

Supplementary Information

Electronic, optical and transport properties of Zn-Porphyrin-C₆₀ MOFs: A combined periodic and cluster modeling.

Kevin Granados-Tavera^{a,b}, Gloria Cárdenas-Jirón^{*a}

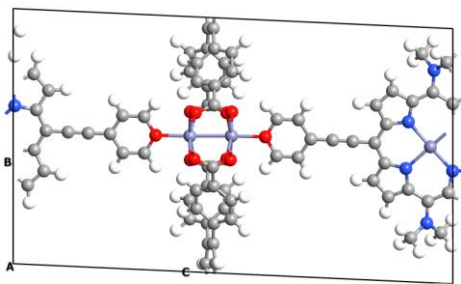
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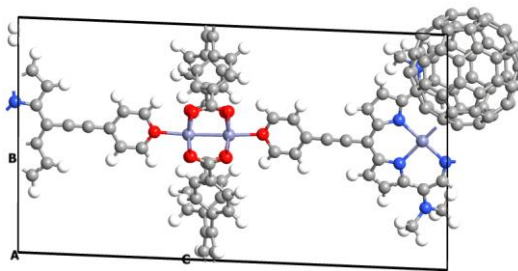
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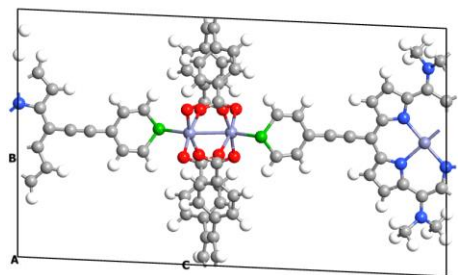
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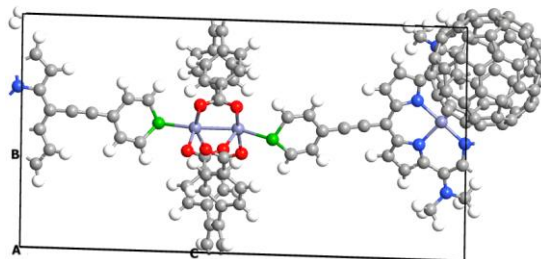
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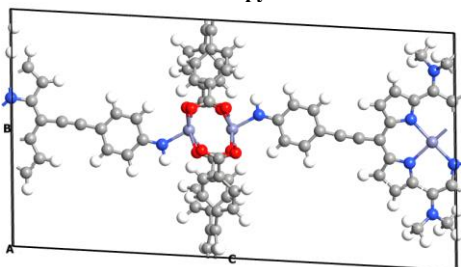
C₆₀@R_{pyr}



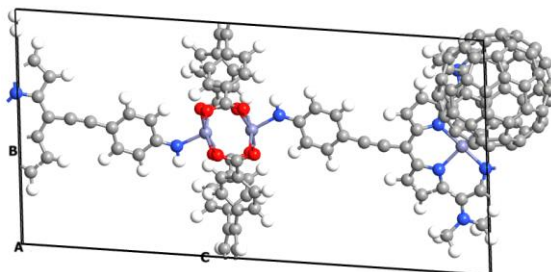
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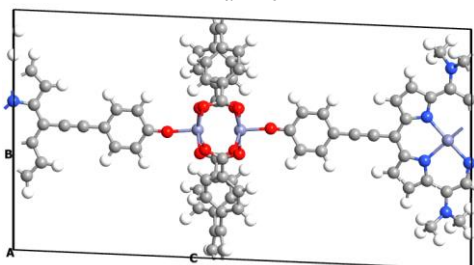
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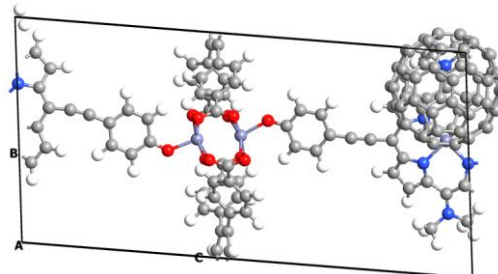
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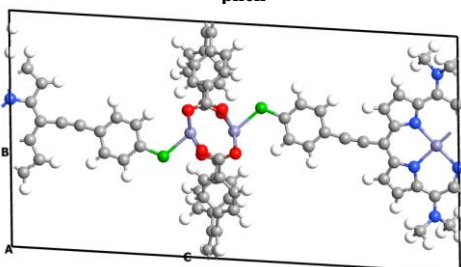
C₆₀@R_{amine}



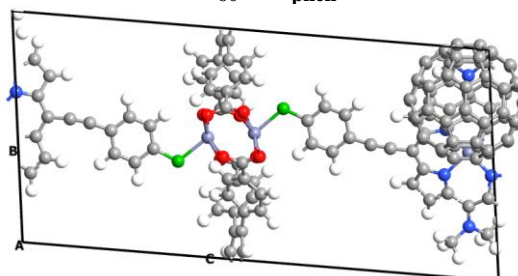
R_{phen}



C₆₀@R_{phen}



R_{sulf}



C₆₀@R_{sulf}

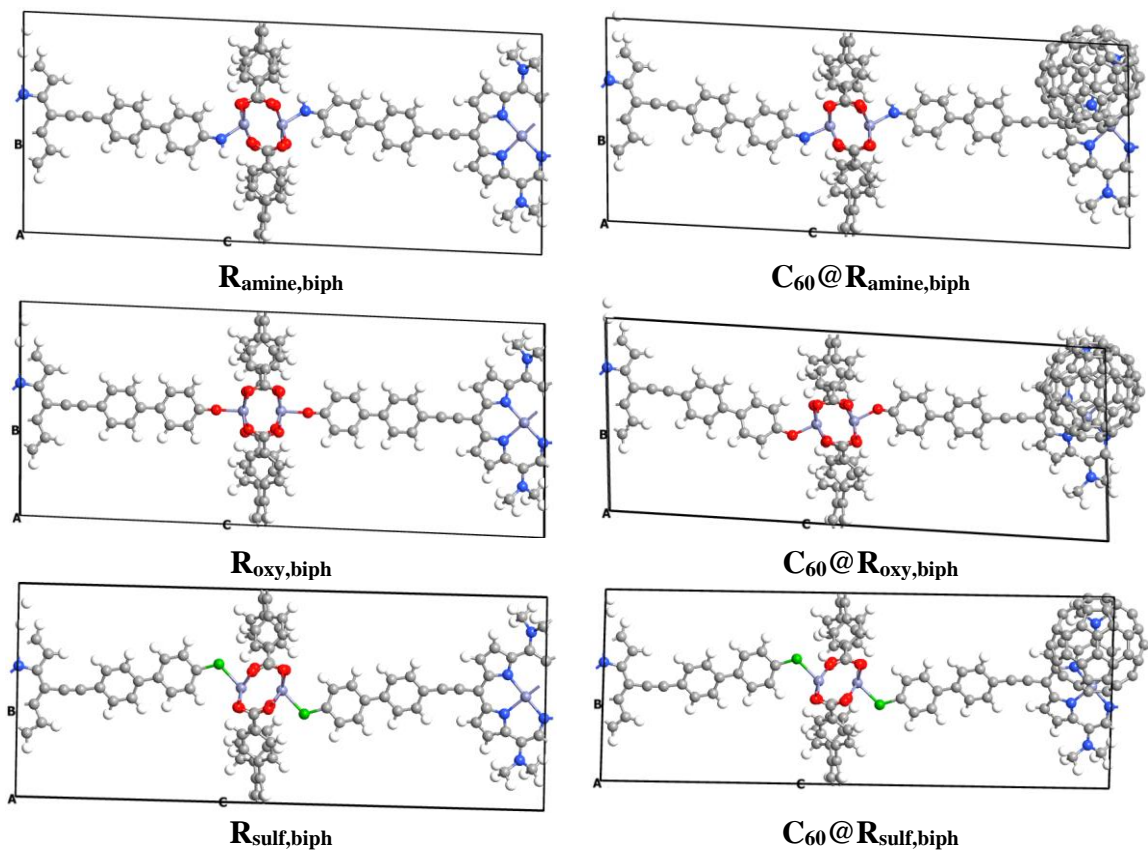


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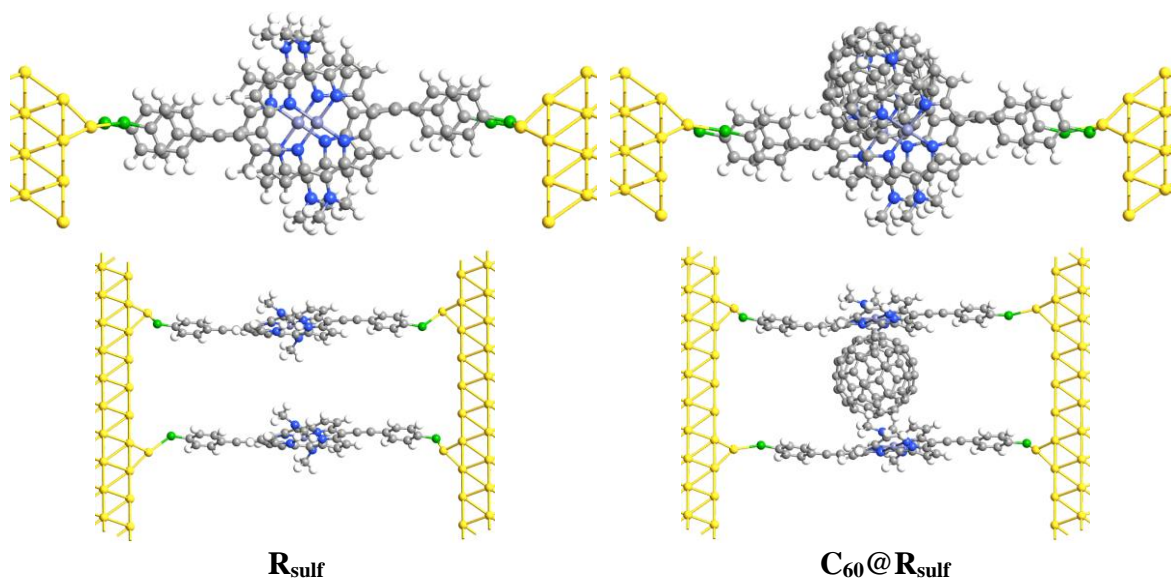


Figure S2. Optimized electronic device structure for a cluster; \mathbf{R}_{sulf} and $\mathbf{C}_{60}@\mathbf{R}_{\text{sulf}}$. Front view (top) and side view (bottom).

Table S1. Lattice parameters of the MOFs with and without \mathbf{C}_{60} .

MOF	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
\mathbf{R}_{py}	11.66	15.68	27.35	92.39	95.49	90.13
\mathbf{R}_{pyr}	11.55	15.74	27.39	92.60	95.19	90.06
$\mathbf{R}_{\text{thiopyr}}$	11.51	15.60	27.89	92.51	94.74	90.20
$\mathbf{R}_{\text{amine}}$	11.70	15.59	29.33	93.66	96.08	89.62
\mathbf{R}_{phen}	11.64	15.59	29.91	92.40	95.65	90.11
\mathbf{R}_{sulf}	11.68	15.51	29.56	94.10	96.51	89.56
$\mathbf{R}_{\text{amine,biph}}$	11.66	15.68	37.28	92.38	95.49	90.13
$\mathbf{R}_{\text{oxy,biph}}$	11.67	15.63	38.59	92.38	95.78	90.06
$\mathbf{R}_{\text{sulf,biph}}$	11.73	15.38	38.42	90.53	96.69	90.75
$\mathbf{C}_{60}@\mathbf{R}_{\text{py}}$	12.85	14.67	27.17	94.67	93.11	90.54
$\mathbf{C}_{60}@\mathbf{R}_{\text{pyr}}$	12.71	14.84	27.34	92.26	95.45	90.81
$\mathbf{C}_{60}@\mathbf{R}_{\text{thiopyr}}$	12.71	14.56	27.74	91.04	92.36	90.29
$\mathbf{C}_{60}@\mathbf{R}_{\text{amine}}$	12.93	14.46	29.03	95.36	94.82	89.67
$\mathbf{C}_{60}@\mathbf{R}_{\text{phen}}$	13.04	14.31	28.81	96.25	94.55	89.65
$\mathbf{C}_{60}@\mathbf{R}_{\text{sulf}}$	13.17	14.20	29.55	97.21	96.49	89.31
$\mathbf{C}_{60}@\mathbf{R}_{\text{amine,biph}}$	13.03	14.45	37.75	93.51	97.79	89.30
$\mathbf{C}_{60}@\mathbf{R}_{\text{oxy,biph}}$	12.94	14.37	37.43	94.67	96.93	89.25
$\mathbf{C}_{60}@\mathbf{R}_{\text{sulf,biph}}$	13.04	14.30	38.27	89.29	96.19	90.60

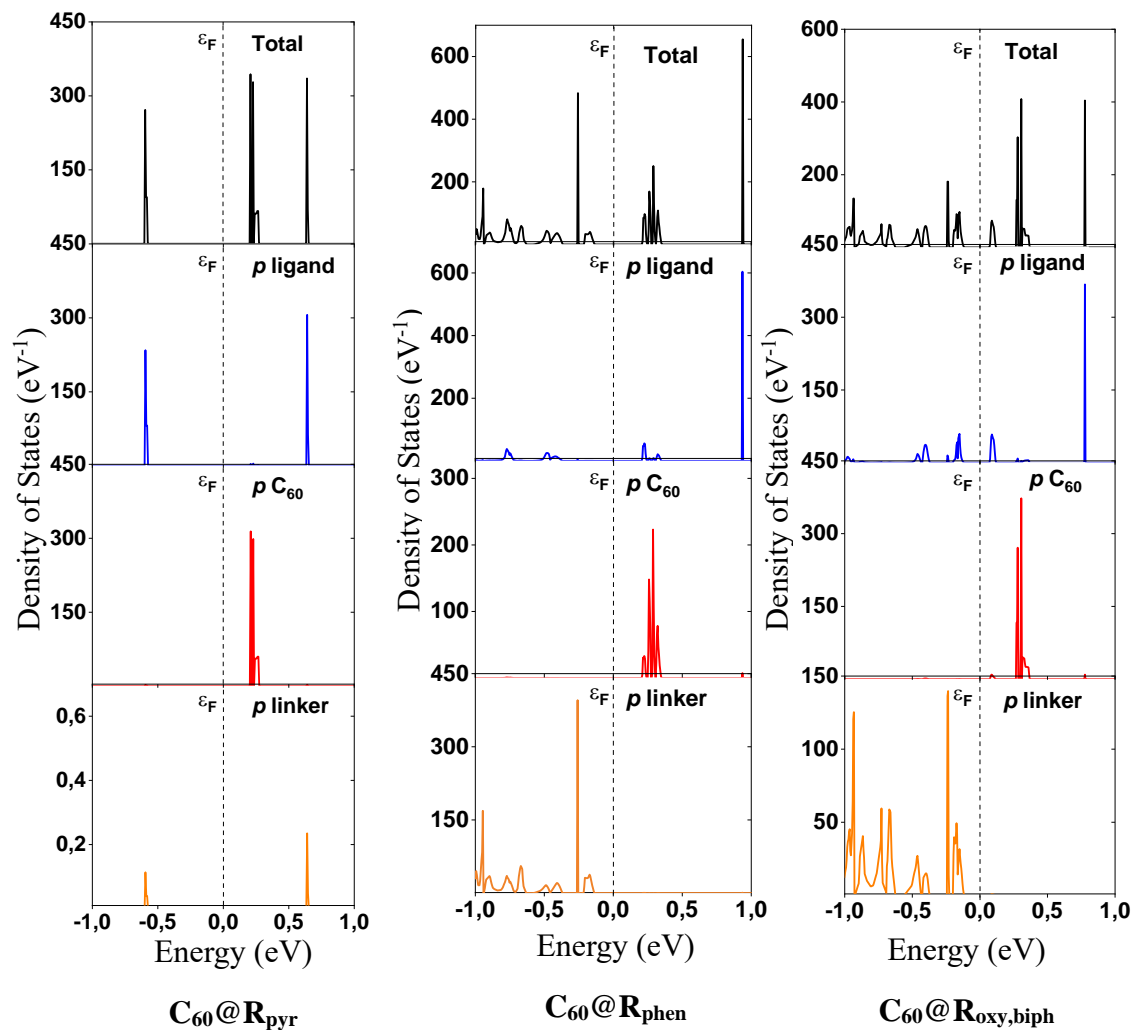


Figure S3. Density of states of $C_{60}@R_{pyr}$, $C_{60}@R_{phen}$ and $C_{60}@R_{oxy,biph}$ (oxygen-functionalized materials) MOFs calculated using the PBE-D3 level. Fermi level energy is indicated by ϵ_F .

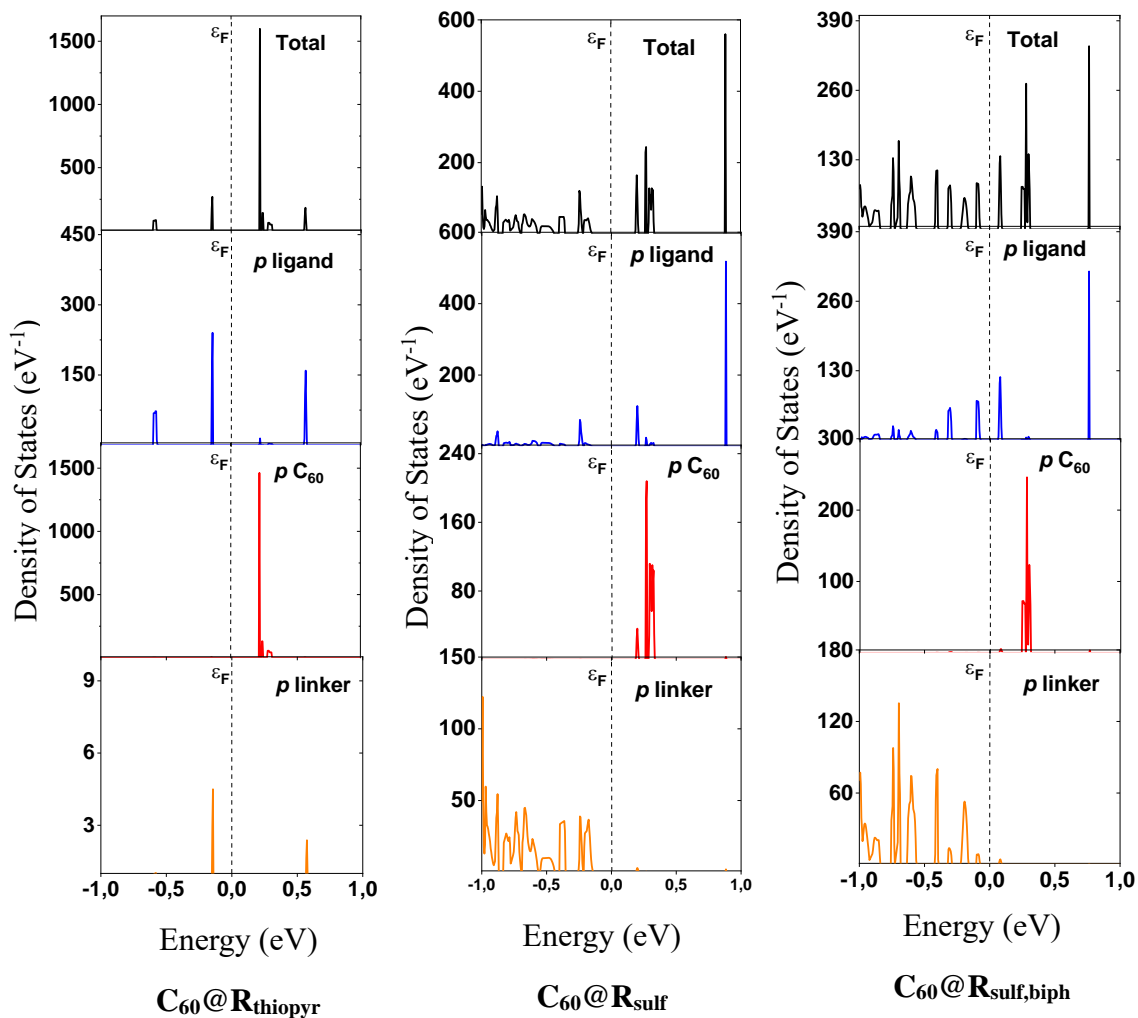
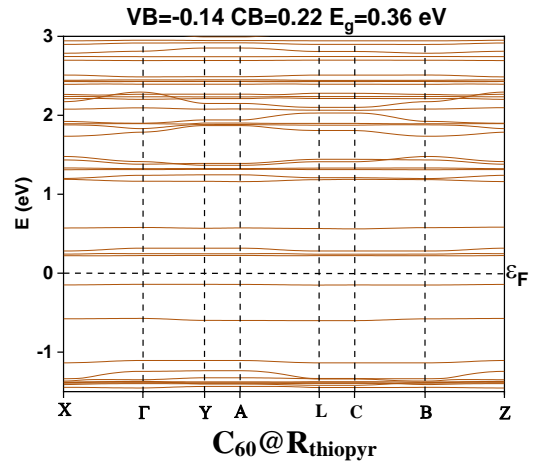
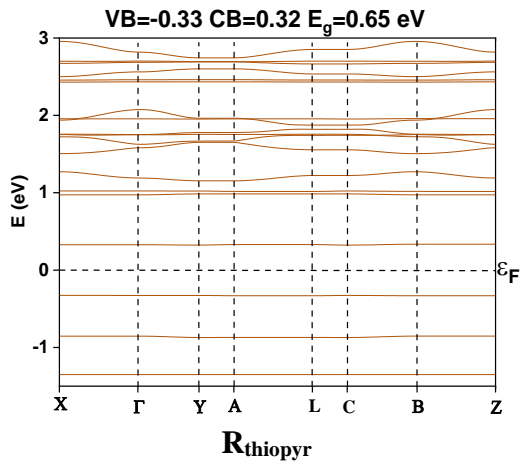
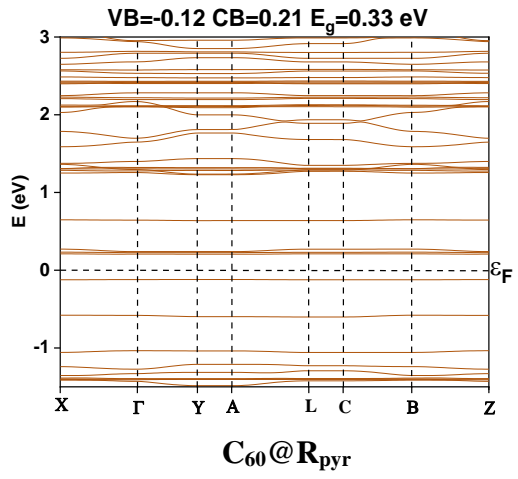
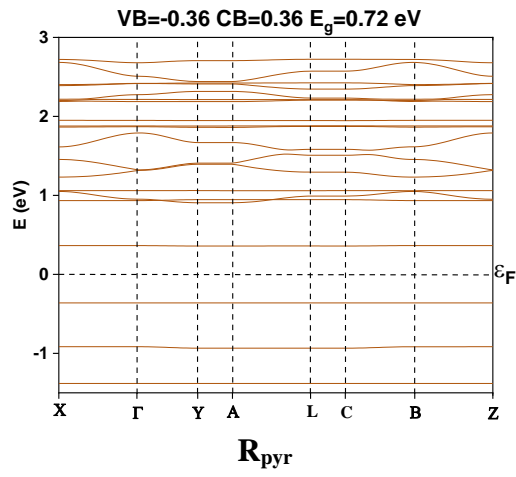
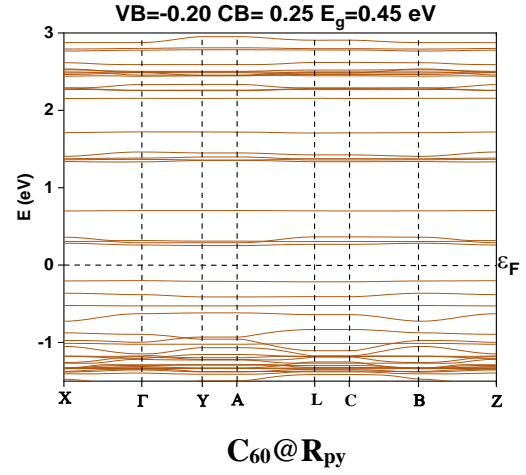
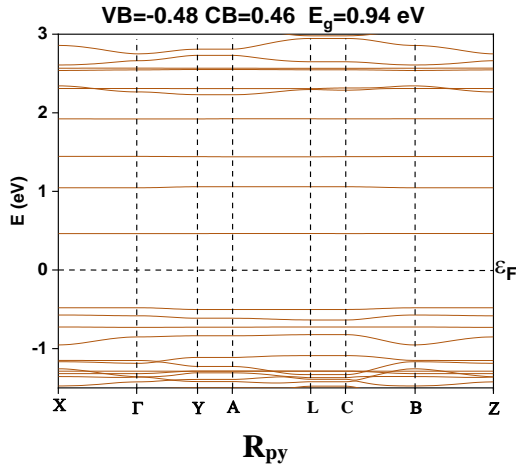
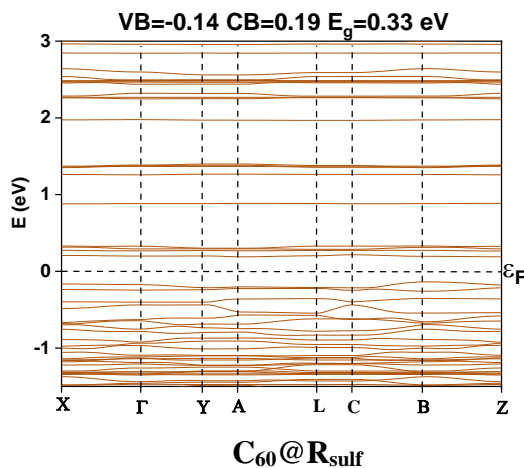
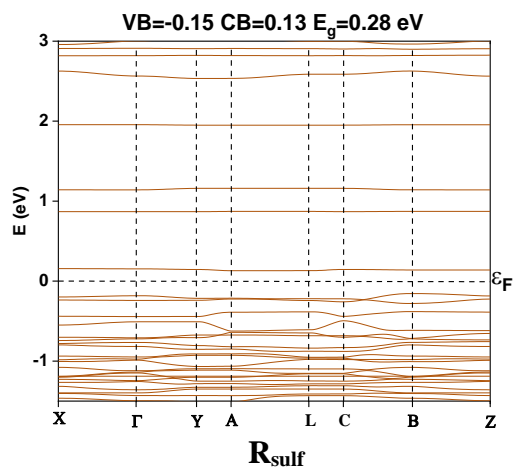
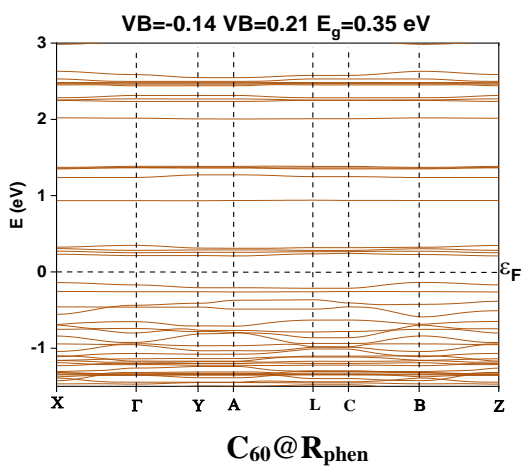
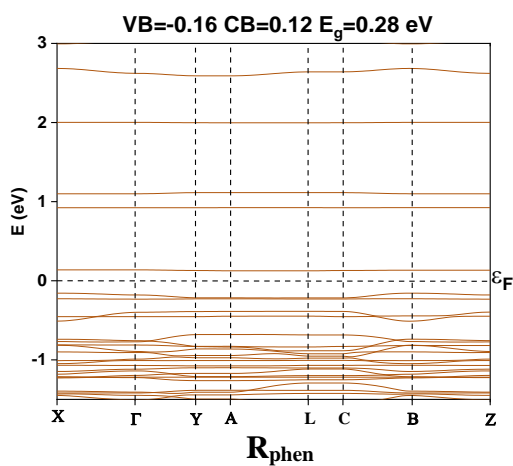
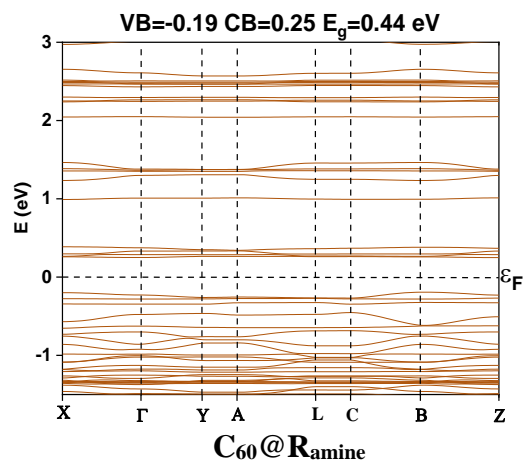
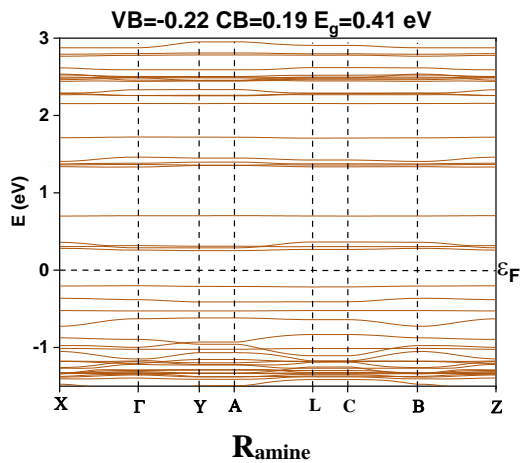


Figure S4. Density of states of $C_{60}@R_{thiopyr}$, $C_{60}@R_{sulf}$ and $C_{60}@R_{sulf,biph}$ (sulfur-functionalized materials) MOFs calculated using the PBE-D3 level. Fermi level energy is indicated by ϵ_F .





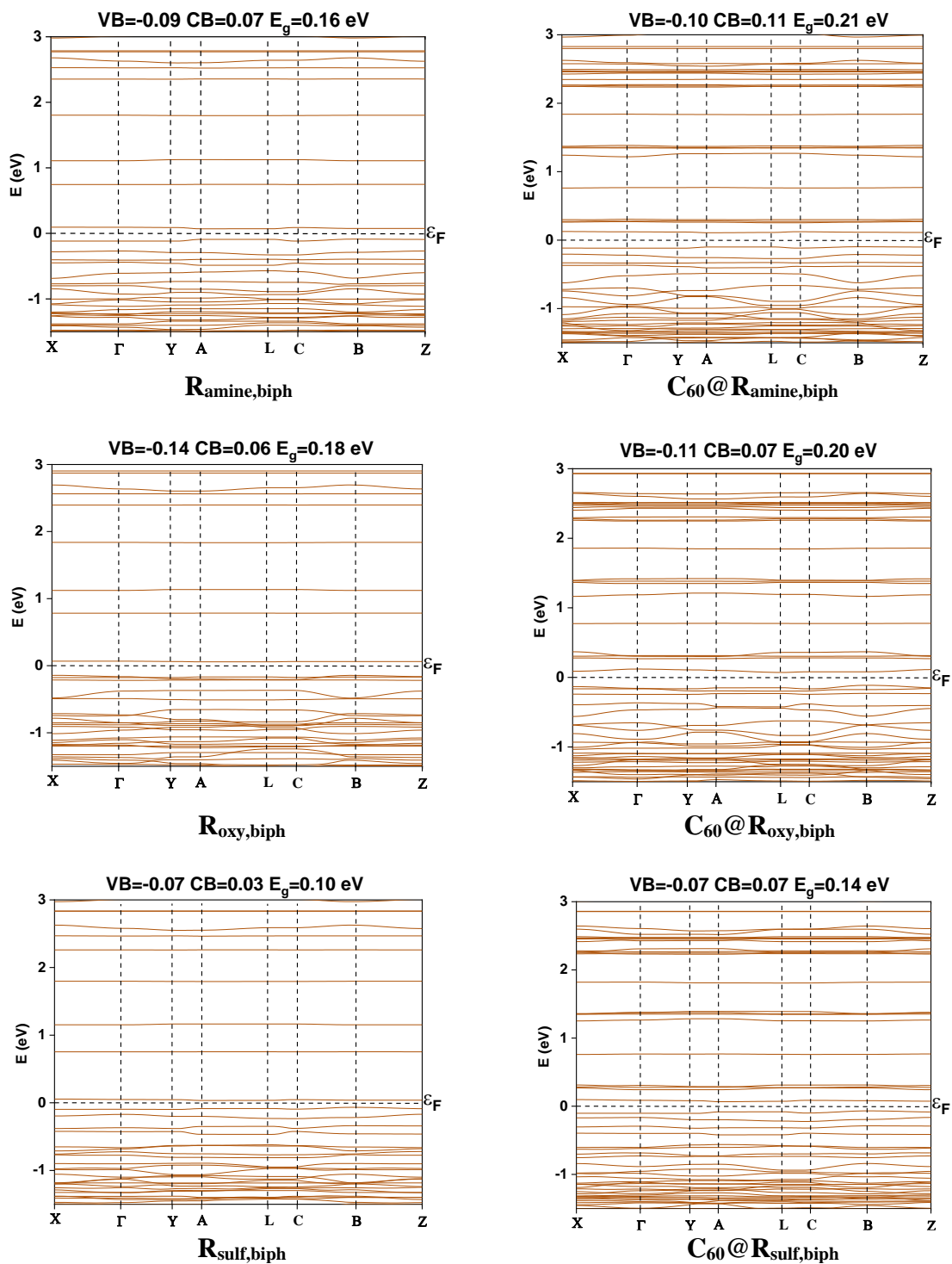


Figure S5. Band structure of the MOFs with and without C_{60} calculated using the PBE-D3 level. Fermi level and band gap energy is indicated by ϵ_F and E_g respectively. The space group of the MOFs is P1. The calculations were performed along the X Γ YALCBZ path of the Brillouin zone. The x-coordinates of the high-symmetry points along this path are 0.00, 0.19, 0.32, 0.40, 0.58, 0.66, 0.81, and 0.99 Å, respectively.

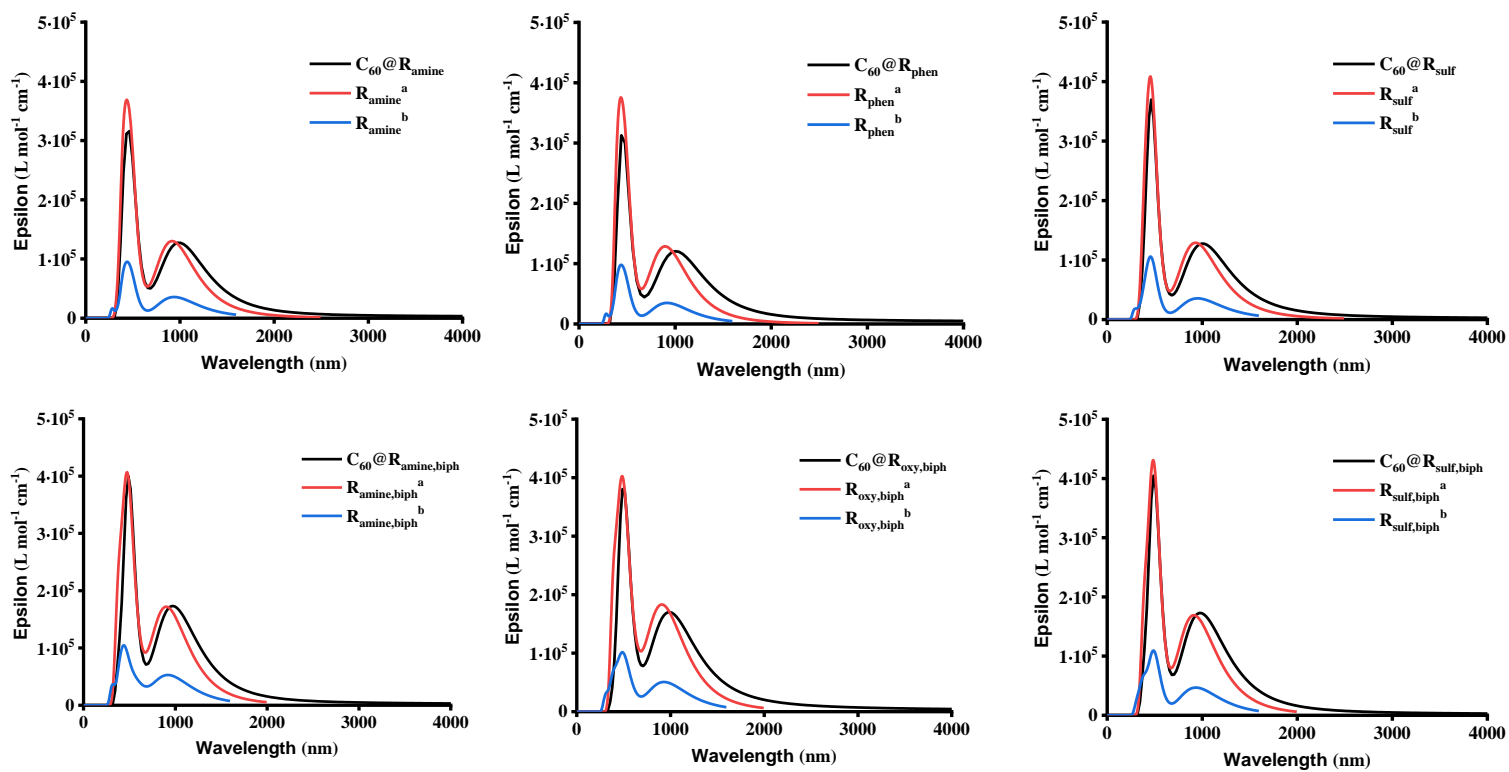
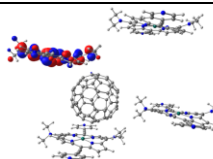
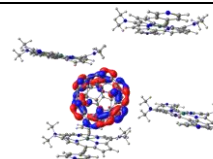
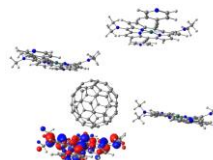
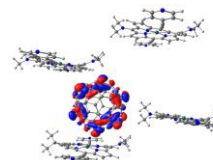
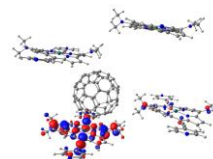
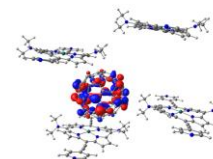
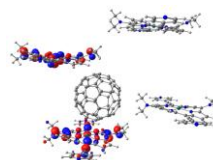
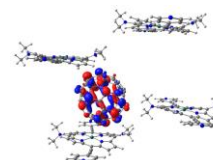
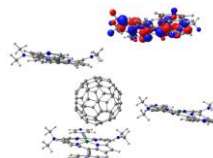
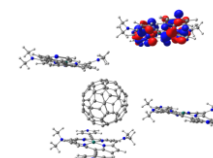
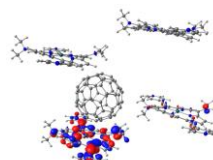
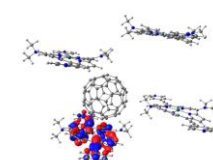
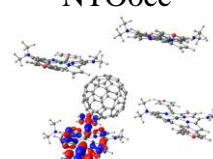
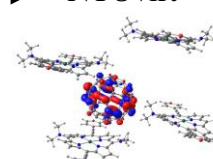
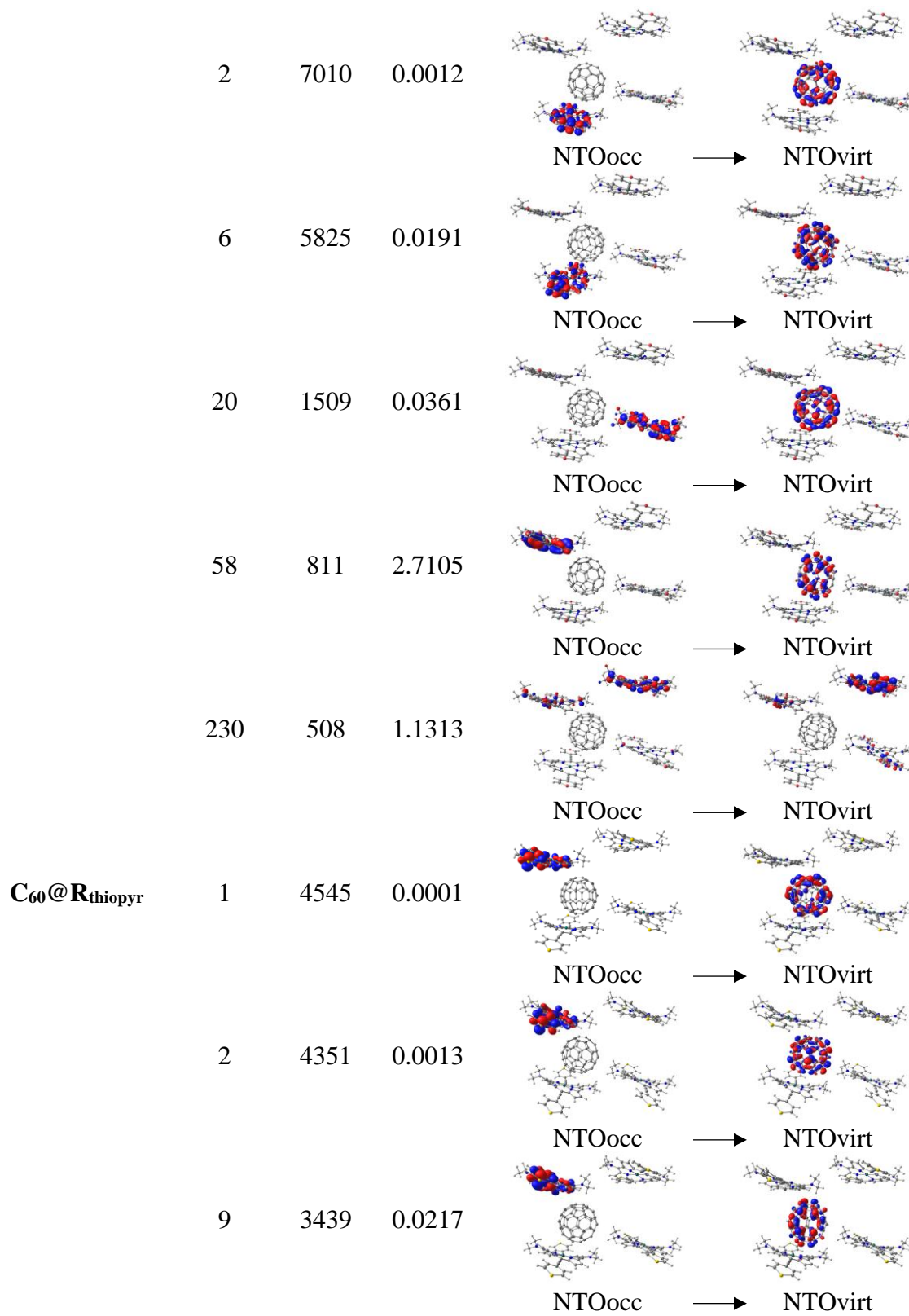
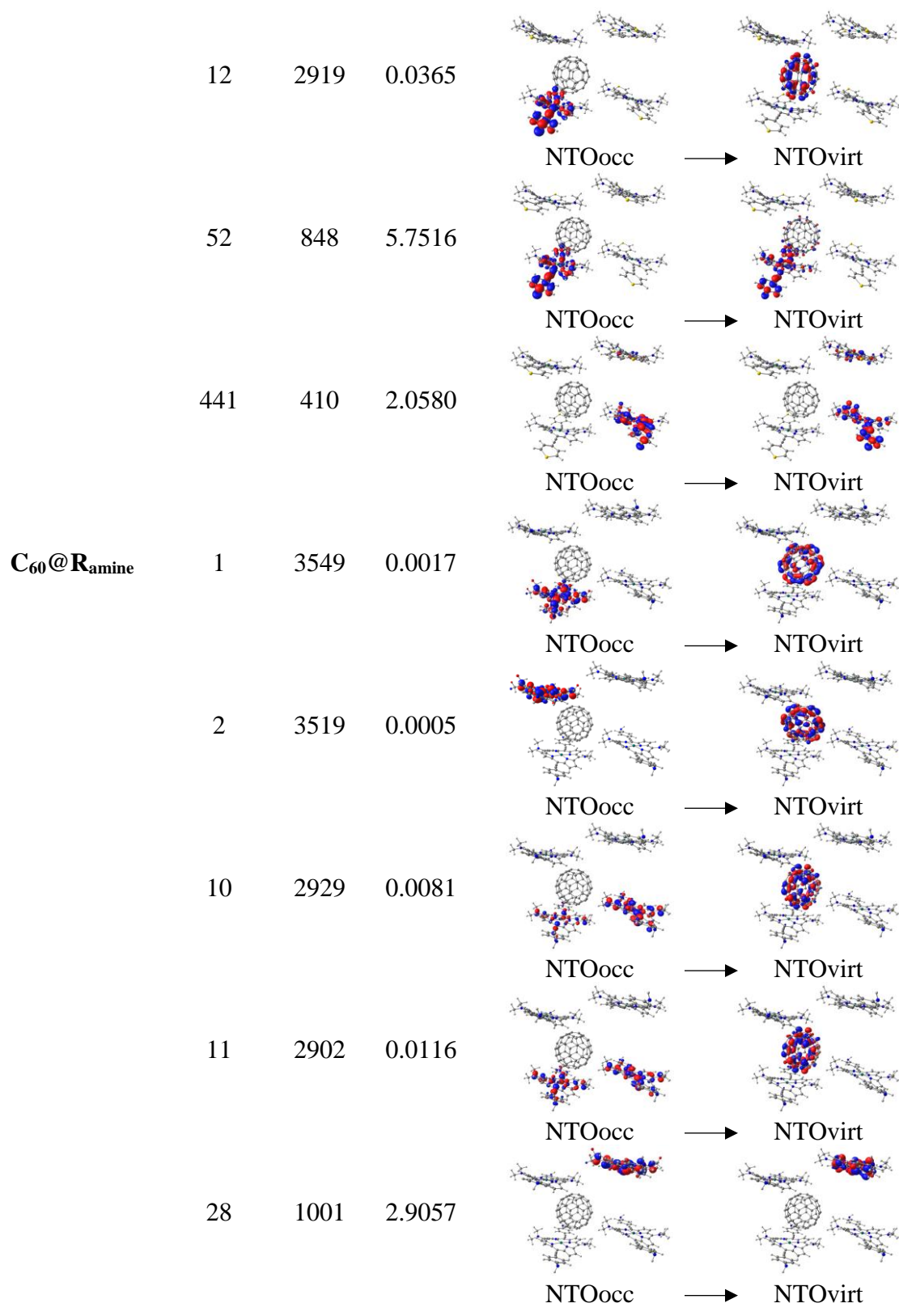


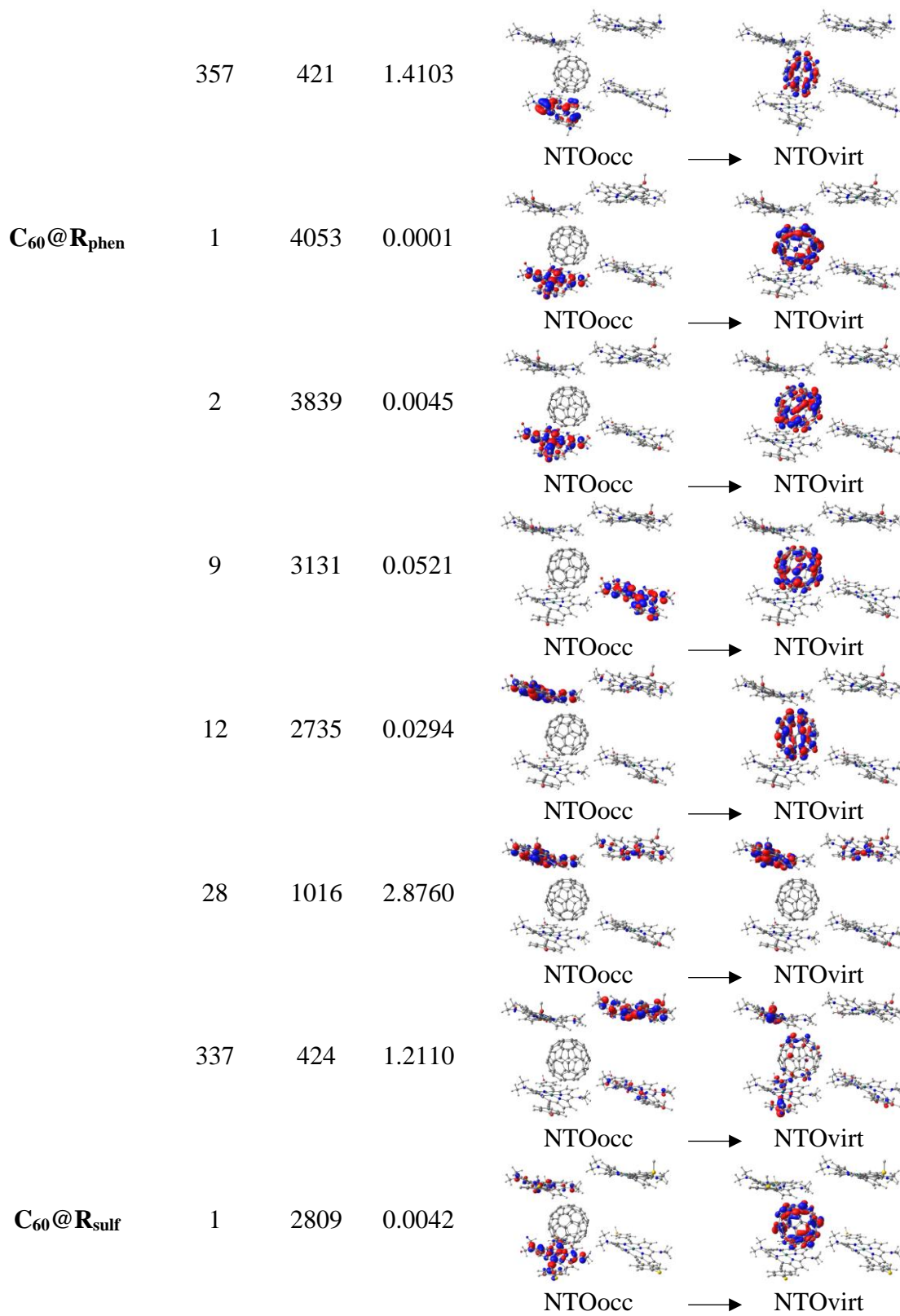
Figure S6. Electronic absorption spectra of MOFs clusters calculated at the TPSSh/6–31G level of theory. ^a MOF cluster without C₆₀. ^b Porphyrin unit.

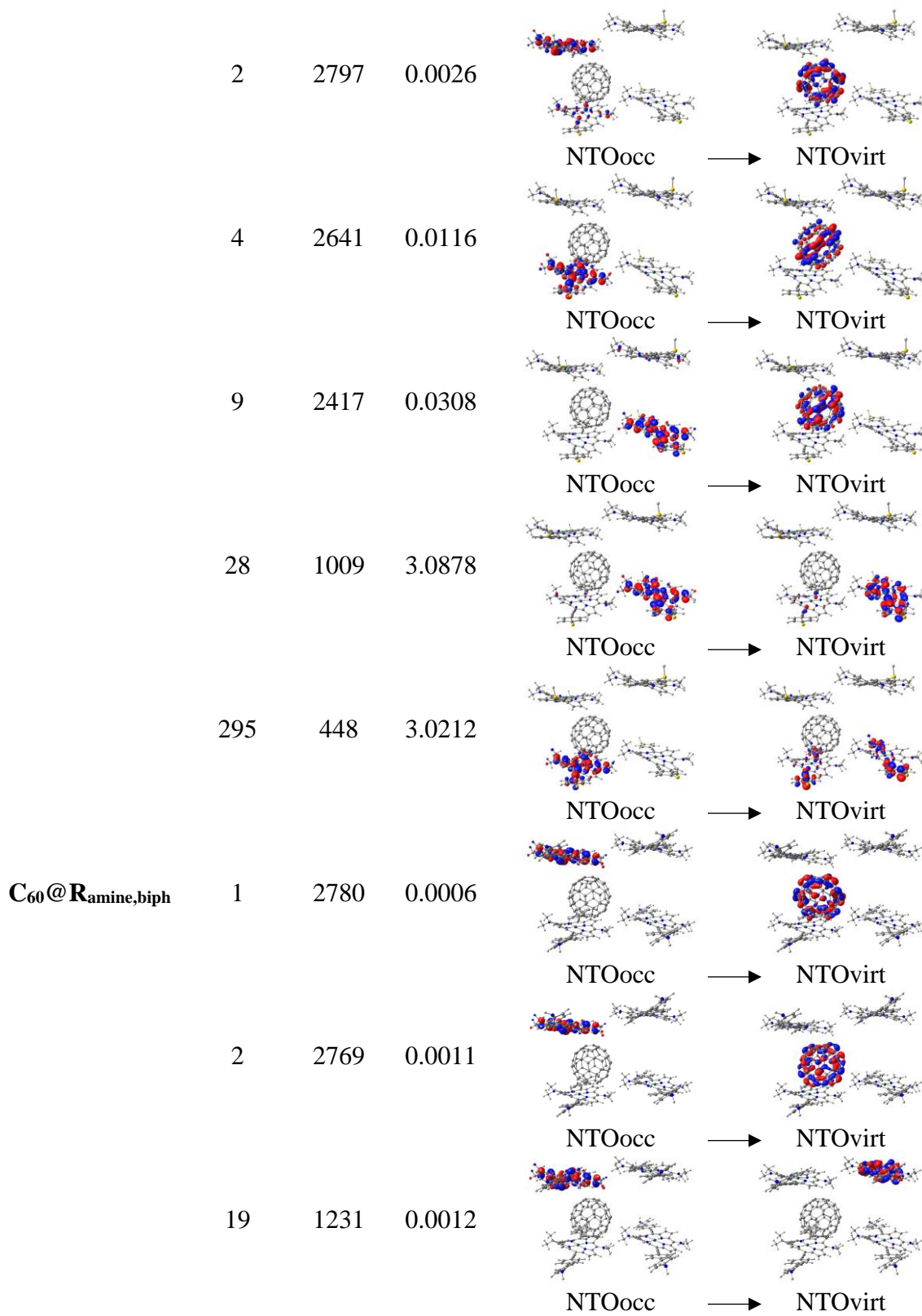
Table S2. Excited states, excitation wavelength (λ), oscillator strengths (f) for model C_{60} @MOFs clusters obtained from TD-DFT calculations (TPSSH/6-31G).

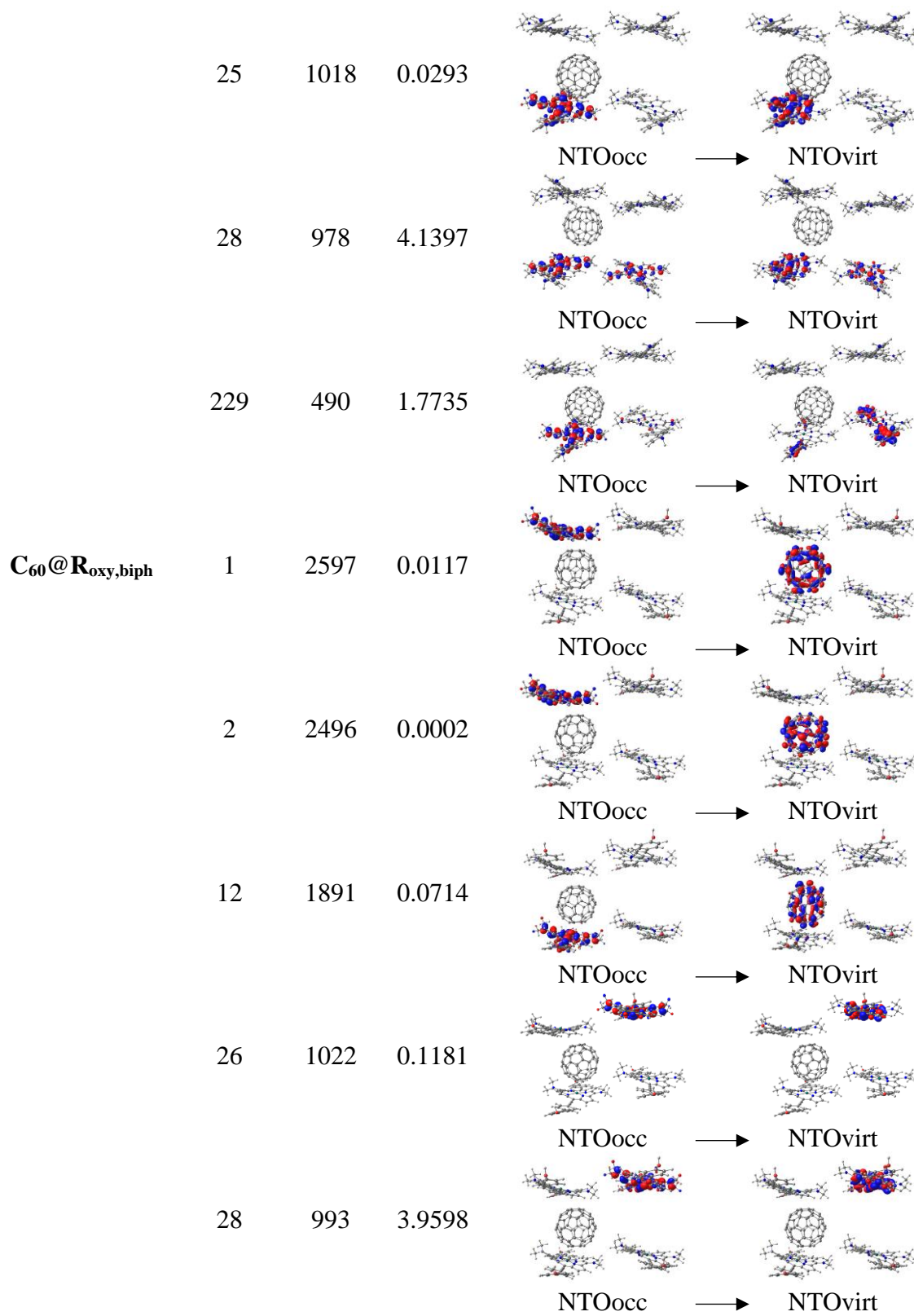
MOF	Excited State	λ (nm)	f	Transition Involved	
$C_{60}@R_{py}$	1	2139	0.0001		
				NTOocc	→ NTOvirt
	2	2064	0.0082		
				NTOocc	→ NTOvirt
	6	1952	0.0284		
				NTOocc	→ NTOvirt
$C_{60}@R_{pyr}$	8	1910	0.0378		
				NTOocc	→ NTOvirt
	28	889	2.6075		
				NTOocc	→ NTOvirt
	346	413	2.2285		
				NTOocc	→ NTOvirt
$C_{60}@R_{pyr}$	1	7161	0.0015		
				NTOocc	→ NTOvirt











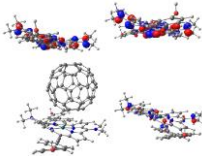
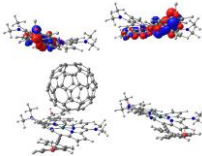
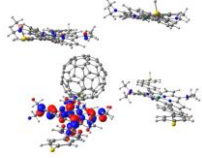
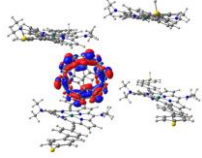
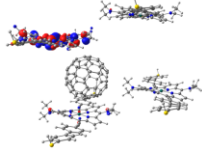
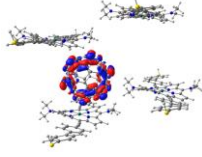
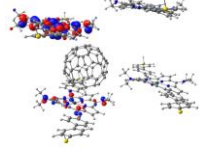
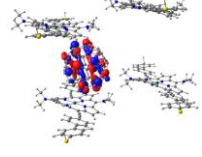
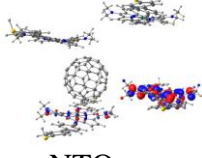
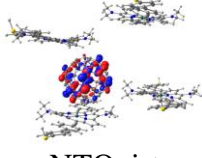
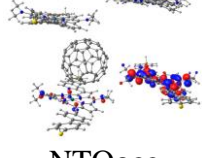
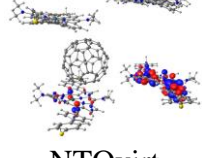
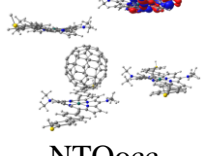
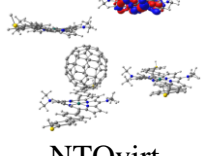
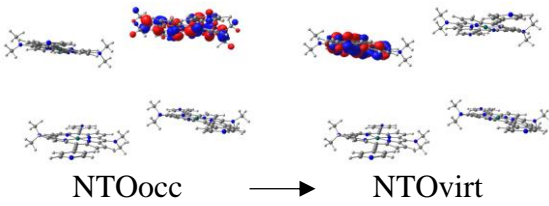
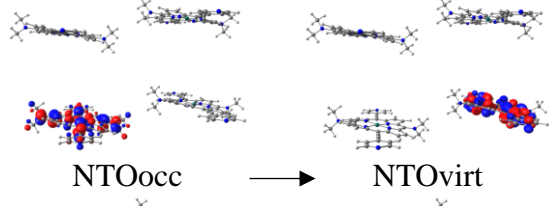
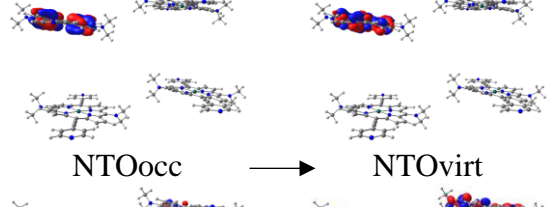
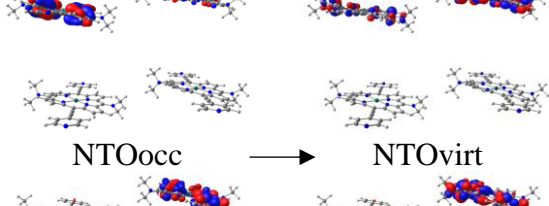
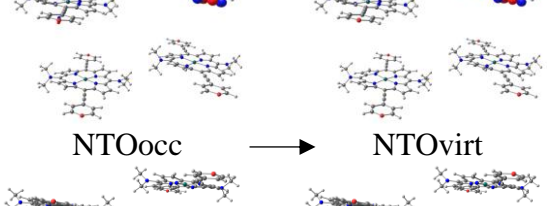
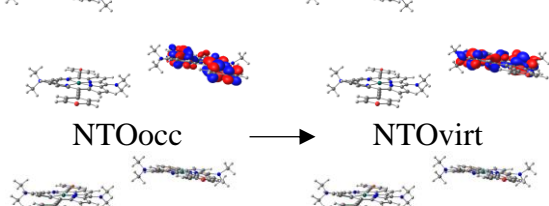
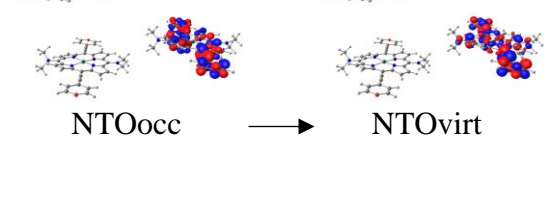
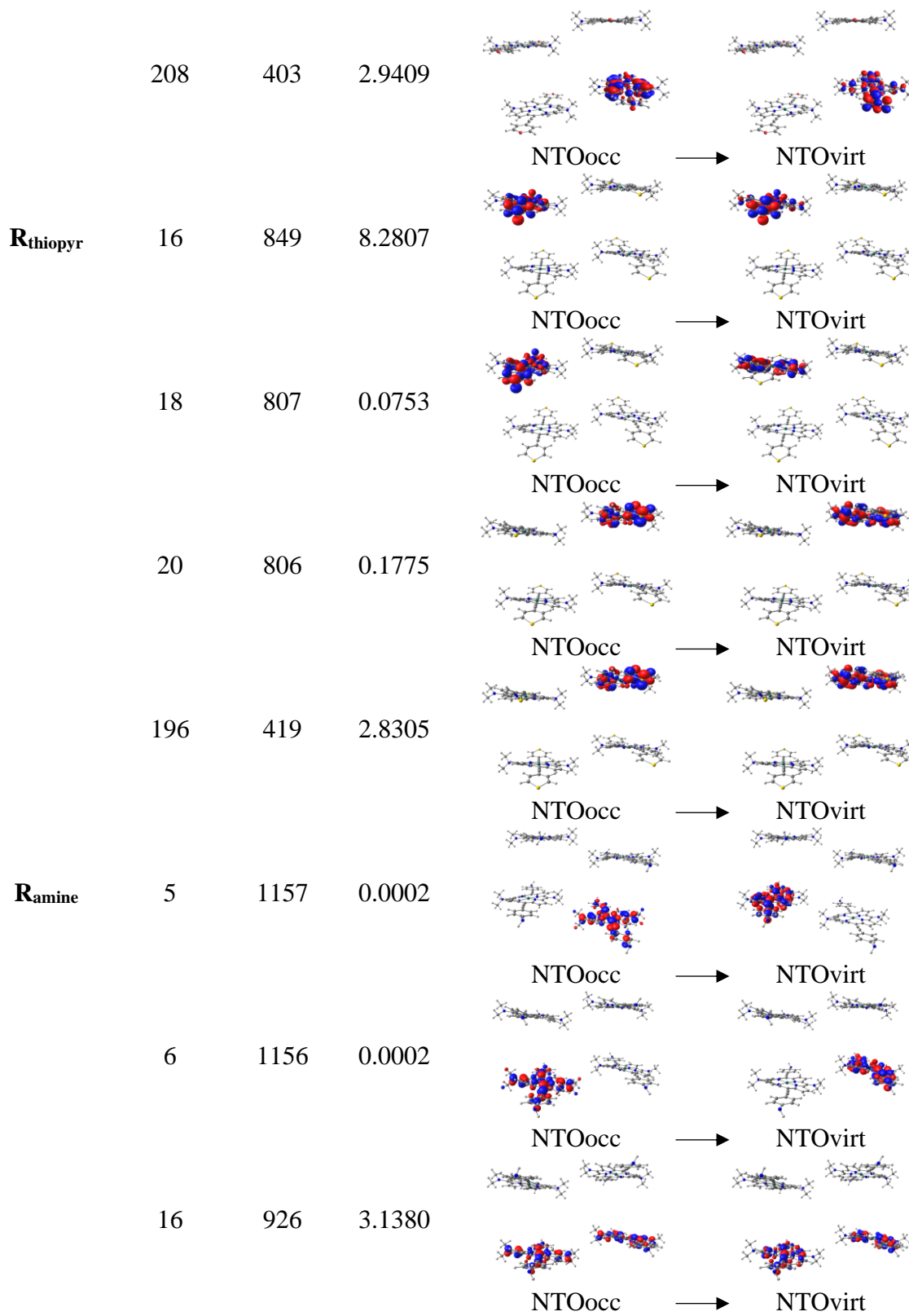
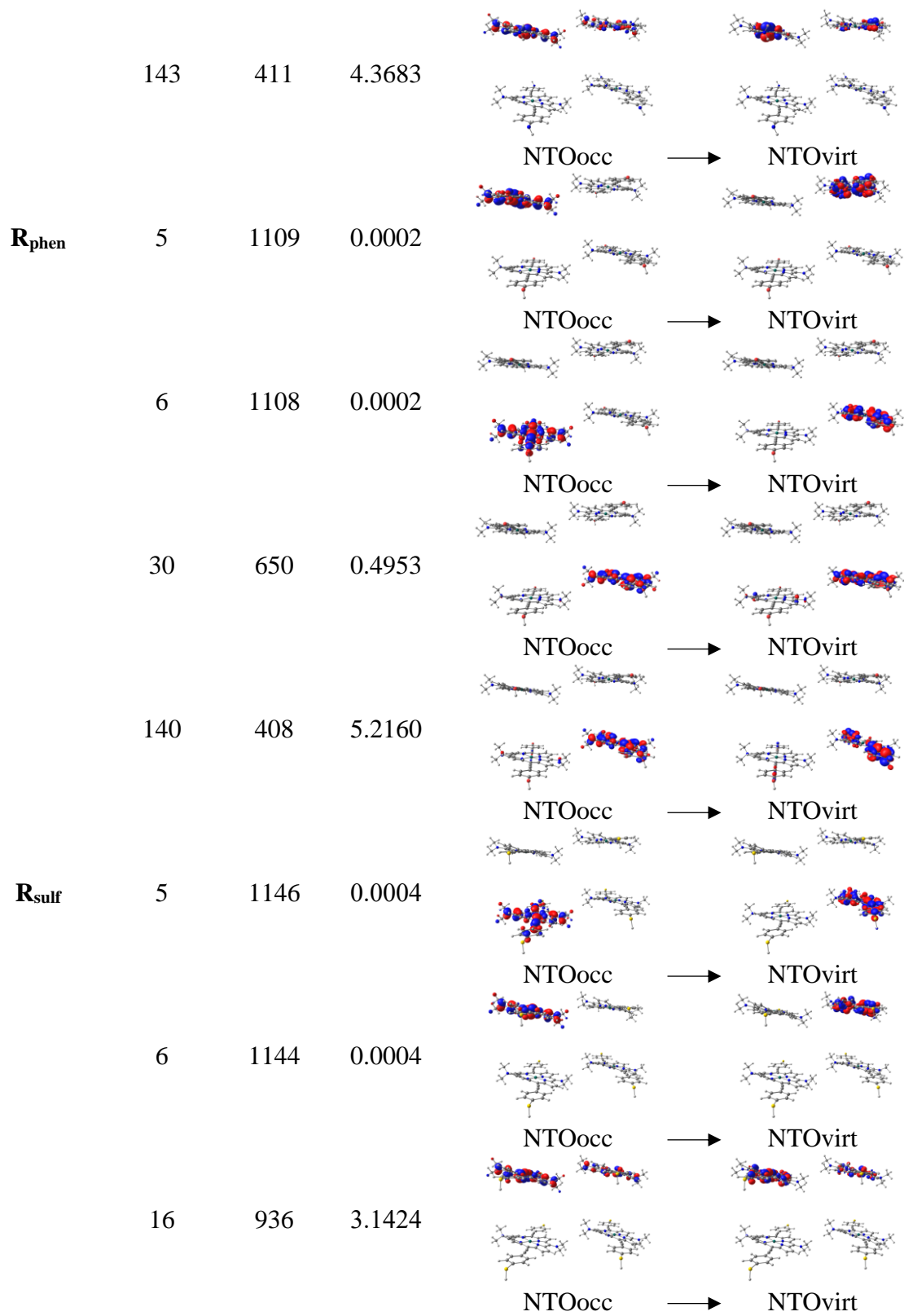
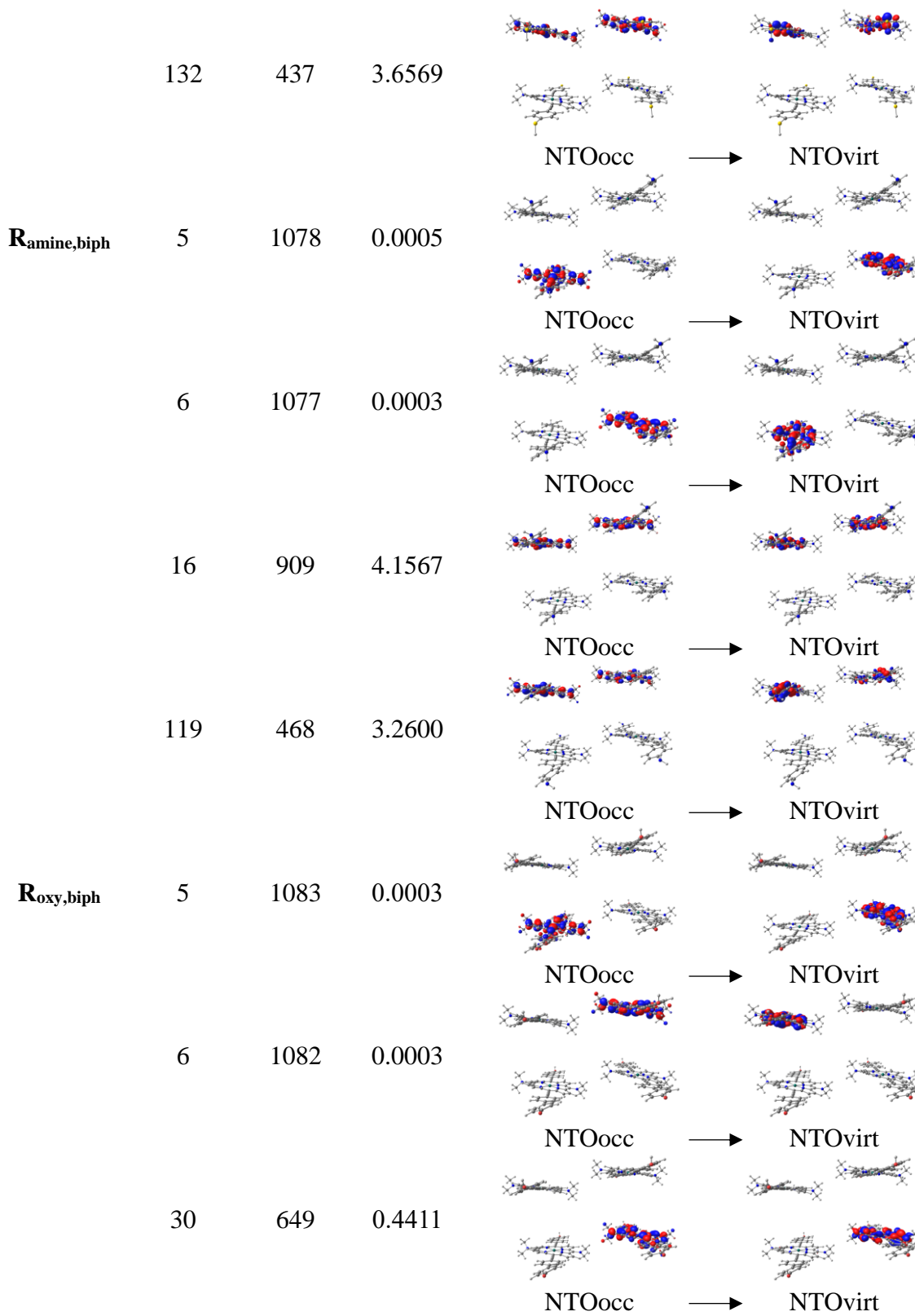
C₆₀@R_{sulf,biph}	225	493	1.2715	 NTOocc	→	 NTOvirt
	1	2706	0.0005	 NTOocc	→	 NTOvirt
	2	2674	0.0024	 NTOocc	→	 NTOvirt
	5	2467	0.0359	 NTOocc	→	 NTOvirt
	7	2383	0.0204	 NTOocc	→	 NTOvirt
	28	987	4.1981	 NTOocc	→	 NTOvirt
	212	494	2.7319	 NTOocc	→	 NTOvirt

Table S3. Excited states, excitation wavelength (λ), oscillator strengths (f) for model MOFs without C_{60} clusters obtained from TD-DFT calculations (TPSSH/6-31G).

MOF	Excited State	λ (nm)	f	Transition Involved
R_{py}	5	1009	0.0003	
	6	1008	0.0003	
	94	474	3.5877	
	136	420	2.6265	
R_{pyr}	15	819	0.0004	
	16	818	0.0029	
	20	794	7.7422	



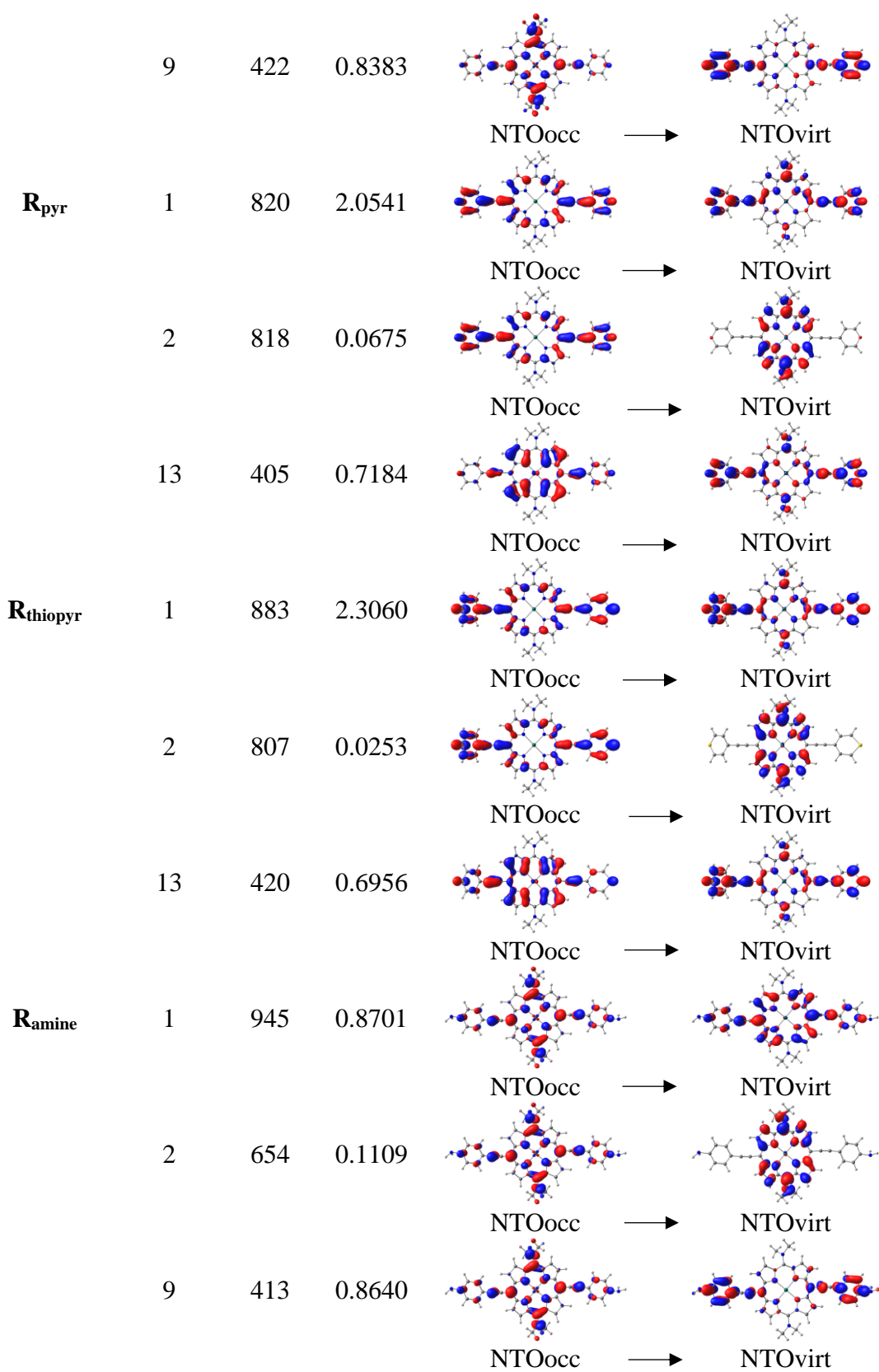


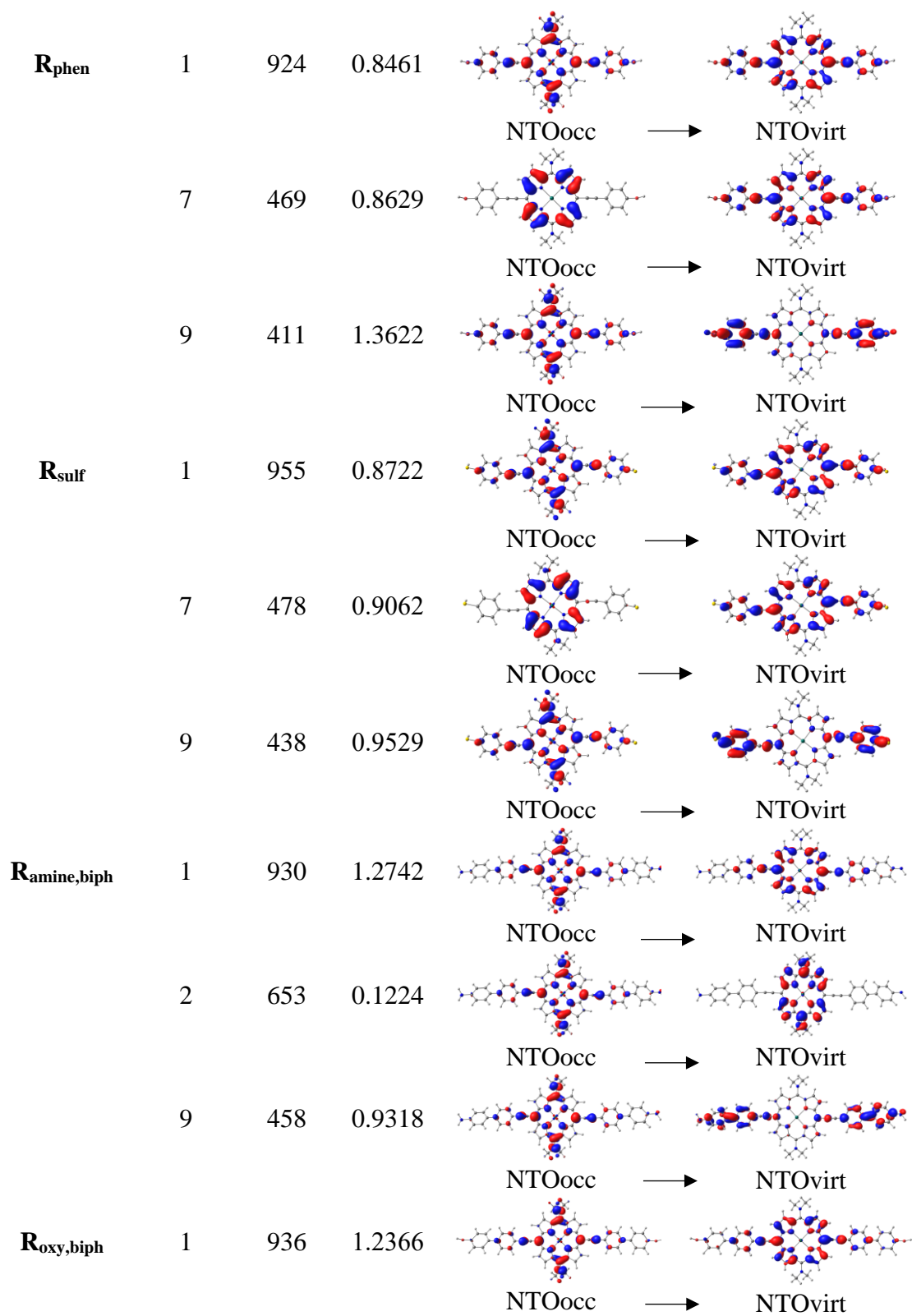


R_{sulf,biph}	116	480	3.3545		→	
				NTOocc		NTOvirt
	5	1082	0.0003		→	
				NTOocc		NTOvirt
	6	1081	0.0003		→	
			NTOocc		NTOvirt	
	30	642	0.4228		→	
				NTOocc		NTOvirt
	105	498	3.2969		→	
				NTOocc		NTOvirt

Table S4. Excited states, excitation wavelength (λ), oscillator strengths (f) for porphyrin unit of MOFs obtained from TD-DFT calculations (TPSSH/6-31G).

MOF	Excited State	λ (nm)	f	Transition Involved		
R_{py}	1	889	0.6189		→	
				NTOocc		NTOvirt
	6	473	0.9734		→	
				NTOocc		NTOvirt





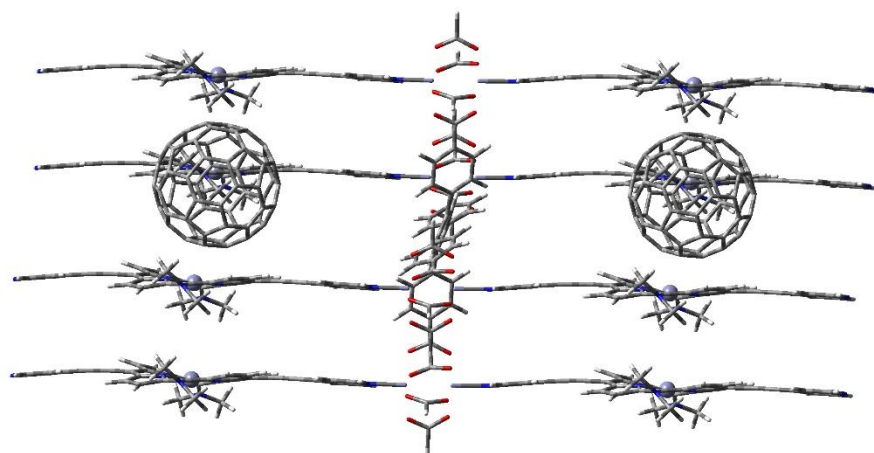
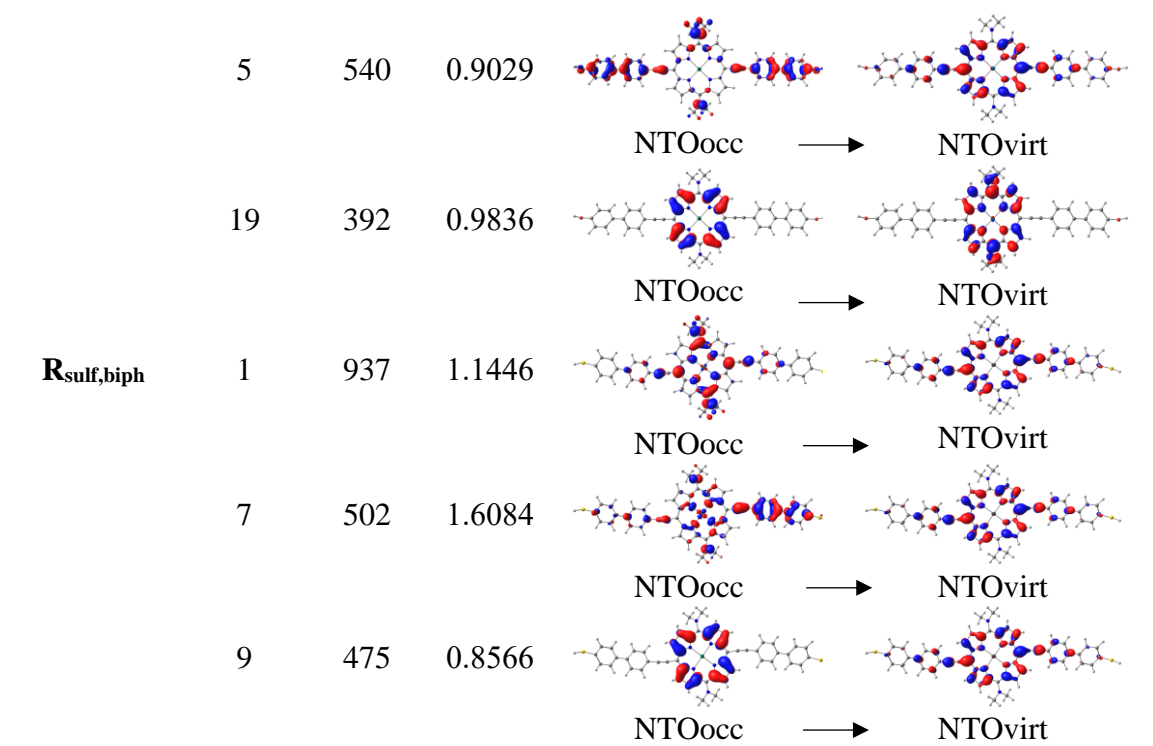


Figure S7. Molecular structure of $C_{60}@R_{py-new}$. Color code: H (white), C (gray), N (blue), O (red), and Zn (purple).