Complexation behavior of trivalent Actinides and Lanthanides with 1,10-Phenanthroline-2,9-dicarboxylic acid based ligands: Insight from Hard Soft Acid Base Principle.

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(2) Figure Captions

1. Figure S1. Molecular structure of [Metal-PHEN]$^{3+}$ Complexes, where M= Am/Eu/U/Ce.

2. Figure S2. Valence level occupied molecular orbitals of a) Metal Complexes, [ML]$^{+}$ and b) [Metal-PHEN]$^{3+}$ Complexes, where M= Am/Eu/U/Ce, L= PDA, TCA1, TCA, THIO.
PDA: 1,10-Phenanthroline-2,9-dicarboxylic acid;
TCA1: 1,10-Phenanthroline-2,9-mono-thio-dicarboxylic Acid (binding through Oxygen);
TCA: 1,10-Phenanthroline-2,9-mono-thio-dicarboxylic Acid (binding through Sulphur);
and THIO: 1,10-Phenanthroline-2,9-di-thio-dicarboxylic Acid.

Table S1.Calculated M-L bond distances (Å) and complexation energies (eV) in gas (ΔE_g) and solvent (ΔE_s) phases for Am and Eu complexes with TZVP/BP86 method

Complex	M-O/M-S	M-N	M-O/M-S	M-N	(ΔE_g)	(ΔE_s)
	Gas	Gas	Solvent	Solvent		
[Am-PDA]$^{+}$	2.182	2.506	2.275	2.523	-40.37	-5.62
[Eu-PDA]$^{+}$	2.227	2.527	2.329	2.562	-41.45	-3.63
[Am-TCA1]$^{+}$	2.223	2.499	2.299	2.519	-39.52	-5.14
[Eu-TCA1]$^{+}$	2.305	2.525	2.372	2.572	-40.98	-3.33
[Am-TCA]$^{+}$	2.638	2.576	-------	-------	-39.17	------
[Eu-TCA]$^{+}$	2.679	2.575	-------	-------	-40.47	------
[Am-THIO]$^{+}$	2.697	2.553	-------	-------	-38.84	------
[Eu-THIO]$^{+}$	2.769	2.550	-------	-------	-40.39	------

Table S2. Calculated Bond distances (d in Å) for $[ML]^+$ complexes obtained from ADF software with TZ2P basis sets and BP86 exchange-correlation functional in the gas phase

	Bond Distances							
→ Ligand	PDA		TCA1		TCA		THIO	
↓ Metal	d_{M-O} Å	d_{M-N} Å	d_{M-O} Å	d_{M-N} Å	d_{M-S} Å	d_{M-N} Å	d_{M-S} Å	d_{M-N} Å
Am	2.193	2.506	2.233	2.500	2.579	2.645	2.566	2.688
Eu	2.222	2.508	2.292	2.503	2.556	2.673	2.539	2.739
U	2.152	2.434	2.141	2.407	2.428	2.613	2.418	2.619
Ce	2.206	2.506	2.213	2.493	2.518	2.677	2.495	2.676

Table S3. Effect of different Exchange correlation functionals (PBE and BLYP) on the M-L bond distance (d in Å) of $[ML]^+$ complexes calculated using def-SV(P)

LIGAND NAME	METAL	B-LYP		PBE	
PDA		d_{M-O}	d_{M-N}	d_{M-O}	d_{M-N}
	Ce	2.223	2.571	2.207	2.545
	Eu	2.233	2.548	2.218	2.531
	U	2.172	2.474	2.147	2.438
	Am	2.198	2.533	2.179	2.508
TCA1	Ce	2.233	2.552	2.217	2.526
	Eu	2.307	2.547	2.292	2.523
	U	2.172	2.469	2.147	2.435
	Am	2.237	2.528	2.217	2.501
TCA	Ce	2.660	2.534	2.654	2.534
	Eu	2.699	5.593	2.669	2.576
	U	2.651	2.459	2.607	2.410
	Am	2.663	2.603	2.629	2.576
THIO	Ce	2.700	2.533	2.682	2.529
	Eu	2.793	2.570	2.753	2.541
	U	2.653	2.439	2.640	2.435
	Am	2.727	2.580	2.688	2.556

Table S4. Calculated Hardness and Softness values of the metal ions, dianionic form of the bare ligands and [M-PHEN]$^{3+}$ complexes in gas and solvent phases using def-SV(P)/BP86 method

COMPLEX NAME	HARDNESS		SOFTNESS	
	Gas Phase	Solv	Gas Phase	Solv
Am^{3+}	0.526	0.270	1.901	3.708
Eu^{3+}	0.682	0.395	1.466	2.533
U^{3+}	0.497	0.258	2.013	3.869
Ce^{3+}	0.630	0.383	1.588	2.609
$[PDA]^{2-}$	0.196	0.126	5.097	7.914
$[TCA/TCA1]^{2-}$	0.187	0.095	5.352	10.571
$[THIO]^{2-}$	0.179	0.099	5.581	10.062
PHEN	0.305	0.177	3.282	5.654
$[Am\text{-}PHEN]^{3+}$	0.176	0.077	5.680	12.943
$[Eu\text{-}PHEN]^{3+}$	0.179	0.072	5.596	13.964
$[U\text{-}PHEN]^{3+}$	0.237	0.135	4.216	7.429
$[Ce\text{-}PHEN]^{3+}$	0.231	0.119	4.324	8.435

Table S5. Calculated values of charges on donor center and Fukui indices for the nucleophilic attack on the donor sites in gas and solvent phases for the dianionic form of the bare ligands using def-SV(P)/BP86 method

GAS PHASE RESULTS:

LIGAND NAME	q_N	q_O/q_S	f^-_k (O) or f^-_k (S)	f^-_k (N)	f_{el} (O or S)	f_{el} (N)
$[PDA]^{2-}$	-0.446	-0.691	0.142	0.040	3.017	3.137
$[TCA1]^{2-}$	-0.445	-0.589	0.068	0.024	1.623	0.933
$[TCA]^{2-}$	-0.445	-0.450	0.290	0.024	2.273	0.933
$[THIO]^{2-}$	-0.439	-0.196	0.202	0.010	2.335	1.189

SOLV PHASE RESULTS:

LIGAND NAME	q_N	q_O/q_S	f^-_k (O) or f^-_k (S)	f^-_k (N)
$[PDA]^{2-}$	-0.496	-0.756	0.129	0.061
$[TCA1]^{2-}$	-0.493	-0.639	0.061	0.028
$[TCA]^{2-}$	-0.493	-0.491	0.331	0.028
$[THIO]^{2-}$	-0.496	-0.227	0.203	0.024

Table S6. Calculated values of Fukui indices for the electrophilic attack on the metal centre of $[M\text{-}PHEN]^{3+}$ complexes in gas and solvent phases using def-SV(P)/BP86 method

COMPLEX NAME	f^{+}_{k} (M)		f_{nu} (M)
	Gas Phase	Solv phase	Gas Phase
$[Am\text{-}PHEN]^{3+}$	0.280	0.531	1.456
$[Eu\text{-}PHEN]^{3+}$	0.152	0.307	1.029
$[U\text{-}PHEN]^{3+}$	0.607	0.905	3.529
$[Ce\text{-}PHEN]^{3+}$	0.327	0.511	1.741

Table S7. Calculated atomic charges on metal and donor centers of Am and Eu complexes ($[ML]^{+}$ and $[ML_2]^{-1}$) in Gas and Solvent phases using TZVP/BP86 method

Complex	q_M	q_N	q_O/ q_S	q_M	q_N	q_O/ q_S
	Gas	Gas	Gas	Solvent	Solvent	Solvent
$[Am\text{-}PDA]^{+}$	2.049	-0.502	-0.758	2.325	-0.476	-0.759
$[Eu\text{-}PDA]^{+}$	1.960	-0.490	-0.738	2.284	-0.453	-0.729
$[Am\text{-}TCA1]^{+}$	2.008	-0.517	-0.726	2.309	-0.485	-0.702
$[Eu\text{-}TCA1]^{+}$	1.882	-0.504	-0.717	2.174	-0.565	-0.709
$[Am\text{-}(PDA)_2]^{-}$	1.724	-0.409	-0.677	1.722	-0.424	-0.701
$[Eu\text{-}(PDA)_2]^{-}$	1.640	-0.394	-0.667	1.647	-0.410	-0.690
$[Am\text{-}(TCA1)_2]^{-}$	1.806	-0.433	-0.634	1.838	-0.451	-0.646
$[Eu\text{-}(TCA1)_2]^{-}$	1.663	-0.449	-0.594	1.657	-0.460	-0.618
$[Am\text{-}(TCA)_2]^{-}$	0.835	-0.396	-0.153	0.901	-0.405	-0.230
$[Eu\text{-}(TCA)_2]^{-}$	0.878	-0.477	-0.184	0.886	-0.489	-0.237
$[Am\text{-}(THIO)_2]^{-}$	0.888	-0.441	0.025	0.910	-0.445	-0.033
$[Eu\text{-}(THIO)_2]^{-}$	0.946	-0.429	0.009	0.975	-0.432	-0.051

Table S8. Calculated atomic charges at metal centers (q_M) of the complexes $[ML]^+$ for different exchange correlation functionals (PBE and BLYP) using def-SV(P)

	q_M							
⟶ Ligand	PDA		TCA1		TCA		THIO	
↓Metal	B-LYP	PBE	B-LYP	PBE	BLYP	PBE	B-LYP	PBE
Am	2.011	2.010	1.958	1.965	1.596	1.590	1.563	1.568
Eu	1.920	1.918	1.834	1.843	1.564	1.557	1.554	1.542
U	2.116	2.118	2.109	2.116	1.526	1.484	1.508	1.479
Ce	2.065	2.059	2.043	2.042	1.616	1.607	1.620	1.606

Table S9. Calculated atomic charges on metal and donor centers of U and Ce complexes ($[ML_2]^{-1}$) in Gas and Solvent phases using TZVP/BP86 method

Complex	q_M	q_N	q_O/ q_S	q_M	q_N	q_O/ q_S
	Gas	Gas	Gas	Solvent	Solvent	Solvent
$[U\text{-}(PDA)_2]^-$	1.547	-0.386	-0.604	1.570	-0.400	-0.633
$[Ce\text{-}(PDA)_2]^-$	1.696	-0.396	-0.668	1.697	-0.413	-0.698
$[U\text{-}(TCA1)_2]^-$	1.566	-0.396	-0.572	1.571	-0.407	-0.587
$[Ce\text{-}(TCA1)_2]^-$	1.718	-0.413	-0.619	1.717	-0.424	-0.640
$[U\text{-}(TCA)_2]^-$	0.253	-0.381	0.002	0.472	-0.403	-0.118
$[Ce\text{-}(TCA)_2]^-$	0.920	-0.400	-0.174	0.987	-0.407	-0.283
$[U\text{-}(THIO)_2]^-$	0.342	-0.400	0.130	0.391	-0.404	0.080
$[Ce\text{-}(THIO)_2]^-$	0.871	-0.406	0.007	0.958	-0.415	-0.087

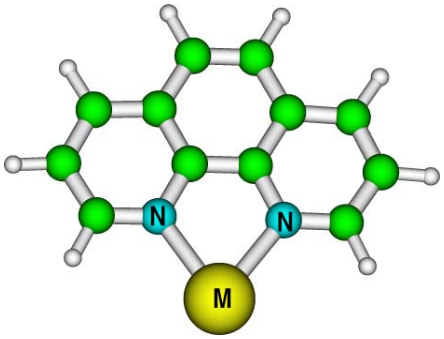
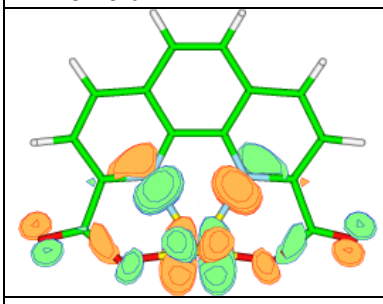
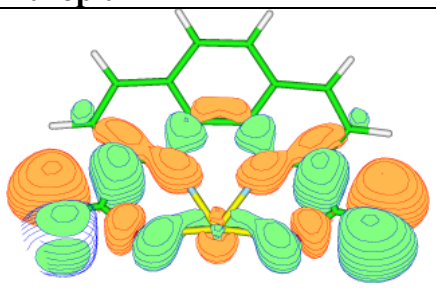


Figure S1. Molecular structure of Metal-PHEN Complexes, where M= Am/Eu/U/Ce.

a)

Americium	Europium
	
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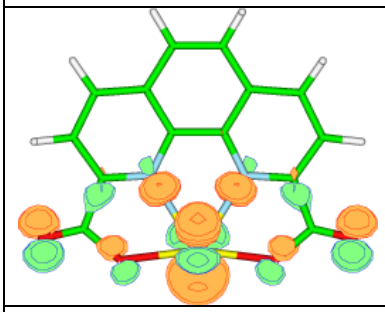	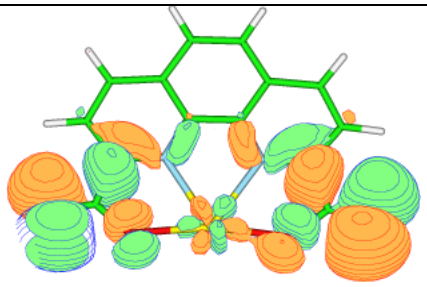
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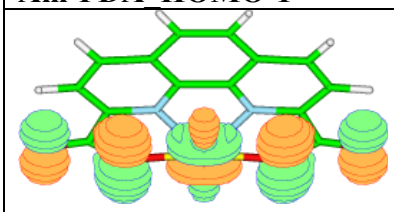	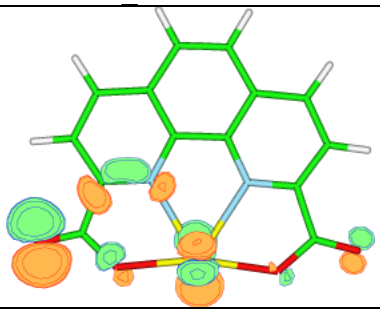
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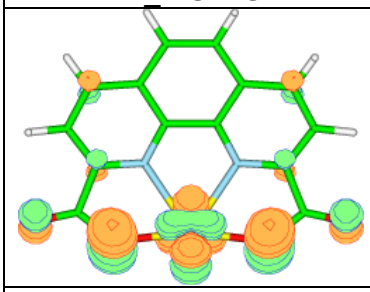	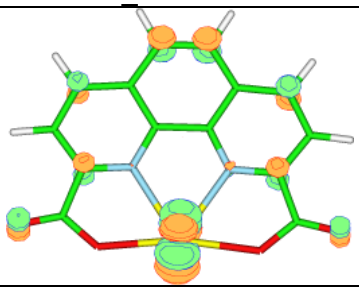
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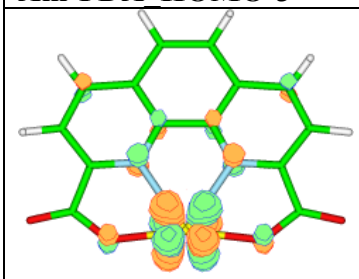	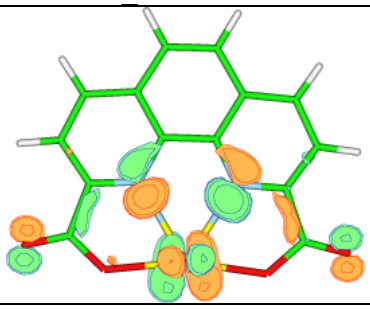

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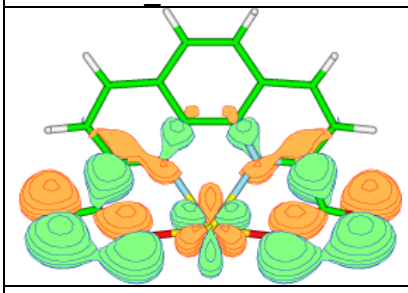	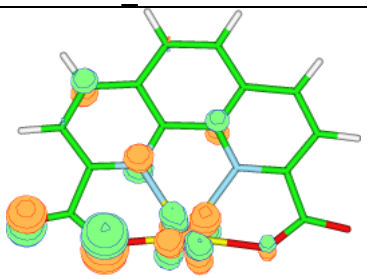
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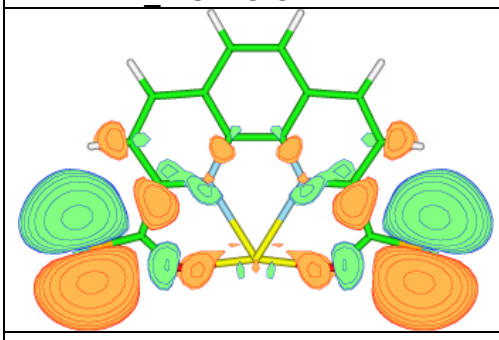	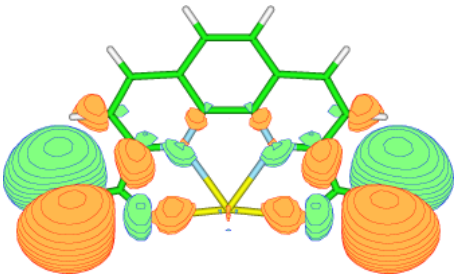
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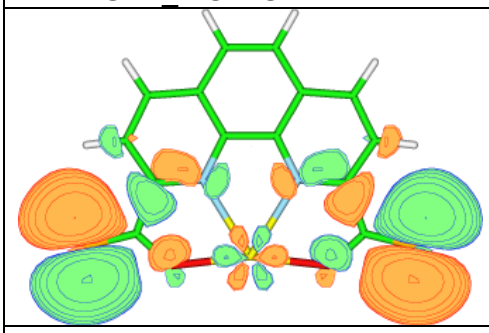	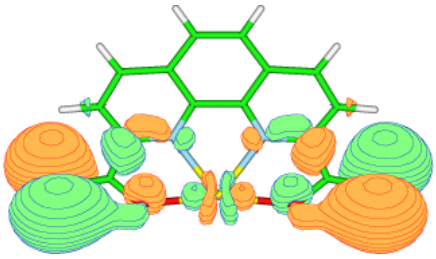
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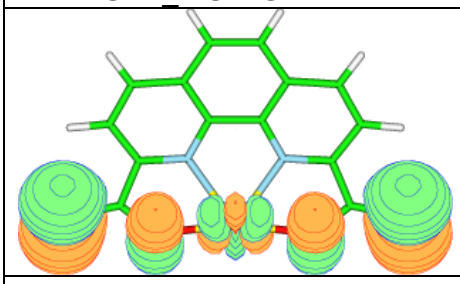	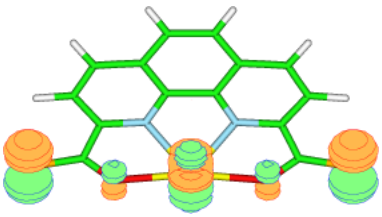
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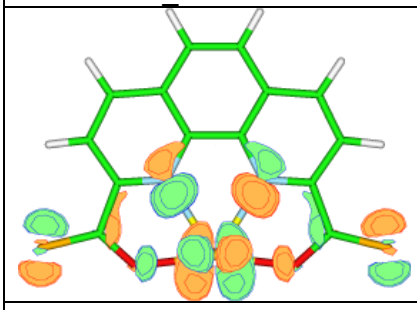	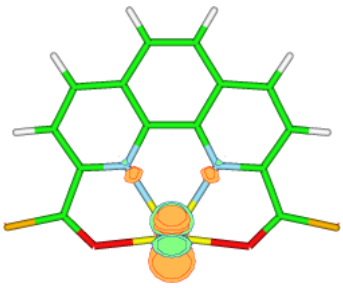
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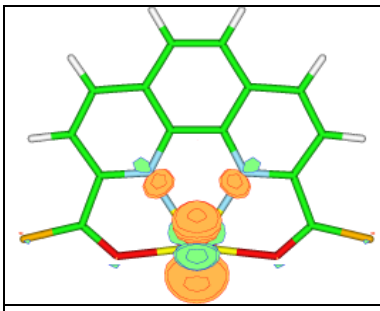	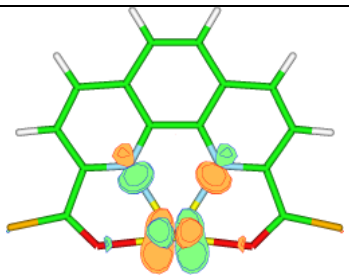
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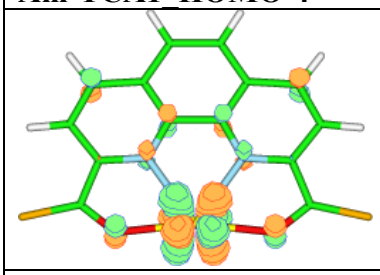	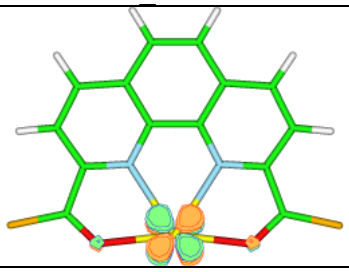
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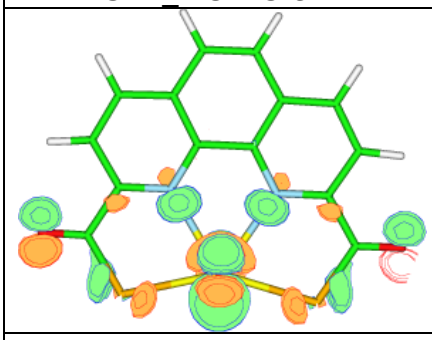	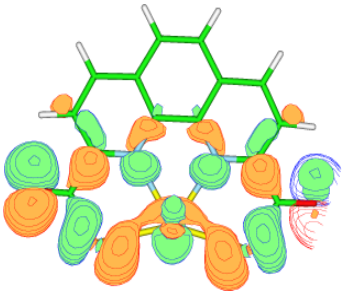
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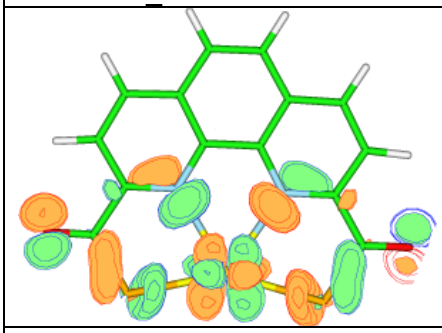	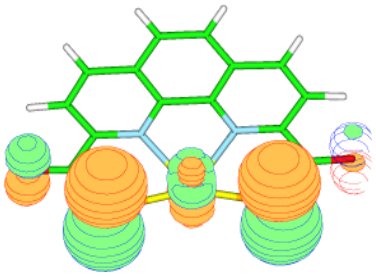
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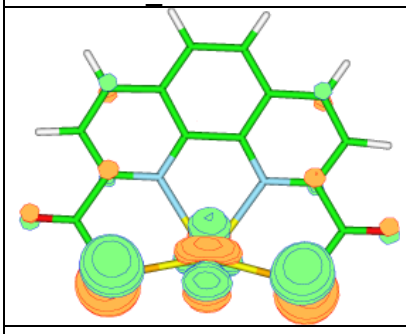	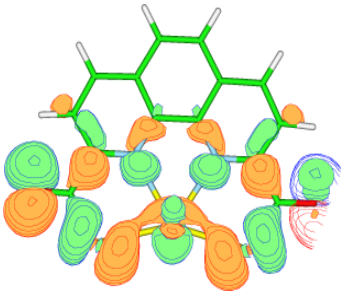
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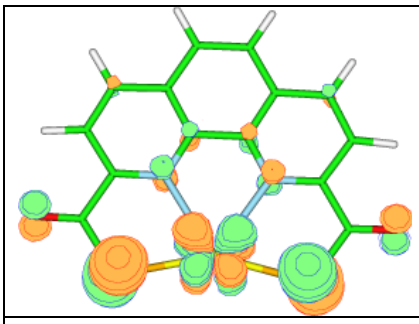	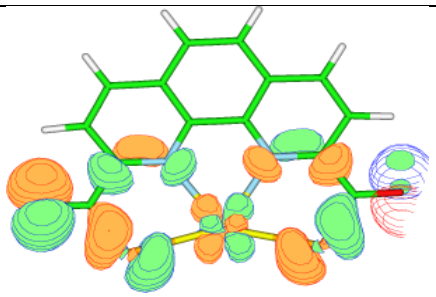
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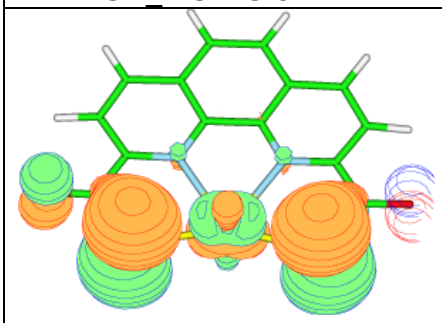	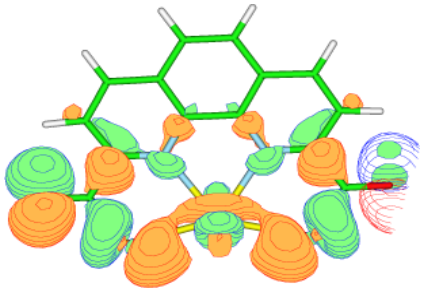
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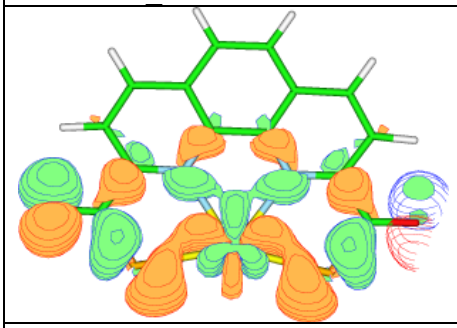	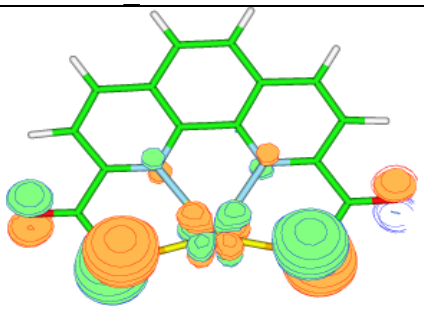
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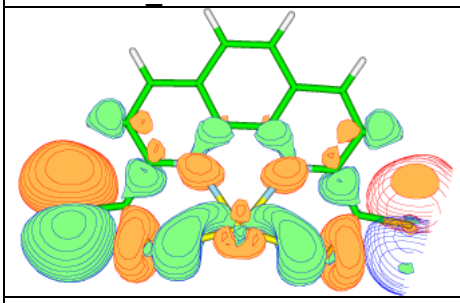	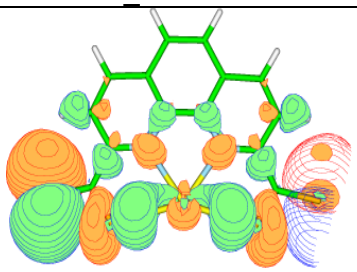
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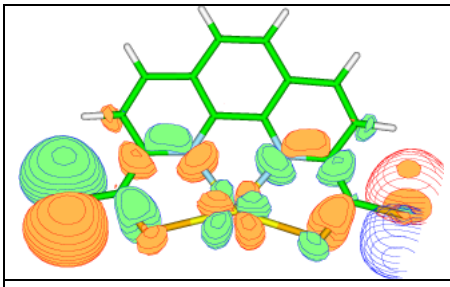	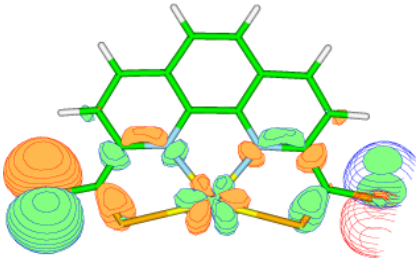
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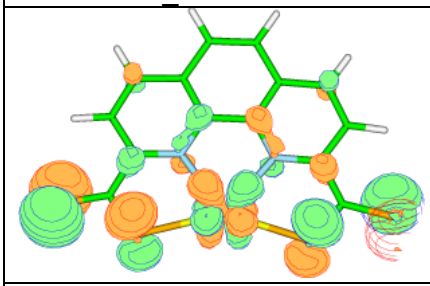	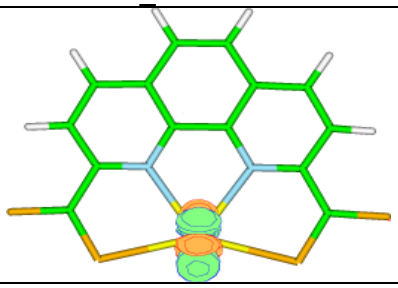
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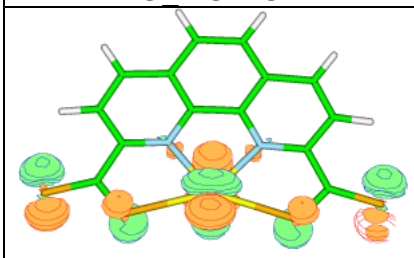	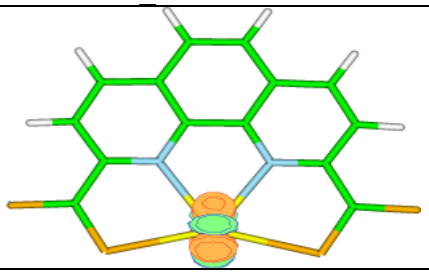
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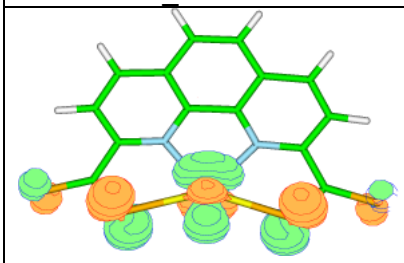	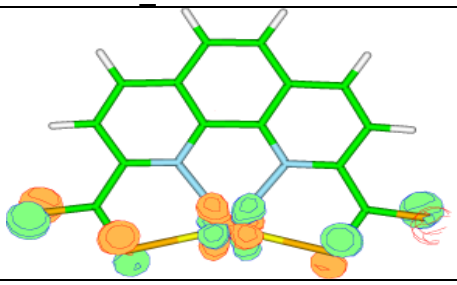
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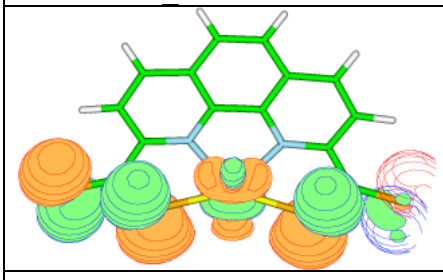	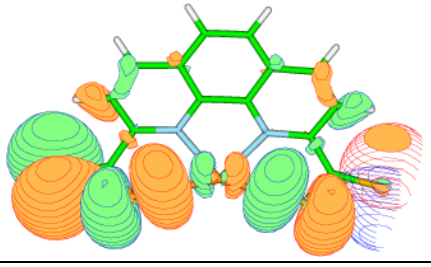
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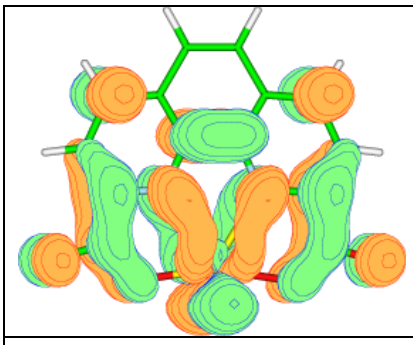	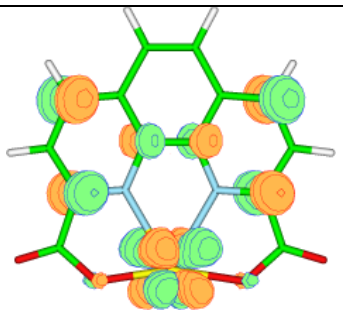
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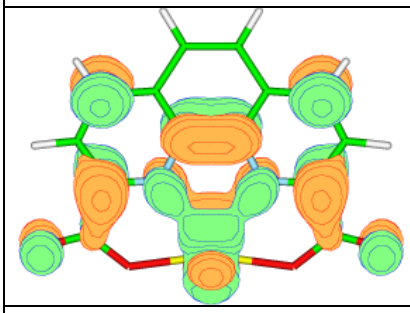	
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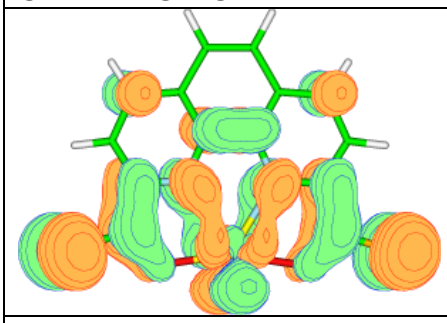	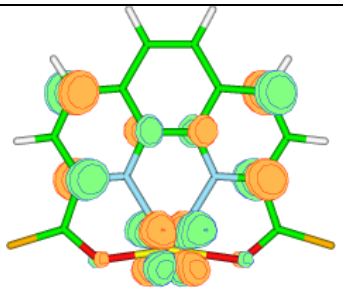
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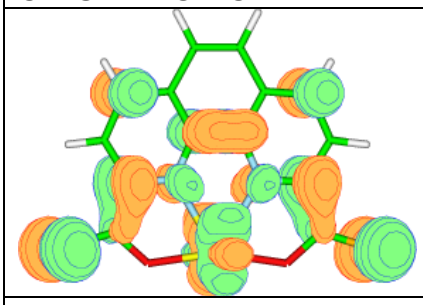	
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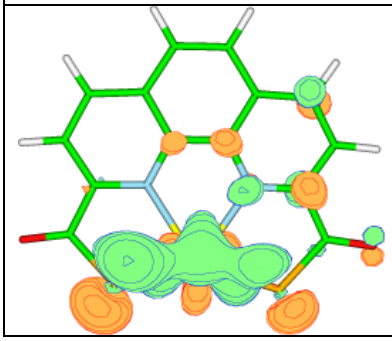	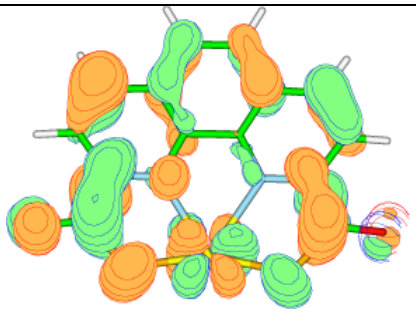

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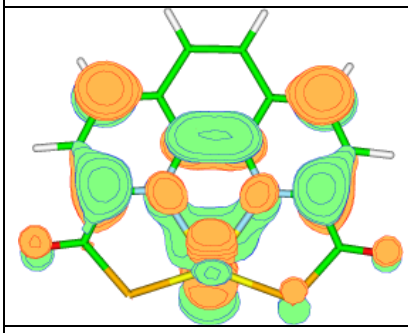	
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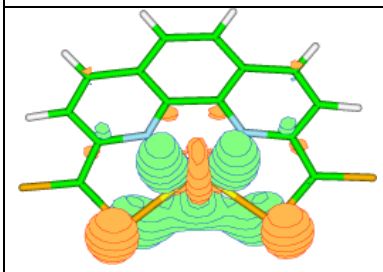	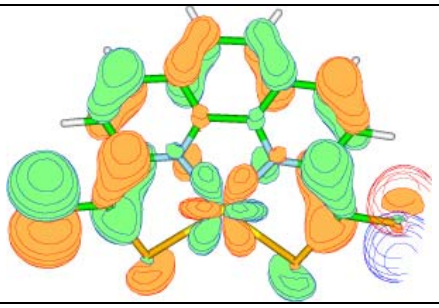
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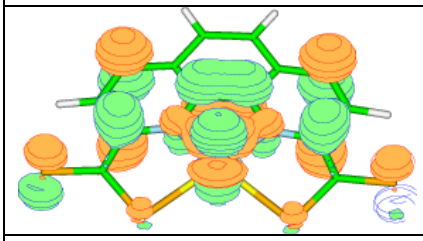	
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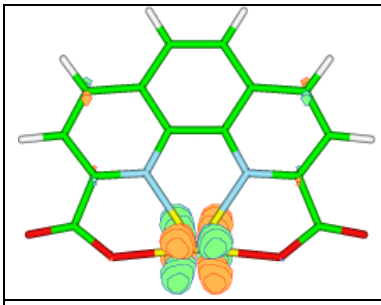	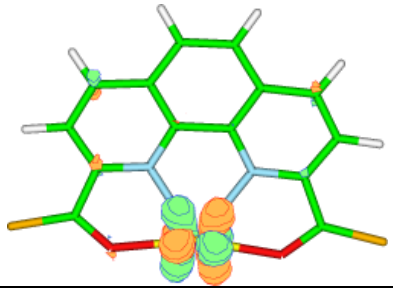
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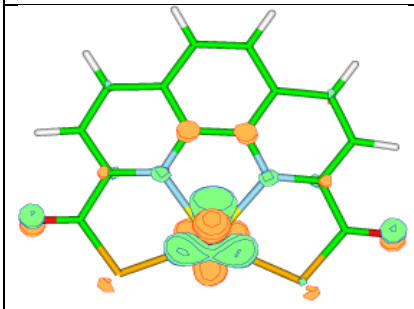
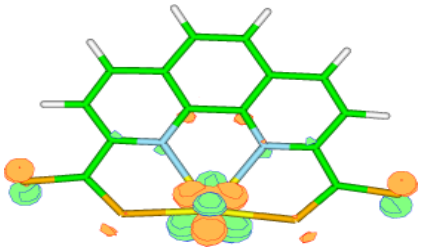
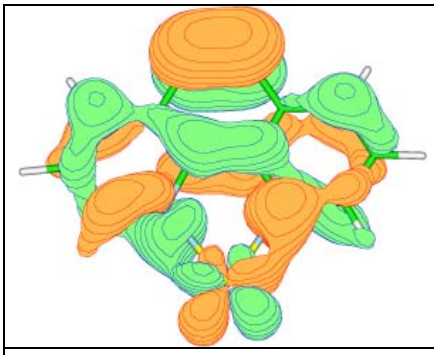
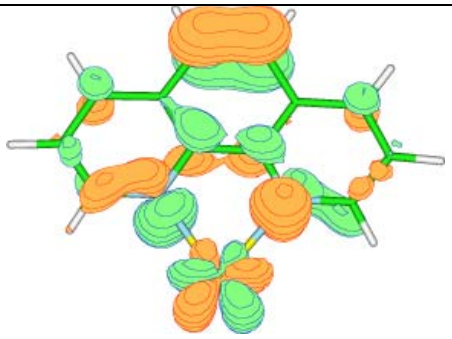
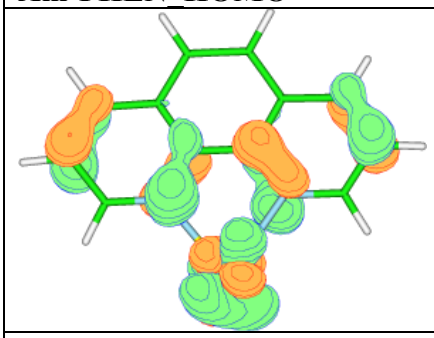
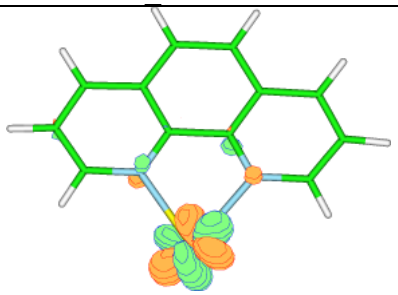
	

Ce-TCA-HOMO	Ce-THIO-HOMO

b)

	
Am-PHEN_HOMO	**Eu-PHEN_HOMO**
	
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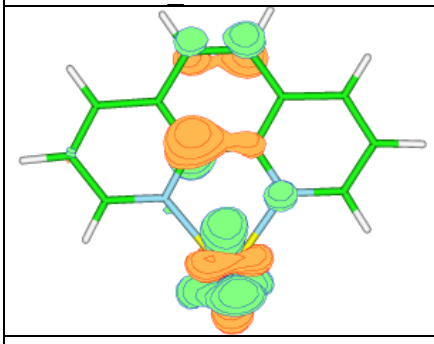	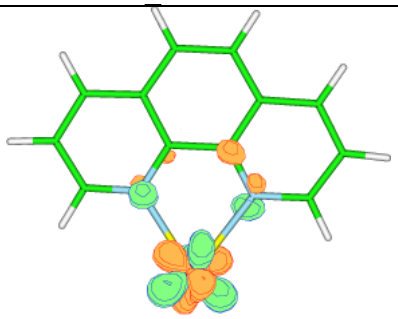
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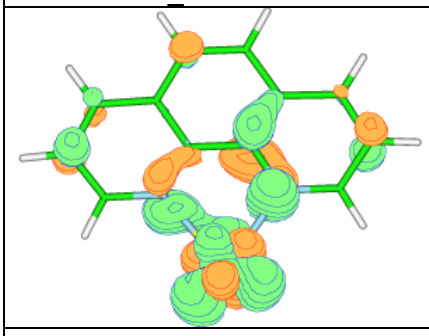
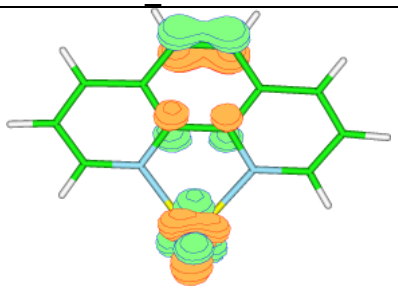
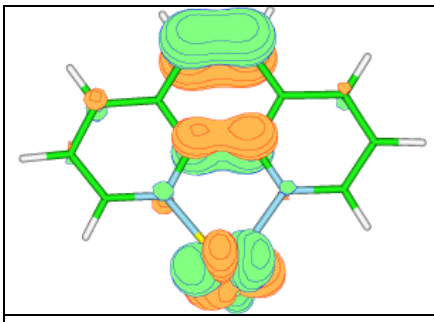
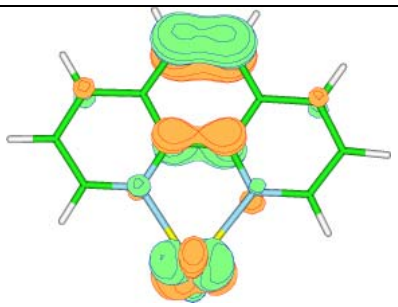
	
Am-PHEN_HOMO-3	**Eu-PHEN_HOMO-3**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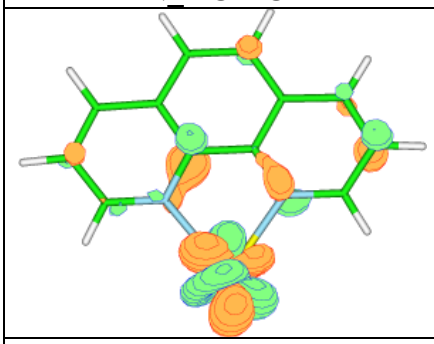	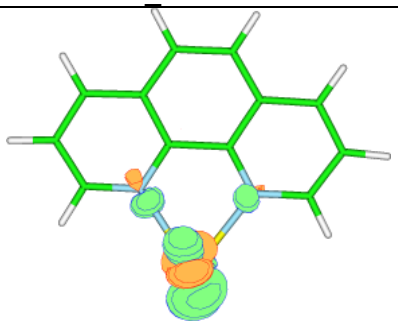
Am-PHEN_HOMO-5	**Eu-PHEN_HOMO-5**

Figure S2. Valence level occupied molecular orbitals of a) Metal Complexes, $[ML]^{+}$ b) $[M\text{-}PHEN]^{3+}$ complexes, where M= Am/Eu/U/Ce, L= PDA, TCA1, TCA, THIO. (1,10-Phenanthroline-2,9-dicarboxylic acid (PDA), 1,10-Phenanthroline-2,9-mono-thio dicarboxylic Acid (binding through Oxygen) (TCA1), 1,10-Phenanthroline-2,9-mono-thio dicarboxylic Acid (binding through Sulphur) (TCA) and 1,10-Phenanthroline-2,9-di-thiodicarboxylic Acid (THIO))