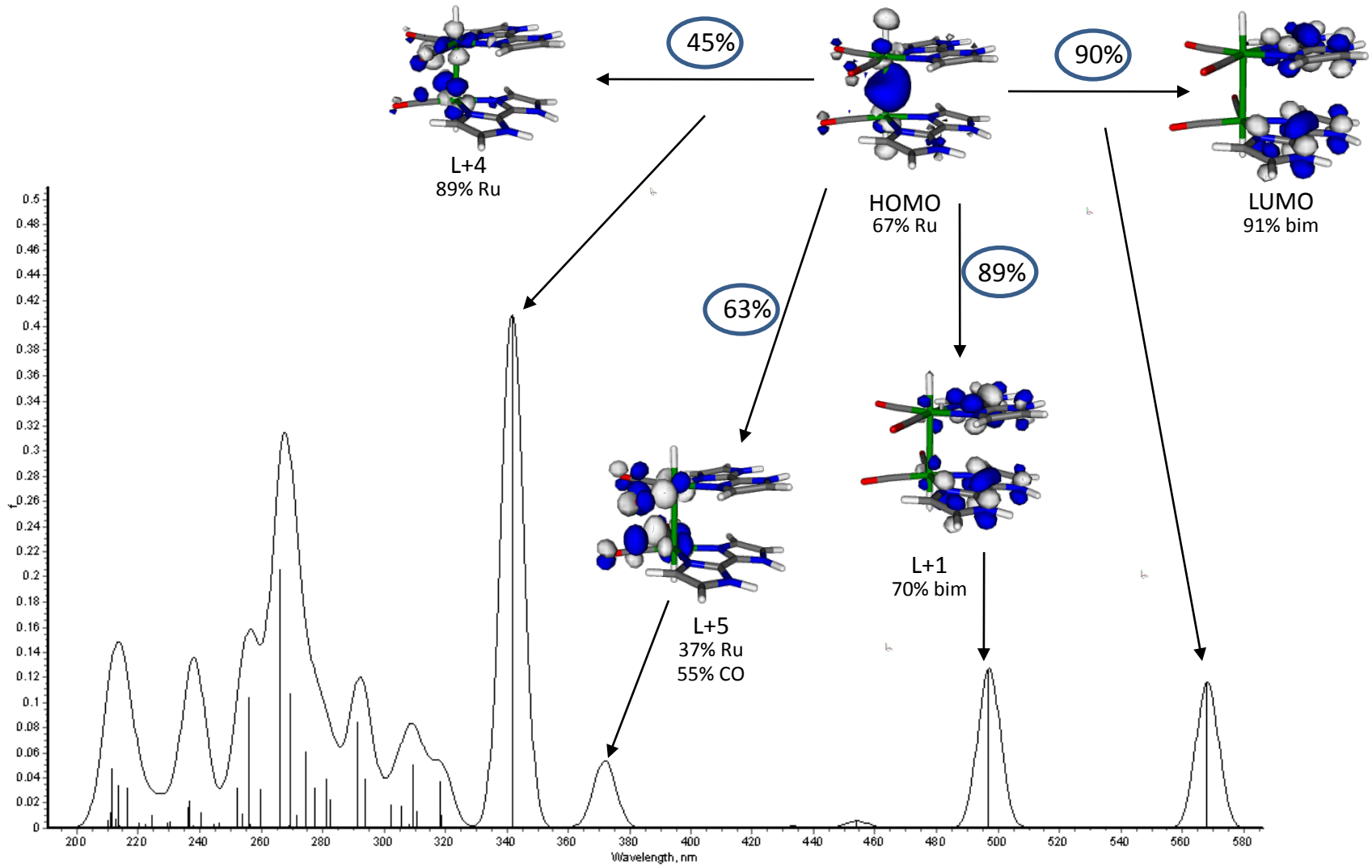
LUMO
90% phen



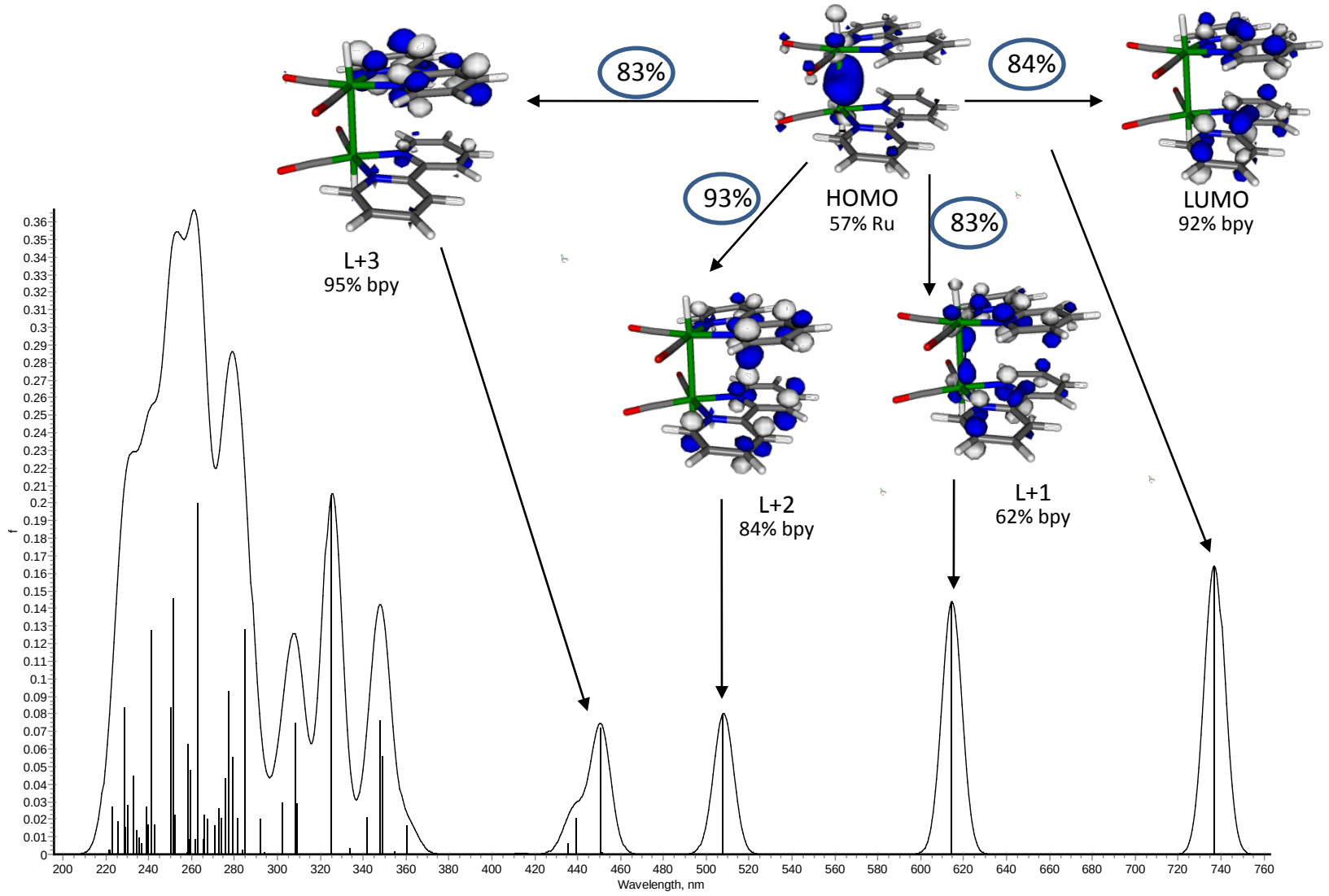
$[Ru(terpy)(CO)]_2H_2$, ~135 dihedral angle



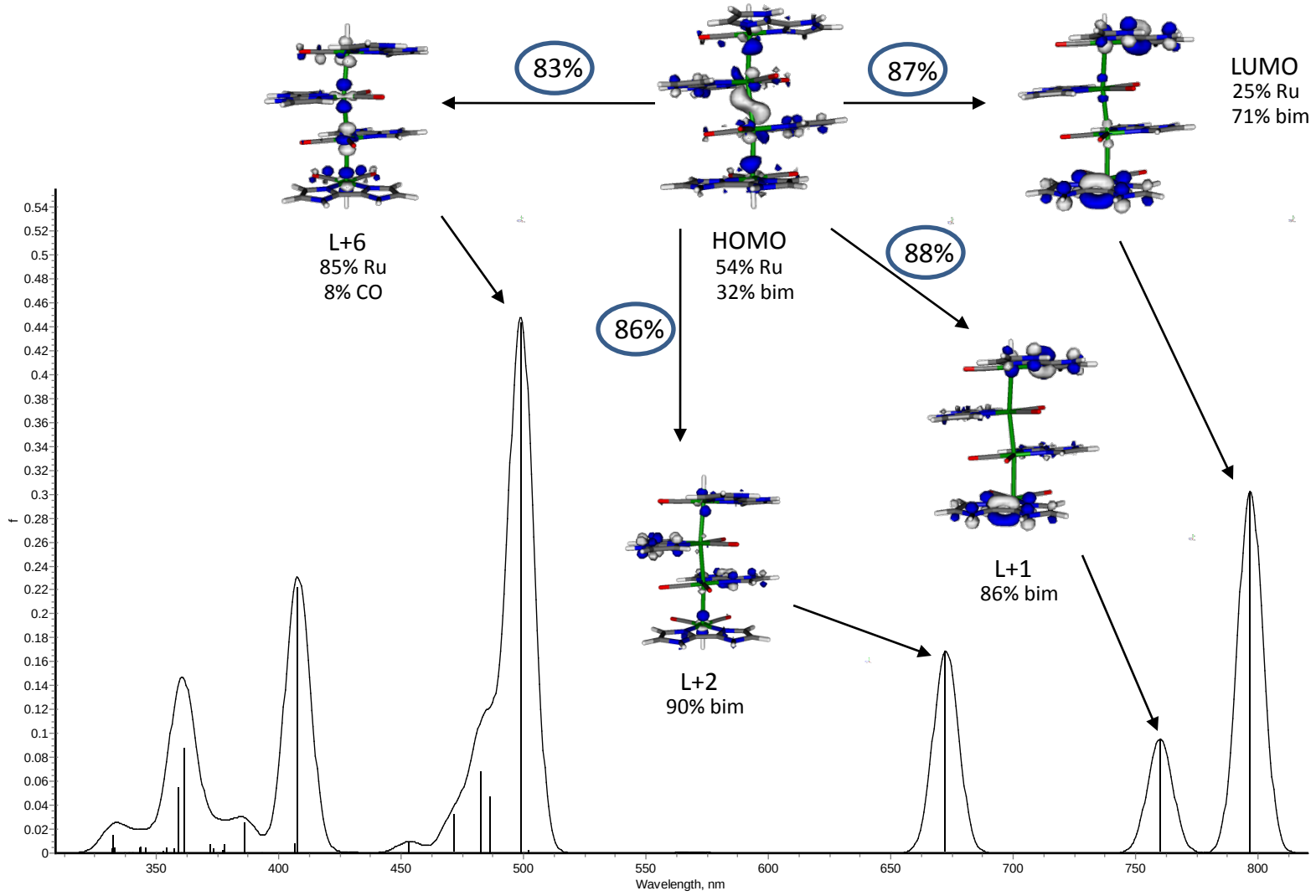
$[Ru(bim)(CO)_2]_2H_2$, ~45 dihedral angle



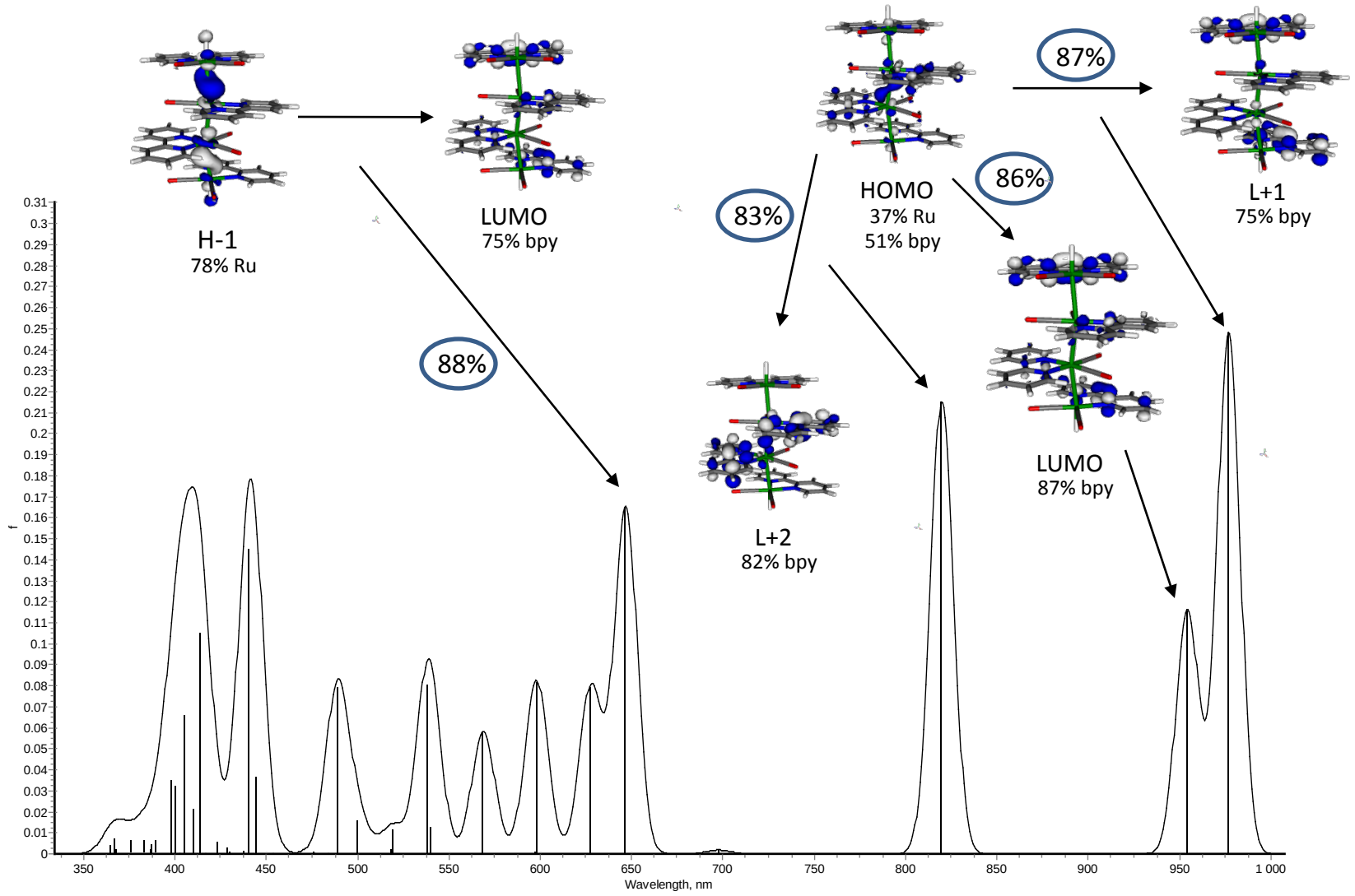
$[Ru(bpy)(CO)_2]_2H_2$, ~45 dihedral angle



$[Ru(bpy)(CO)]_4H_2$, ~135 dihedral angle



$[Ru(bim)(CO)]_4H_2$, ~135 dihedral angle



Similar Low-Energy Excitations

n=2, **Diherdal angle = ~135**			
Complex	Excitation	% in composition	λ (nm)
$[Ru(bim)(CO)_2]_nH_2$	HOMO –> LUMO	90	544
$[Ru(bpy)(CO)_2]_nH_2$	HOMO –> LUMO	82	732
$[Ru(bpy(COOH)_2)(CO)_2]_nH_2$	HOMO –> LUMO	75	824
$[Ru(bpy(OH)_2)(CO)_2]_nH_2$	HOMO –> LUMO	86	758
$[Ru(bpy(t\text{-}but)_2)(CO)_2]_nH_2$	HOMO –> LUMO	84	733
$[Ru(phen)(CO)_2]_nH_2$	HOMO –> LUMO	83	733
$[Ru(phen(O)_2)(CO)_2]_nH_2$	HOMO –> LUMO+2	82	718
$[Ru(phen(OH)_2)(CO)_2]_nH_2$	HOMO –> LUMO	82	745
$[Ru(terpy)(CO)_2]_nH_2$	HOMO –> LUMO	74	786

Similar Low-Energy Excitations

n=4, **Diherdal angle = ~135**			
Complex	Excitation	% in composition	λ (nm)
$[Ru(bim)(CO)_2]_nH_2$	HOMO –> LUMO+2	86	673
$[Ru(bpy)(CO)_2]_nH_2$	HOMO –> LUMO+2	78	820
$[Ru(bpy(COOH)_2)(CO)_2]_nH_2$	HOMO –> LUMO+2	65	880
$[Ru(bpy(OH)_2)(CO)_2]_nH_2$	HOMO –> LUMO+2	79	929
$[Ru(bpy(t\text{-}but)_2)(CO)_2]_nH_2$	HOMO –> LUMO+2	80	840
$[Ru(phen)(CO)_2]_nH_2$	HOMO –> LUMO+4	74	827
$[Ru(phen(O)_2)(CO)_2]_nH_2$	HOMO –> LUMO+6	80	800
$[Ru(phen(OH)_2)(CO)_2]_nH_2$	HOMO –> LUMO+2	51	831
$[Ru(terpy)(CO)_2]_nH_2$	HOMO –> LUMO+4	65	930