Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information Material

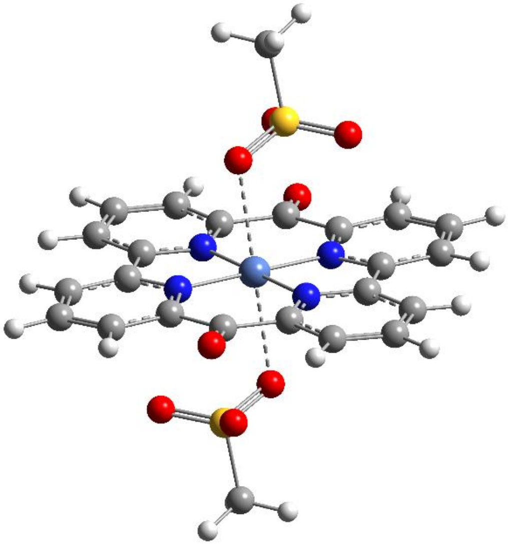
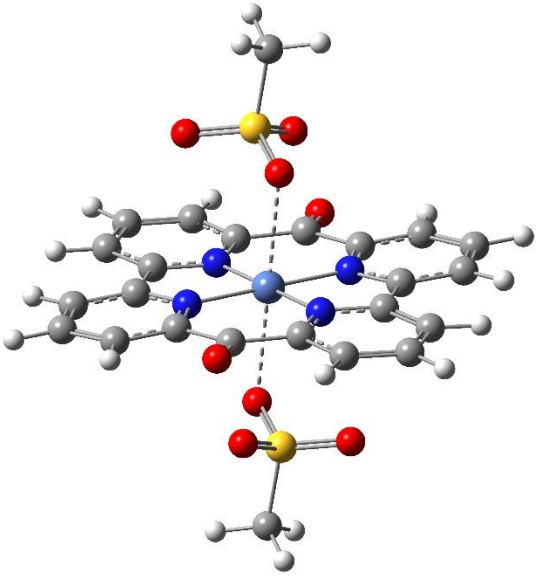
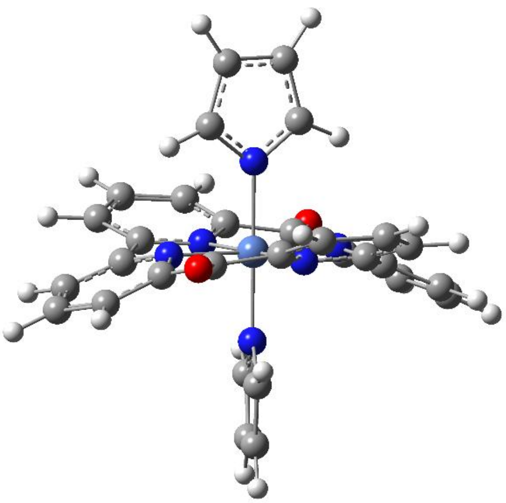
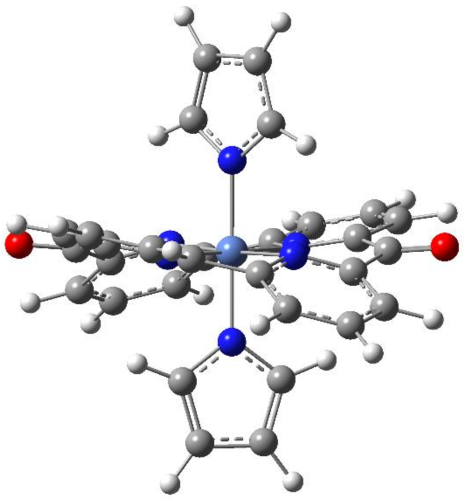
Theoretical modeling of the singlet-triplet spin transition in different Ni(II)-diketo-pyrphyrin based metal-ligand octahedral complexes

Alex A. Farcaș[a,b] and Attila Bende*,[a]

[a]National Institute for Research and Development of Isotopic and Molecular Technologies, Donat Street, No. 67-103, Ro-400293, Cluj-Napoca, Romania.

[b]Faculty of Physics, "Babeş-Bolyai" University, Mihail Kogalniceanu Street No. 1, Ro-400084 Cluj-Napoca, Romania.

Table S1. The equilibrium geometry conformations of the four proposed metal-organic complexes for the singlet spin configuration calculated at B3LYP*-D3/def2-TZVP and CAM-B#LYP-17-D3 levels of theory.

Geom.	B3LYP*-D3	CAM-B3LYP-17-D3
DP⊕Mes		
DP⊕Py		

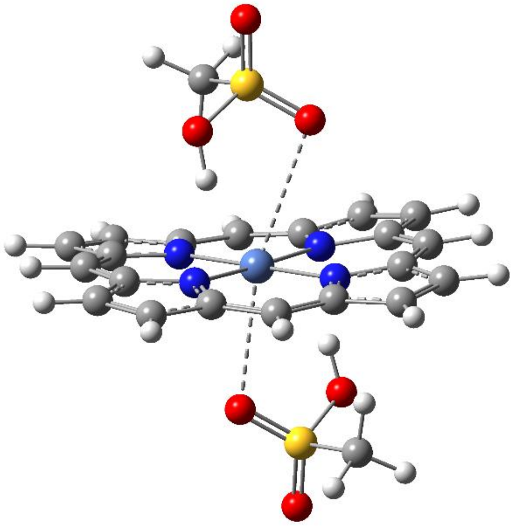
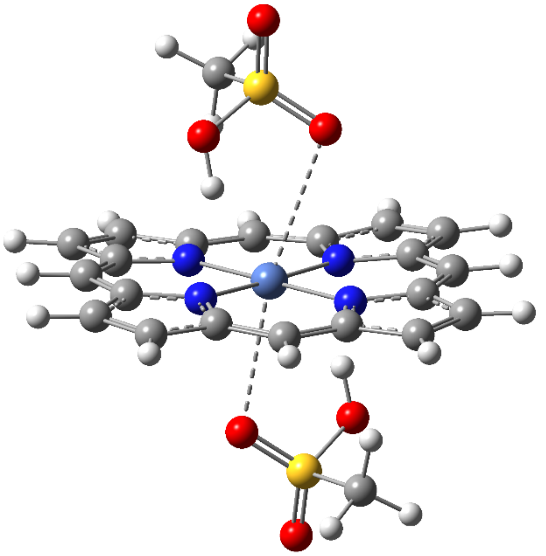
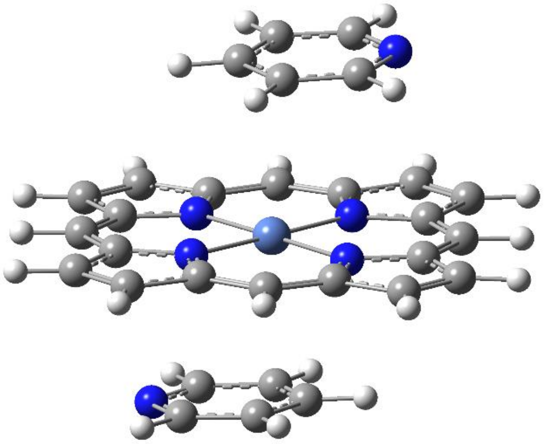
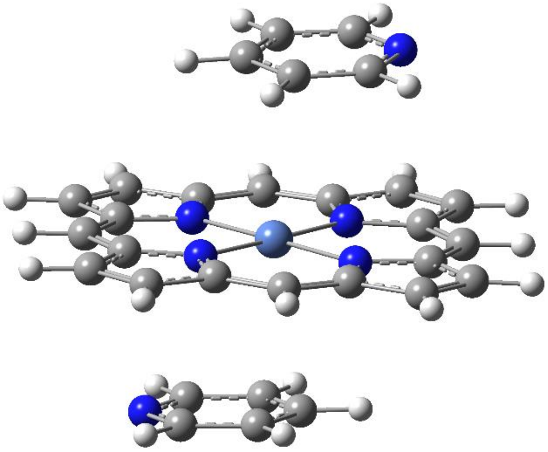
P⊕Mes		
P⊕Py		

Table S2. The equilibrium geometry conformations of the four proposed metal-organic complexes for the triplet spin configuration calculated at B3LYP*-D3/def2-TZVP and CAM-B#LYP-17-D3 levels of theory.

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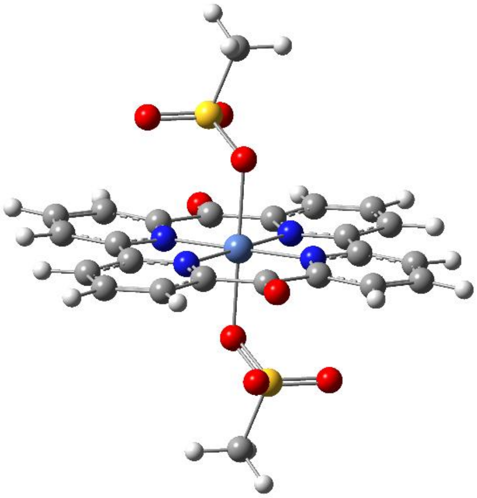
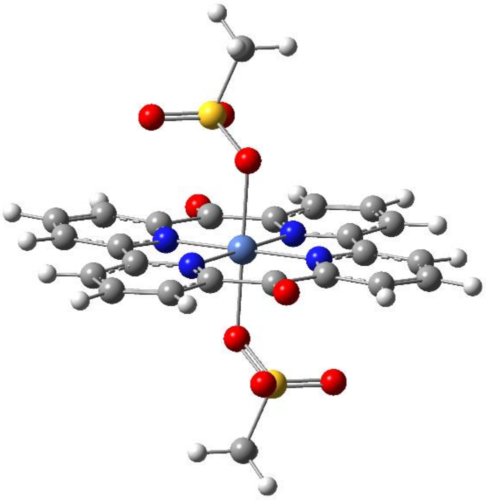
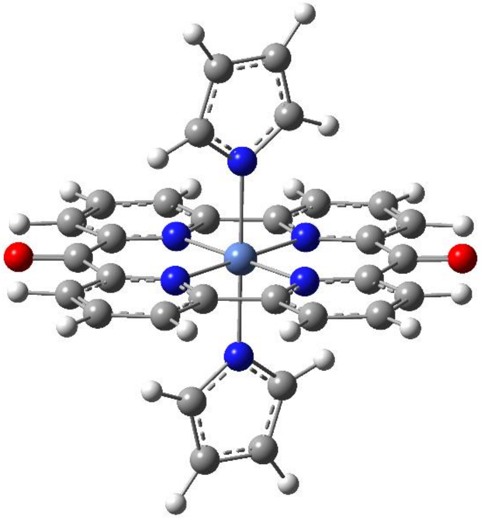
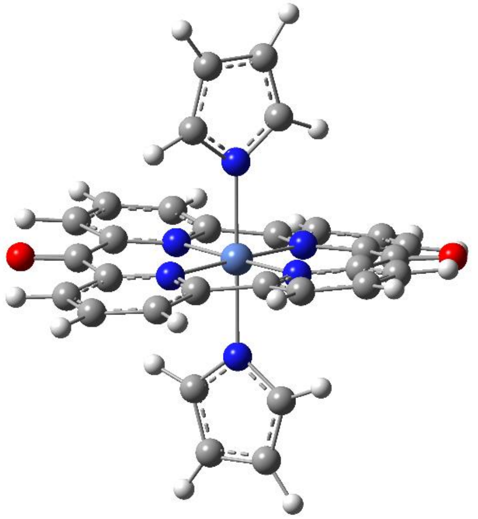
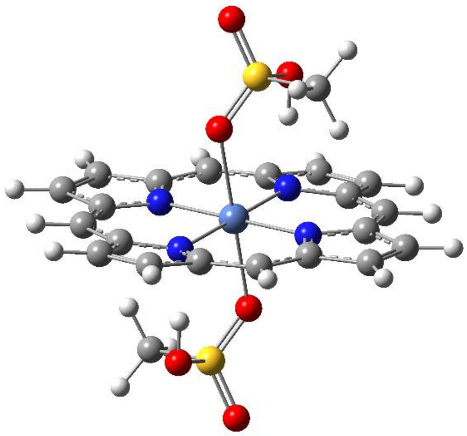
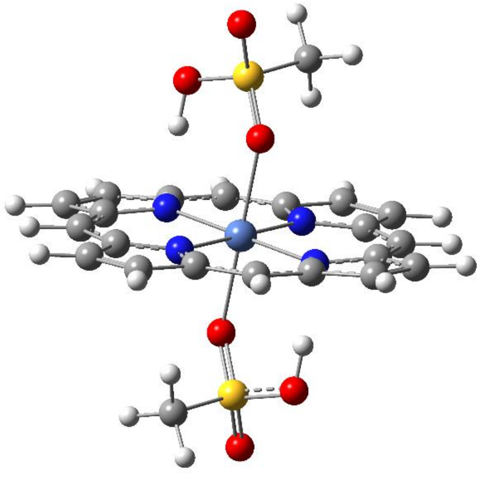
DP⊕Mes		
DP⊕Py		
P⊕Mes		

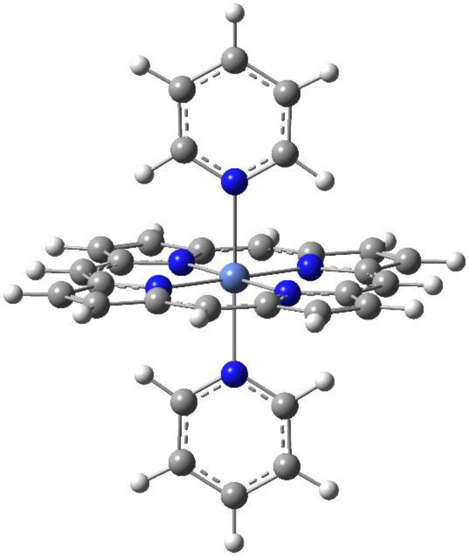
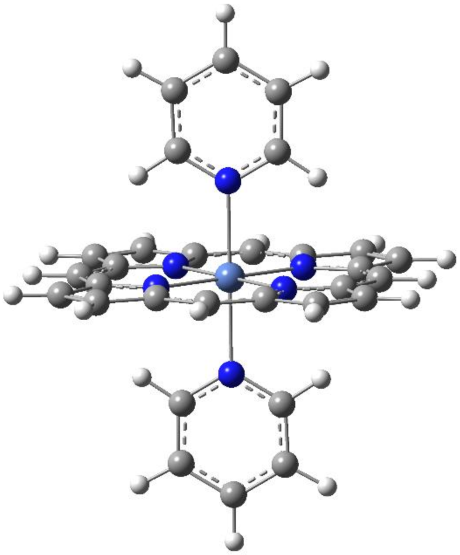
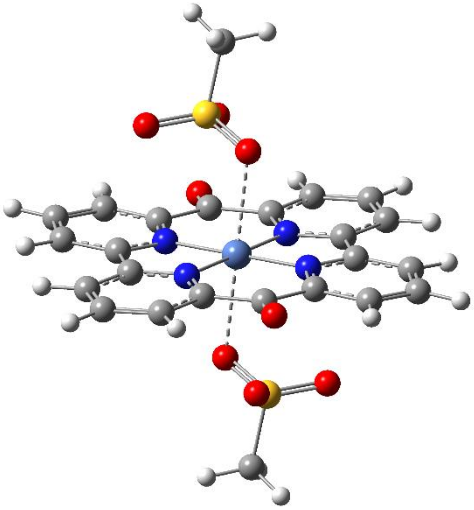
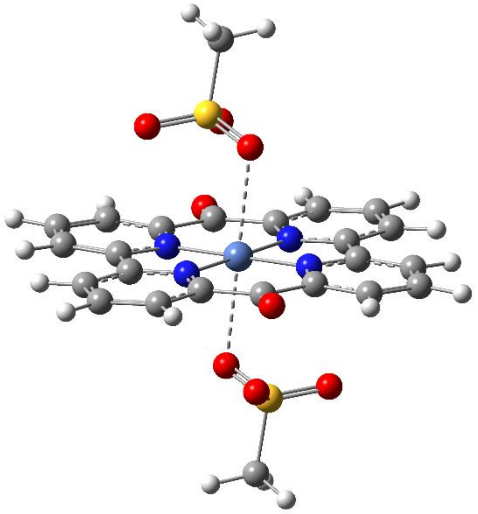
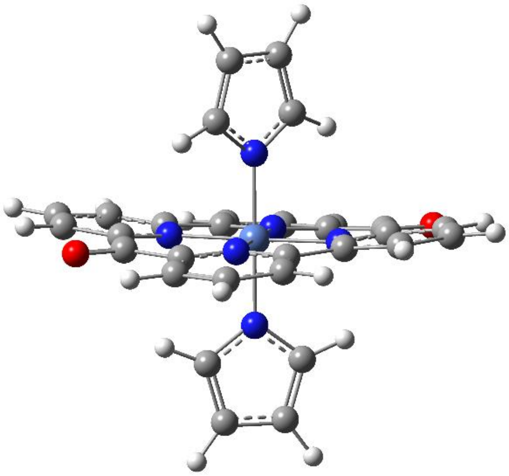
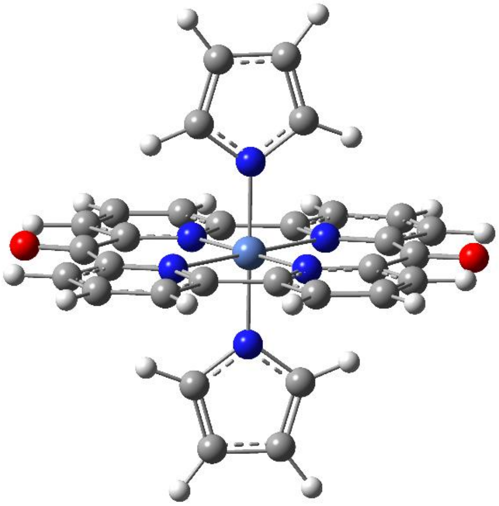
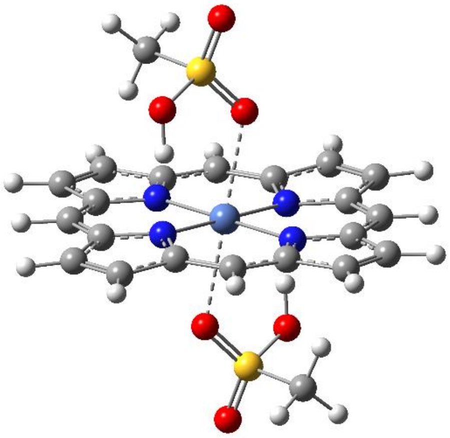
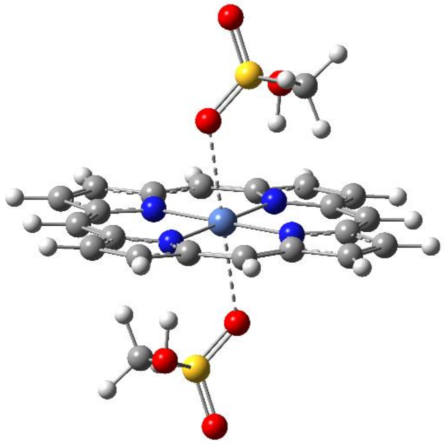
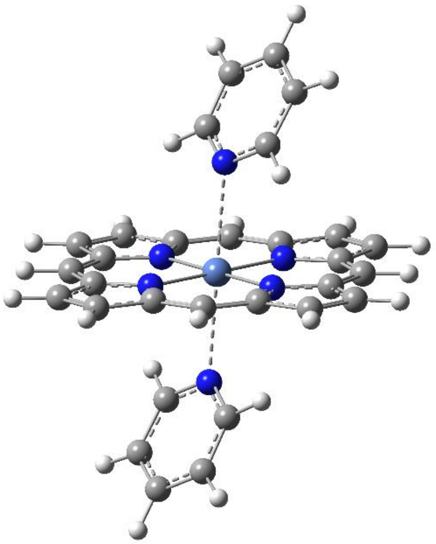
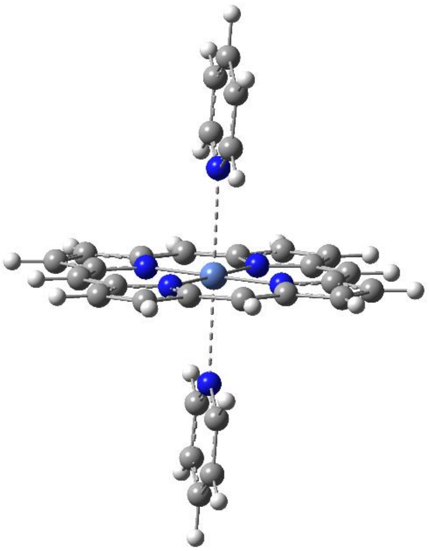
P⊕Py		

Table S3. The equilibrium geometry conformations of the four proposed metal-organic complexes for the MECP geometry configuration calculated at B3LYP*-D3/def2-TZVP and CAM-B3LYP-17-D3 levels of theory.

Geom.	**B3LYP*-D3**	**CAM-B3LYP-17-D3**
DP⊕Mes		

DP⊕Py		
P⊕Mes		
P⊕Py		

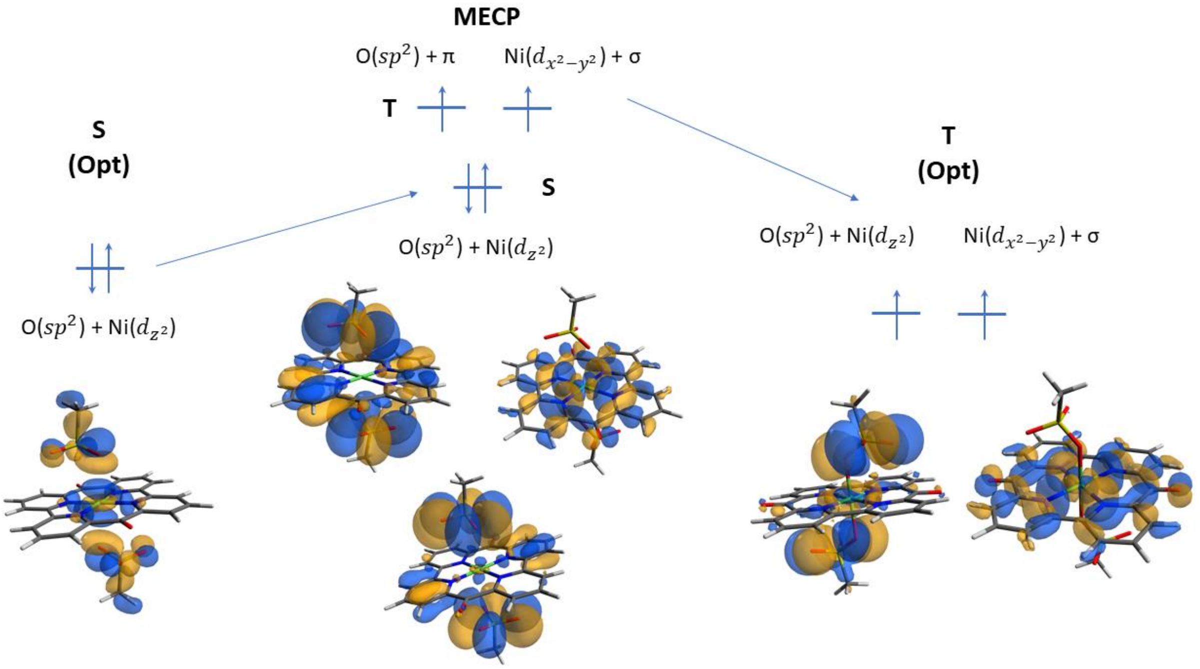


Figure S1. The orbitals transition scheme between the equilibrium geometries with singlet and triplet spin states for the DP⊕Mes metal-organic complex obtained at CAM-B3LYP-17-D3 level of theory.

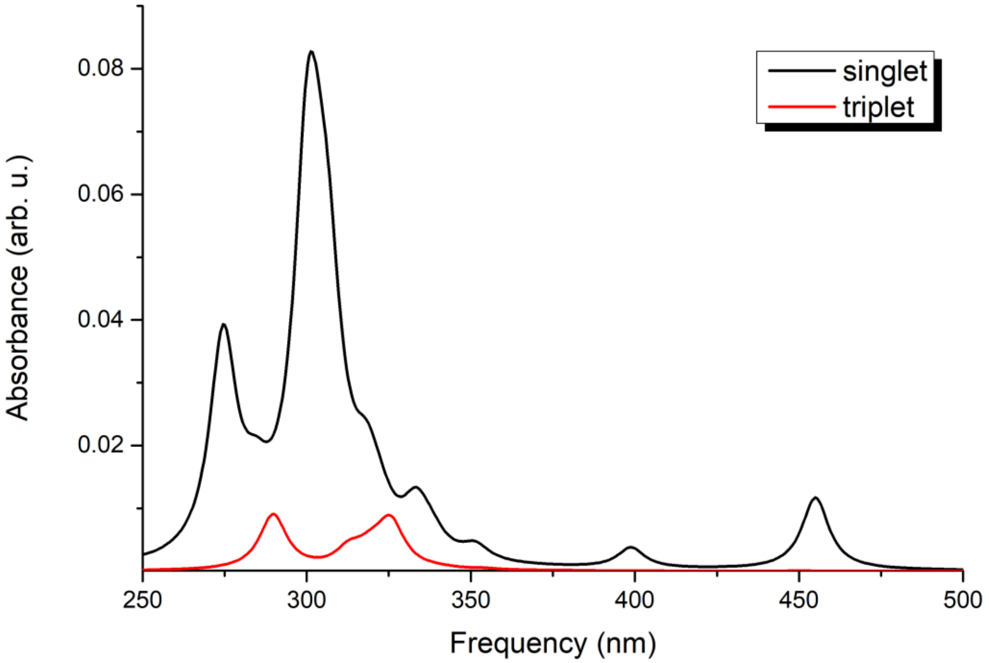
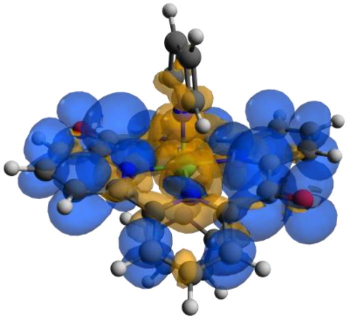
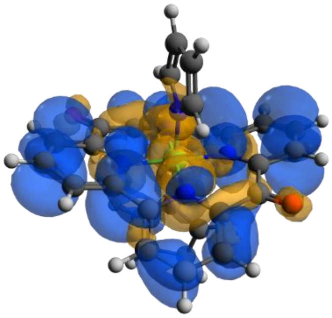
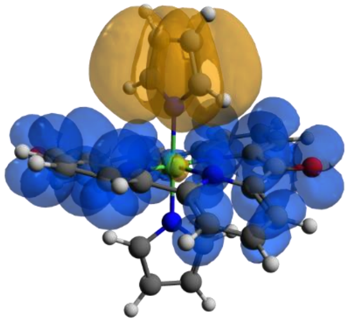
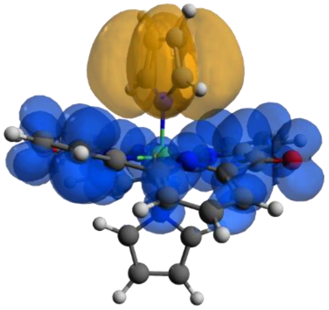
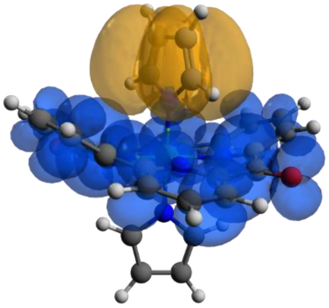
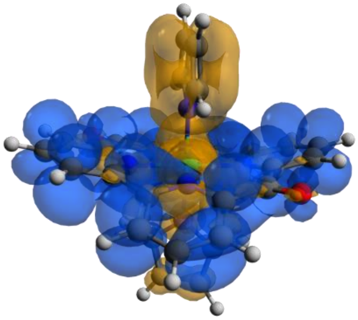
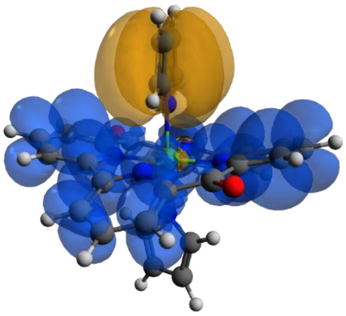
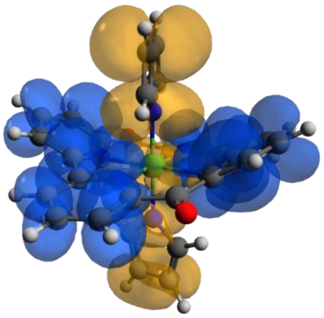
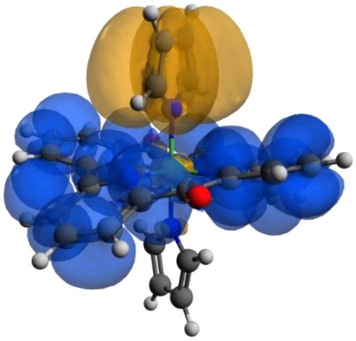
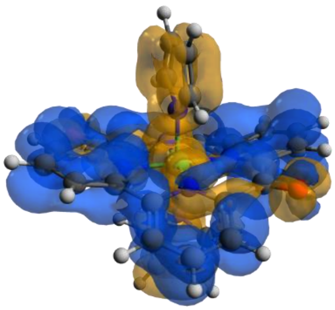


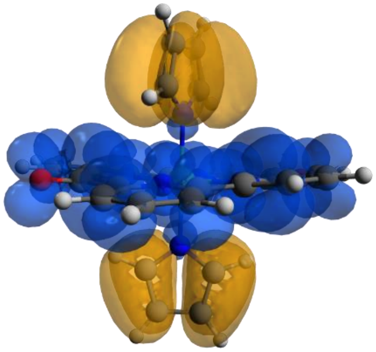
Figure S2. The theoretical UV-Vis absorption spectra with both the singlet and triplet spin configurations, computed for the DP⊕Mes metal-organic complex considering the TD-DFT framework at CAM-B3LYP-17/def2-TZVP level of theory.

Table S4. The most relevant electronic excited states and their oscillator strengths in parenthesis ($f_{osc} > 0.003$ for singlet and $f_{osc} > 0.001$ for triplet) for the DP⊕Py metal-organic complex with octahedral coordination computed at TD-DFT/CAM-B3LYP-17-D3/def2-TZVP level of theory considering both the singlet and triplet spin configurations. (VL = vertical ligand; PL = planar ligand; M = metal)

El. Excited State	Singlet		El. Excited State	Triplet	
	Trans.	Freq.		Trans.	Freq.
S_2	π → π, VL → PL, M → PL	869.2 (0.0355)	T_3	VL → PL	713.6 (0.0240)
S_4	n → π, VL → PL, M → PL	665.8 (0.0534)	T_6	VL → PL	655.2 (0.0010)
S_6	VL, M → PL	573.4 (0.0116)	T_8	VL → PL	640.9 (0.0130)
S_8	VL → PL	557.5 (0.0140)	T_9	VL → M π → π	596.3 (0.0067)
S_{11}	VL → PL	499.1 (0.0043)	T_{13}	VL → PL	546.8 (0.001
S_{13}	VL, M → PL	455.7 (0.0138)	T_{16}	VL, M → PL	540.5 (0.0099)
S_{17}	VL, M → PL	439.8 (0.0037)	T_{18}	VL → PL	537.7 (0.0005)
S_{26}	VL, M → PL	355.5 (0.0070)	T_{20}	VL → PL	538.6 (0.0010)
S_{29}	VL, M → PL	345.8 (0.0057)	T_{24}	VL, M → PL	516.2 (0.0019)
S_{30}	π → π VL, M → PL				

Table S5. The orbital shapes of the Natural Difference Orbitals (NDO) obtained as the difference between the corresponding ground state and the electronic excited state densities for the DP⊕Py metal-organic complex with octahedral coordination computed at TD-DFT/CAM-B3LYP-17-D3/def2-TZVP level of theory (blue is the positive and orange means the negative densities).

 S_2	 S_4	 S_6
 S_8	 S_{11}	 S_{13}
 S_{17}	 S_{26}	 S_{29}
	 S_{30}	



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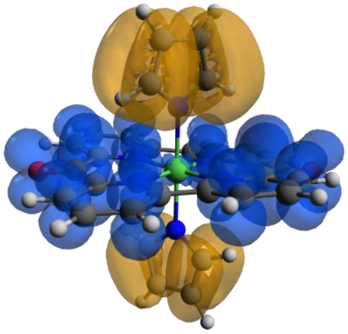

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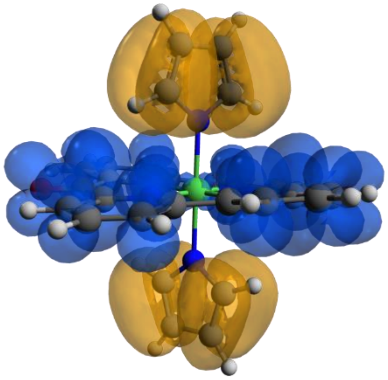

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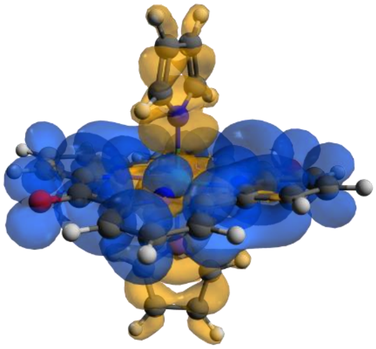

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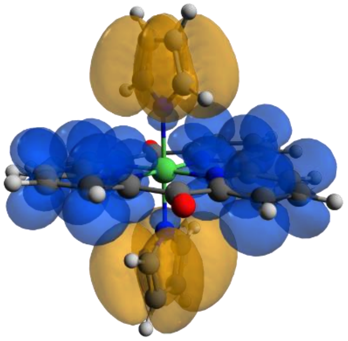

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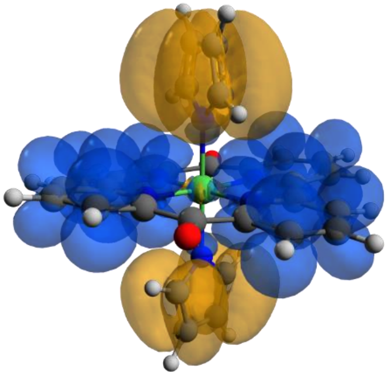

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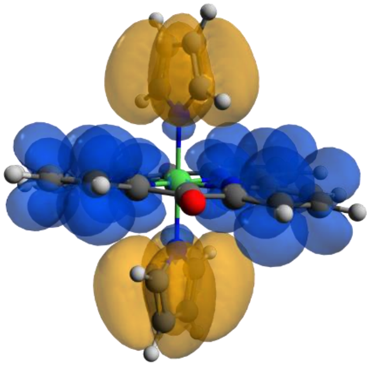

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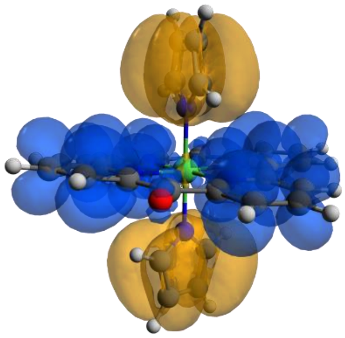

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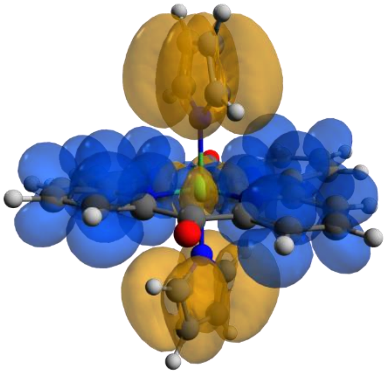

T_{24}