

## Supplementary Information

### Electronic, optical and transport properties of Zn-Porphyrin-C<sub>60</sub> MOFs: A combined periodic and cluster modeling.

Kevin Granados-Tavera<sup>a,b</sup>, Gloria Cárdenas-Jirón\*<sup>a</sup>

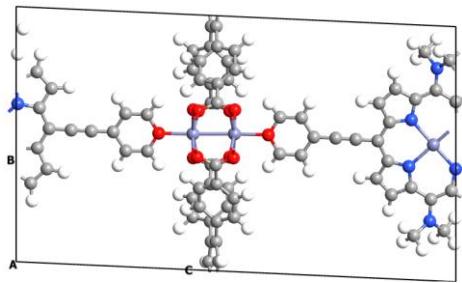
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<sup>b</sup>Facultad de Ciencias Básicas, Universidad de la Amazonía, Florencia, Colombia

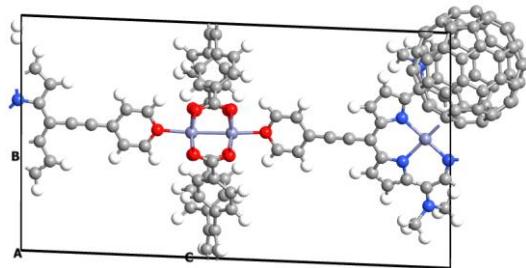
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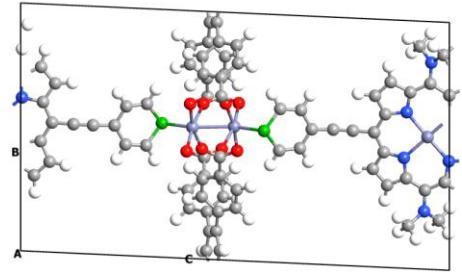
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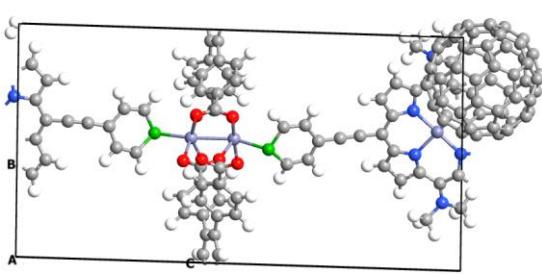
$\mathbf{R}_{\text{pyr}}$



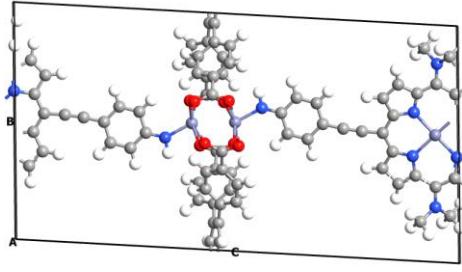
$\mathbf{C}_{60}@\mathbf{R}_{\text{pyr}}$



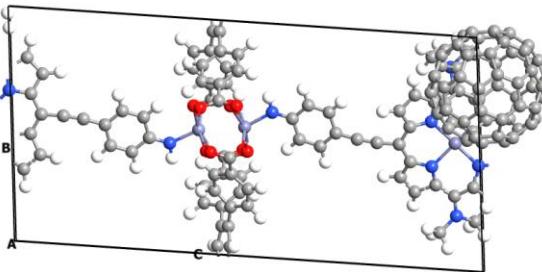
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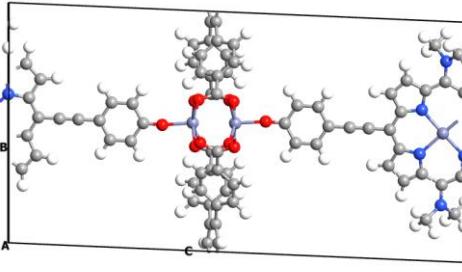
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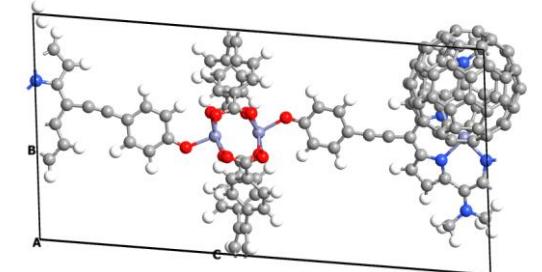
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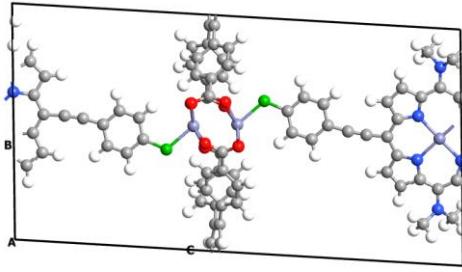
$\mathbf{C}_{60}@\mathbf{R}_{\text{amine}}$



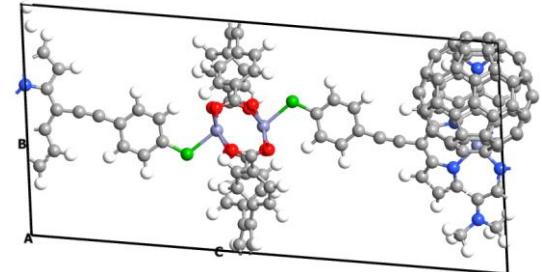
$\mathbf{R}_{\text{phen}}$



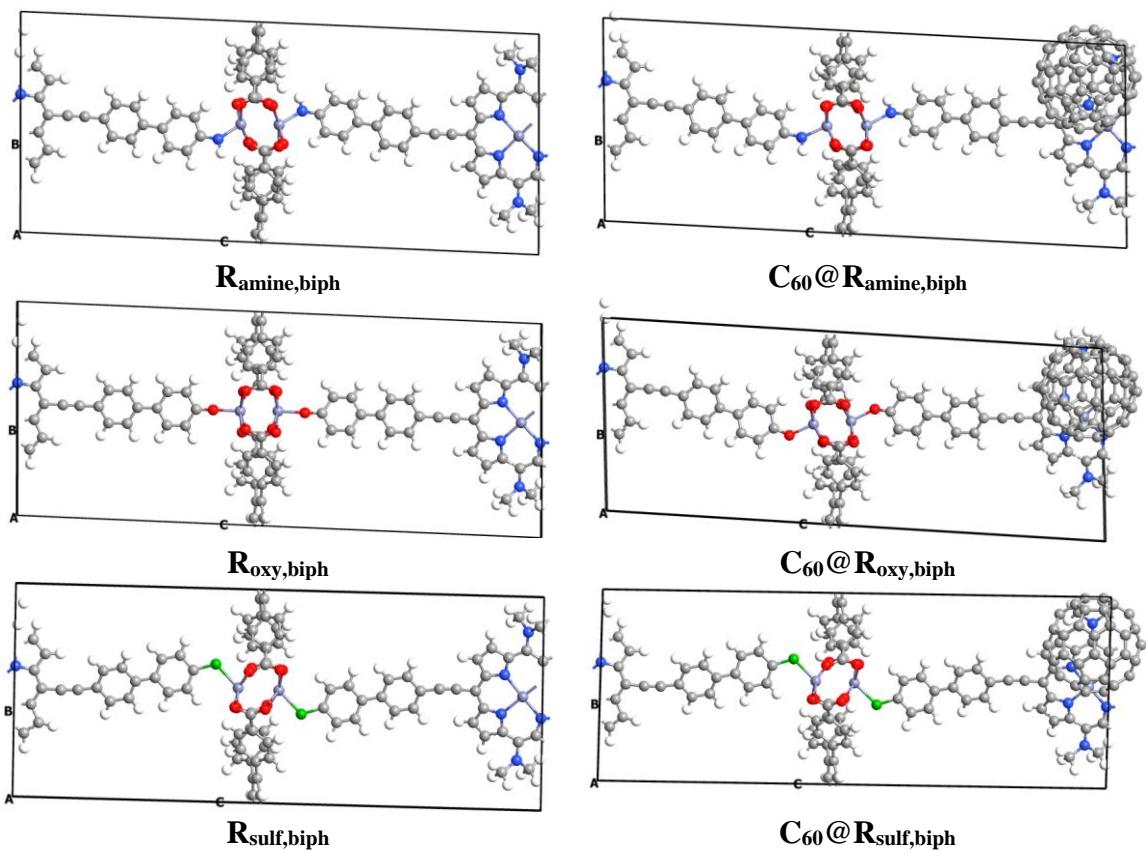
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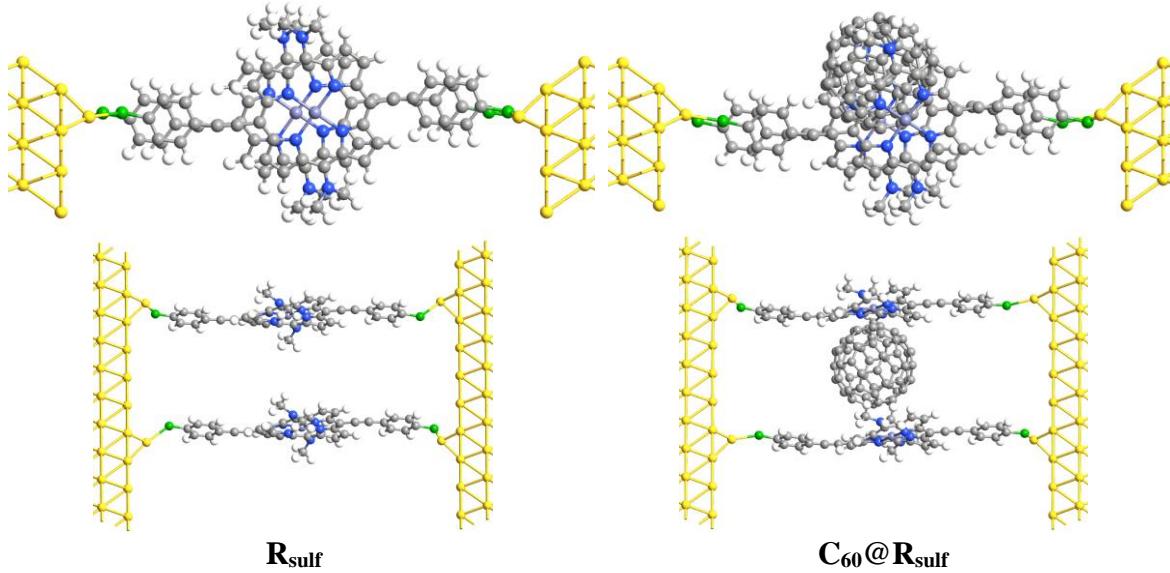
$\mathbf{R}_{\text{sulf}}$



$\mathbf{C}_{60}@\mathbf{R}_{\text{sulf}}$



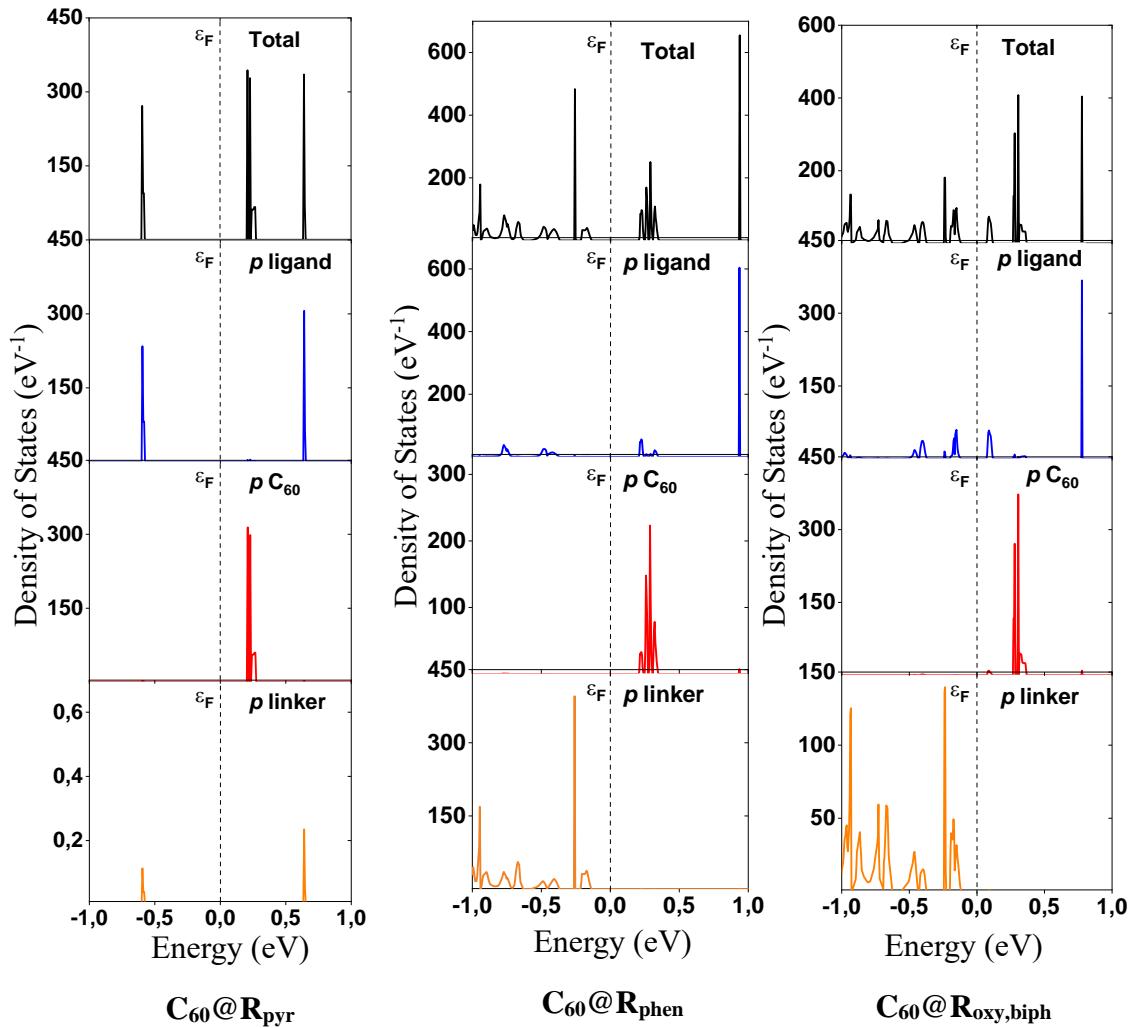
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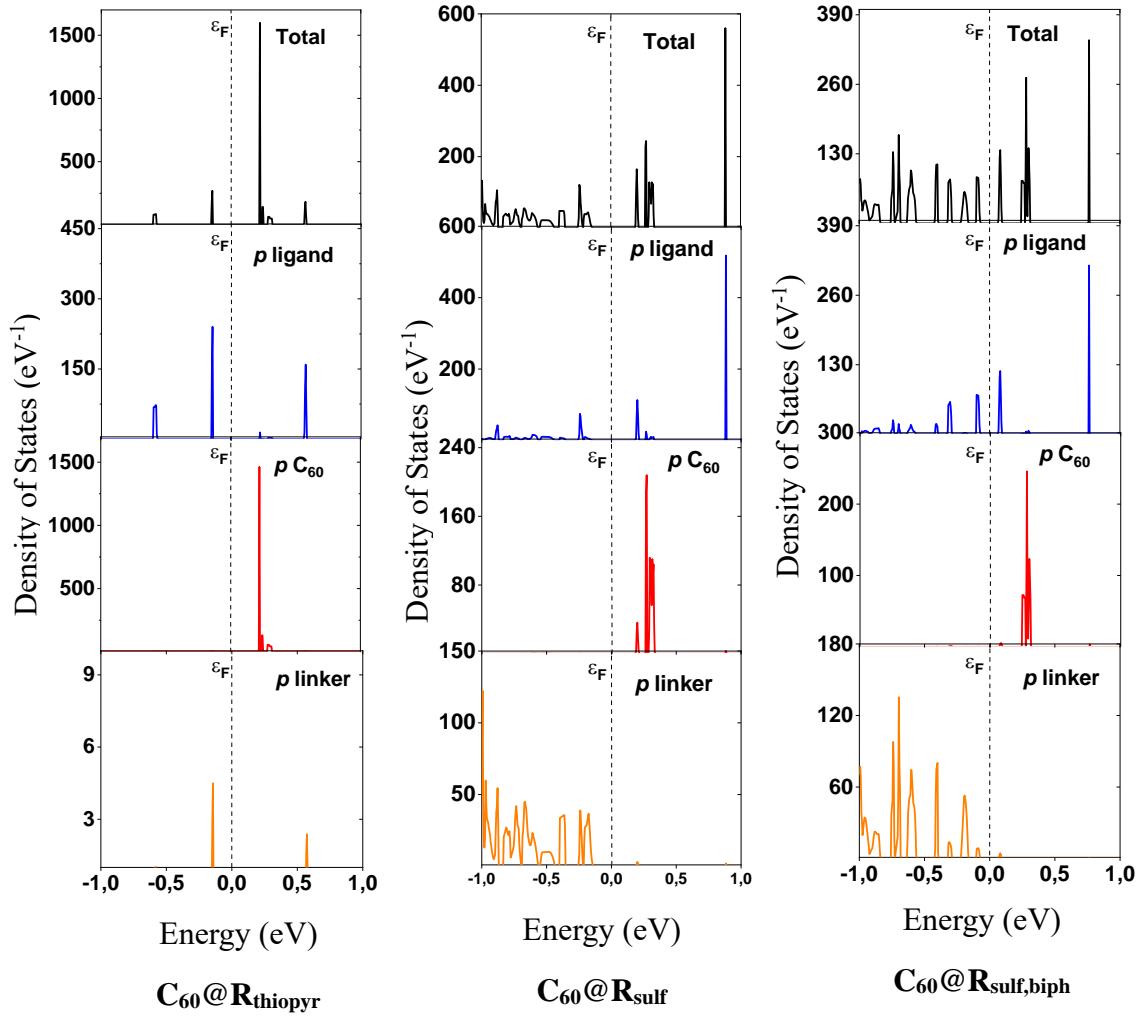
**Figure S2.** Optimized electronic device structure for a cluster;  $\mathbf{R}_{\text{sulf}}$  and  $\mathbf{C}_{60}@\mathbf{R}_{\text{sulf}}$ . Front view (top) and side view (bottom).

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

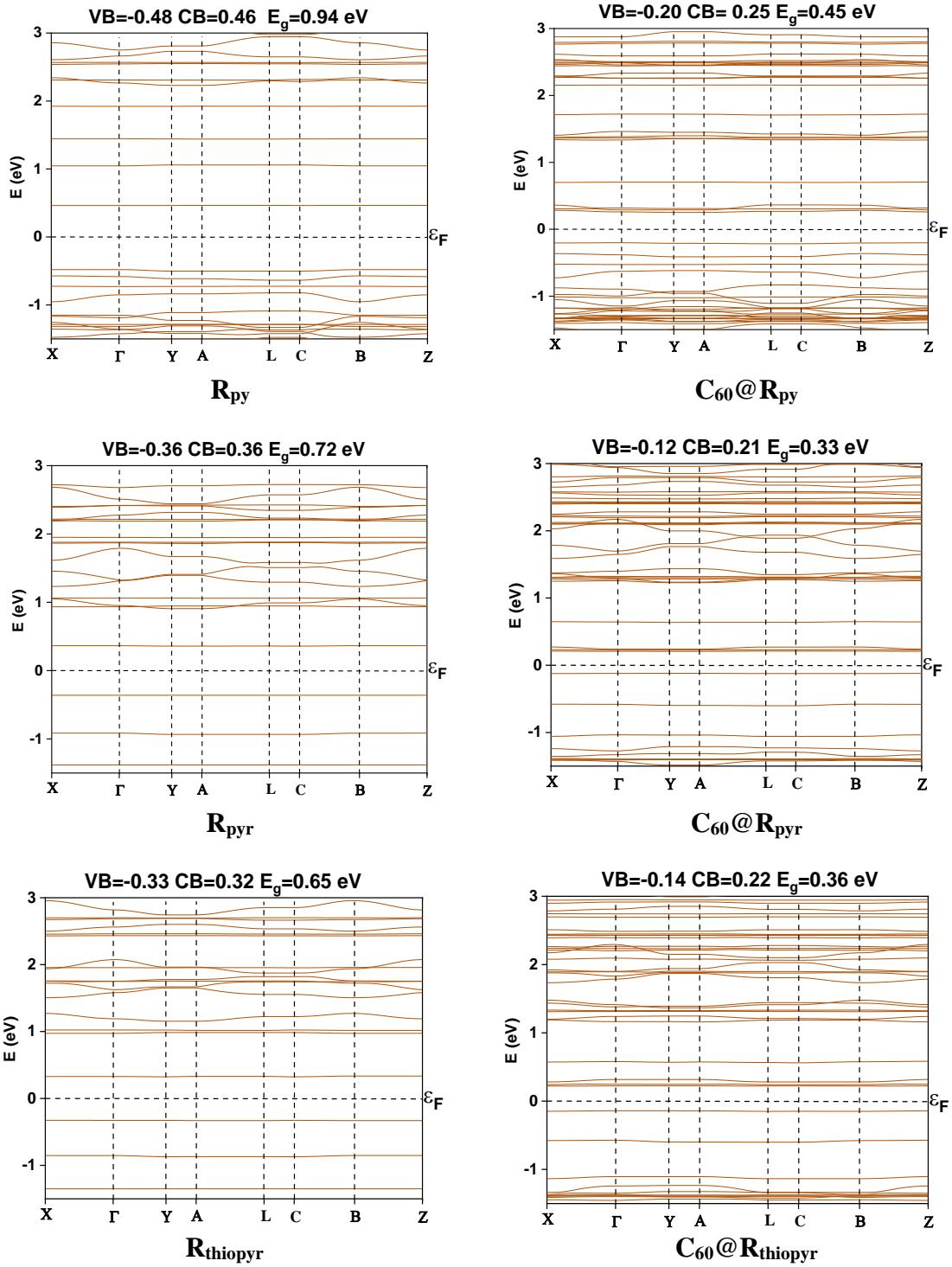
MOF	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$
$\mathbf{R}_{\text{py}}$	11.66	15.68	27.35	92.39	95.49	90.13
$\mathbf{R}_{\text{pyr}}$	11.55	15.74	27.39	92.60	95.19	90.06
$\mathbf{R}_{\text{thiopyr}}$	11.51	15.60	27.89	92.51	94.74	90.20
$\mathbf{R}_{\text{amine}}$	11.70	15.59	29.33	93.66	96.08	89.62
$\mathbf{R}_{\text{phen}}$	11.64	15.59	29.91	92.40	95.65	90.11
$\mathbf{R}_{\text{sulf}}$	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

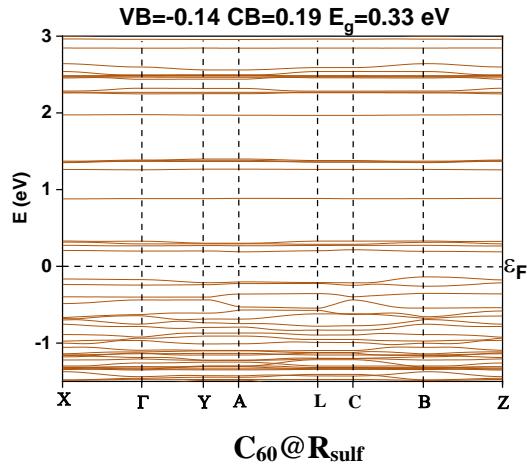
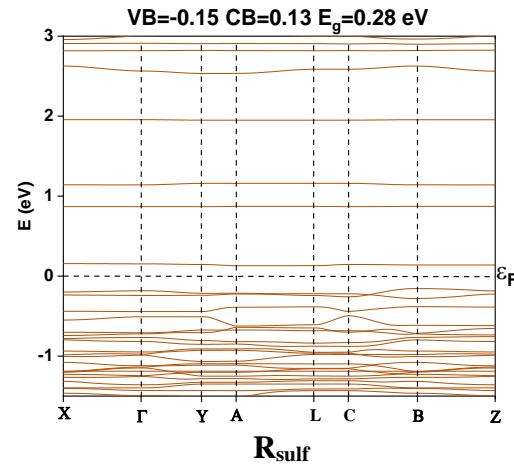
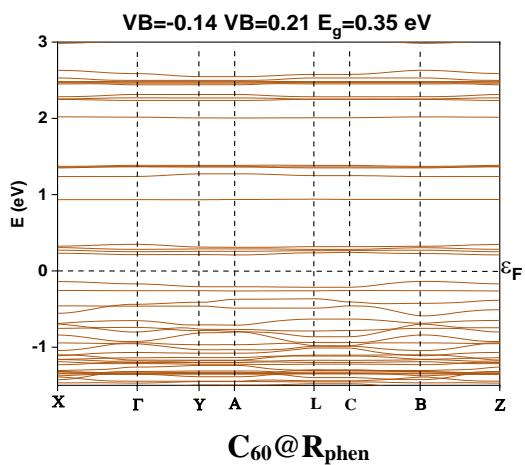
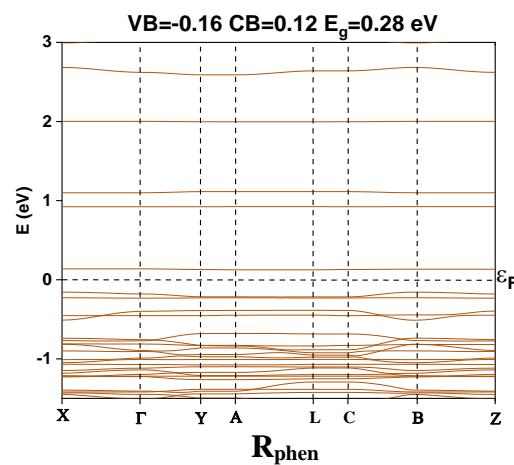
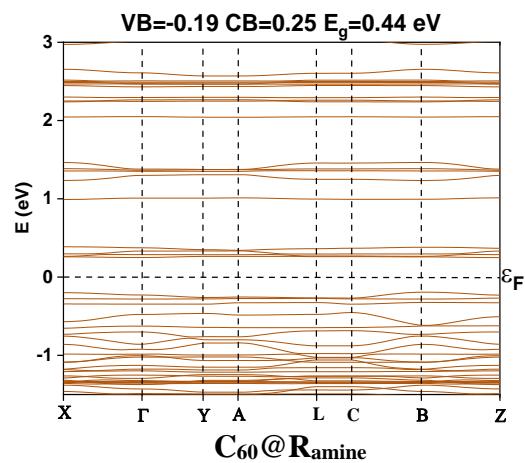
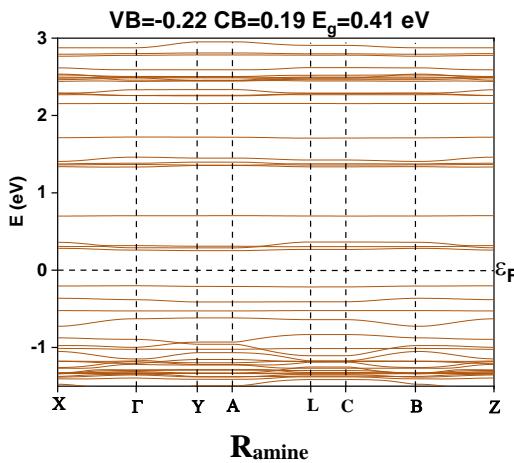


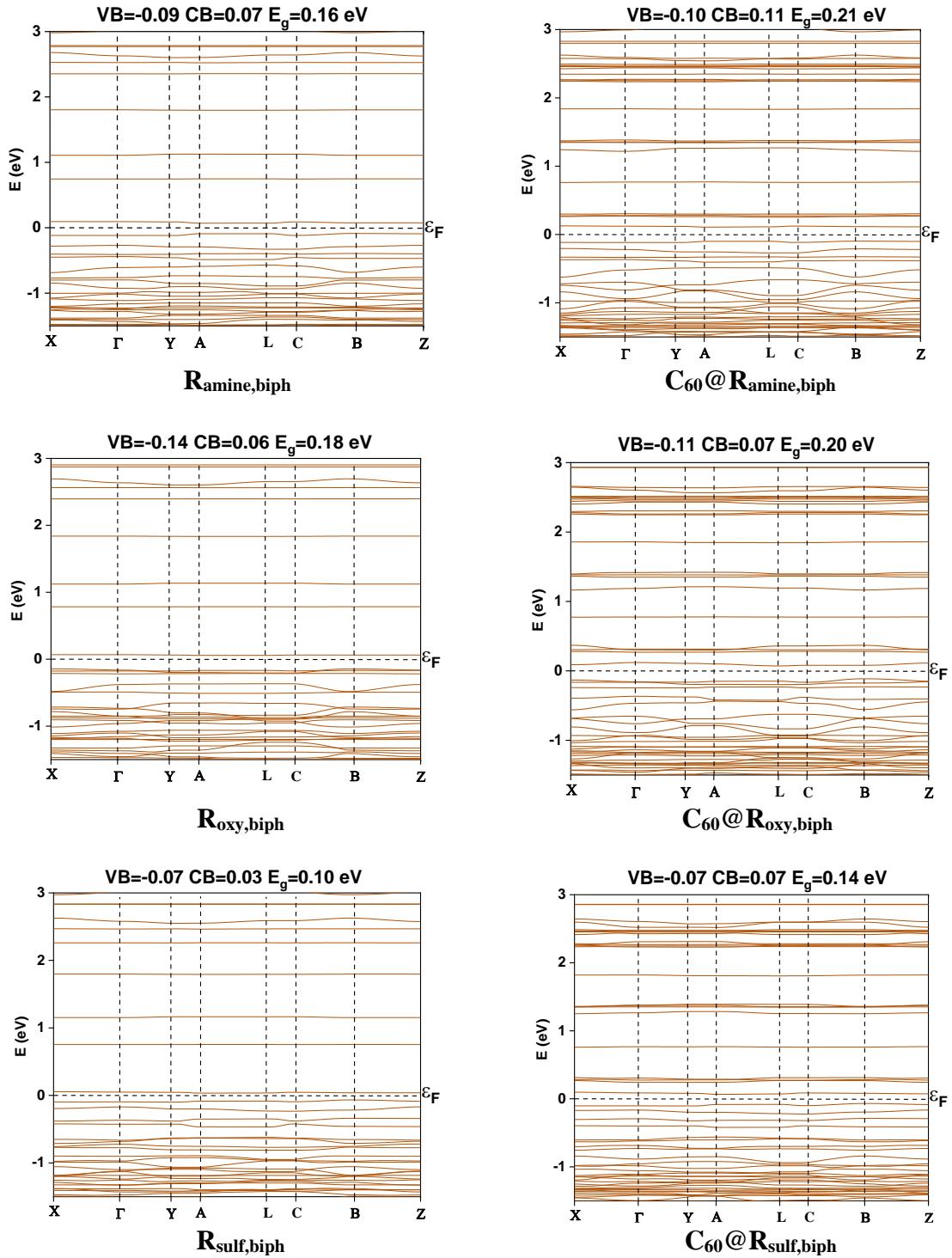
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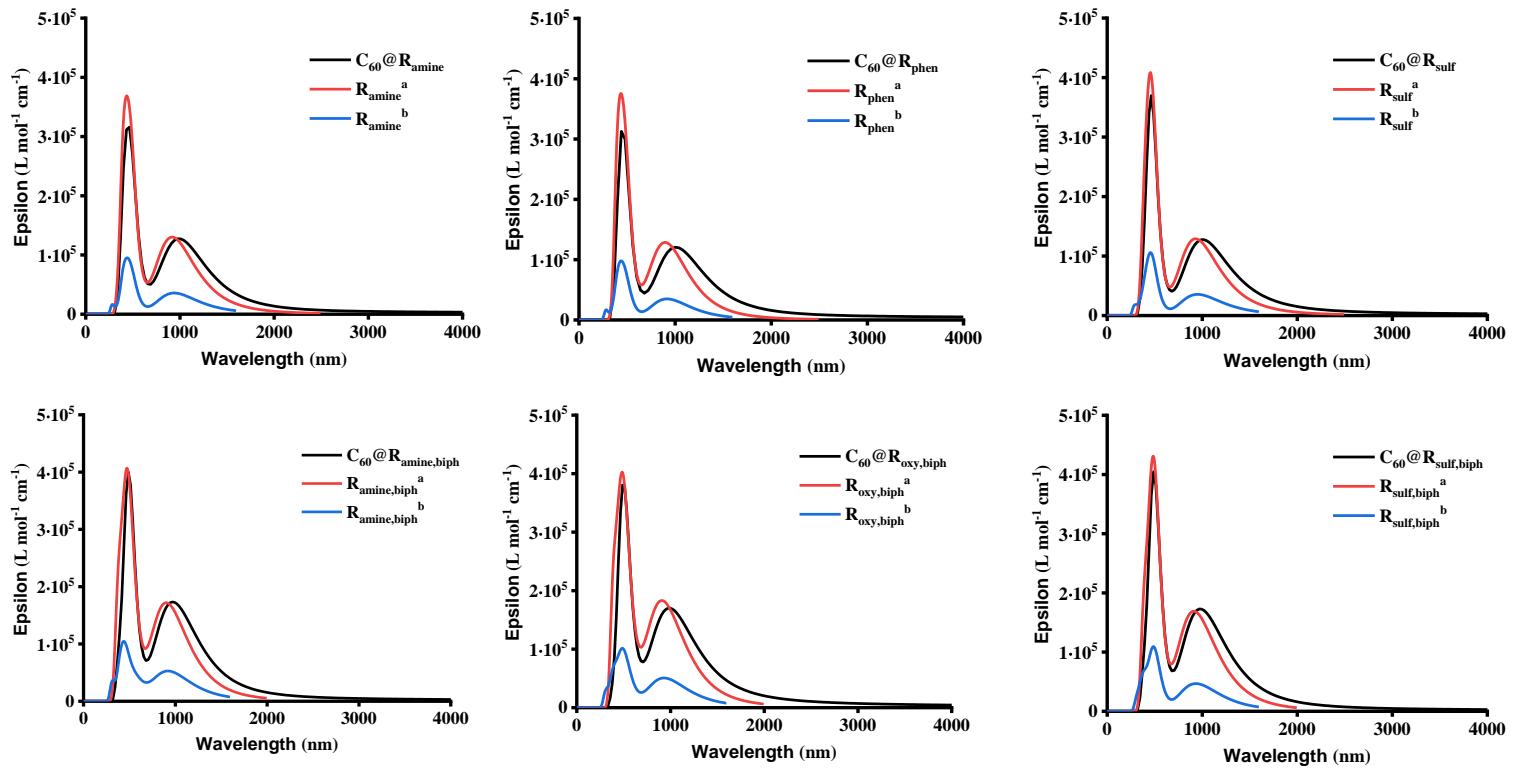
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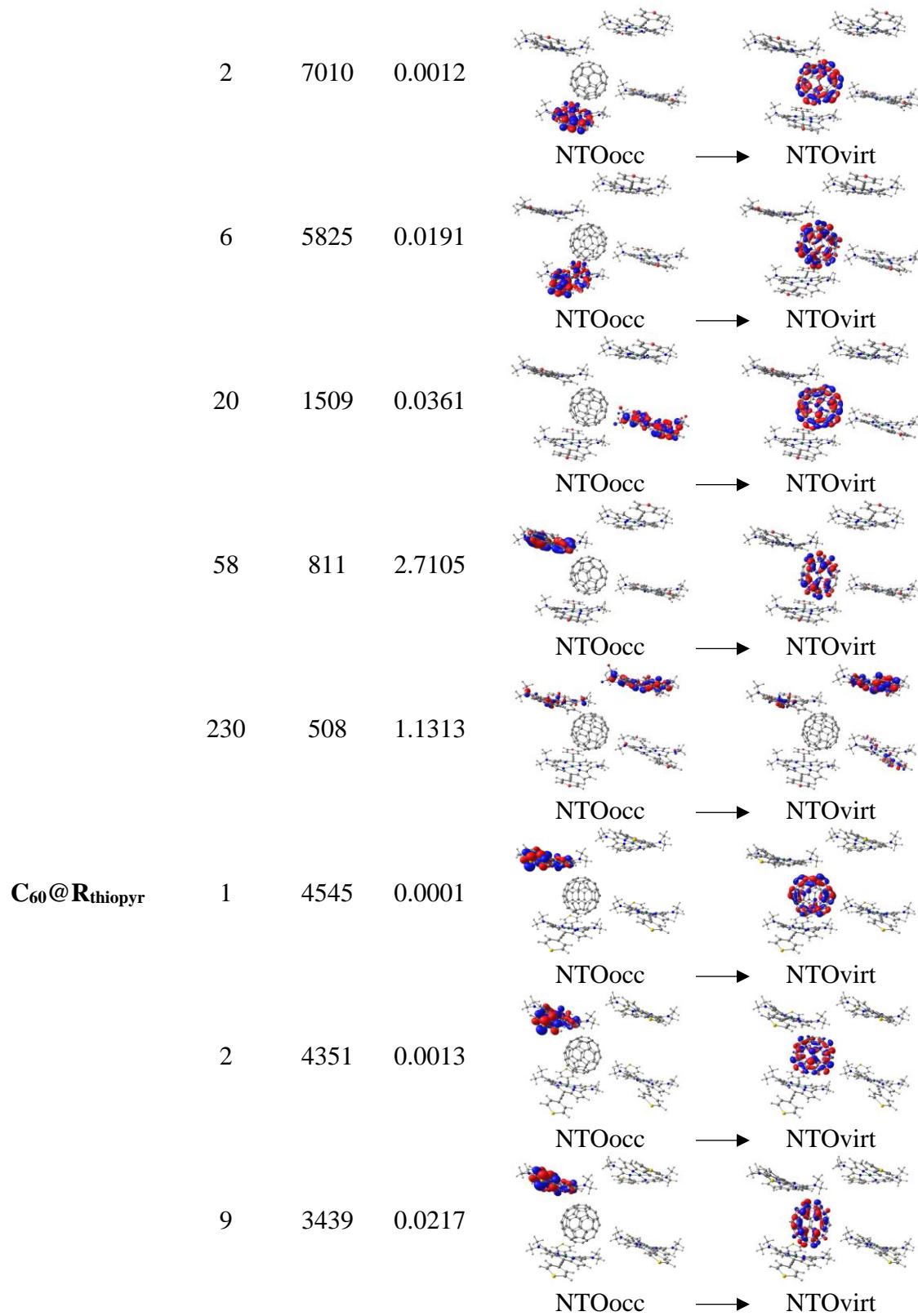
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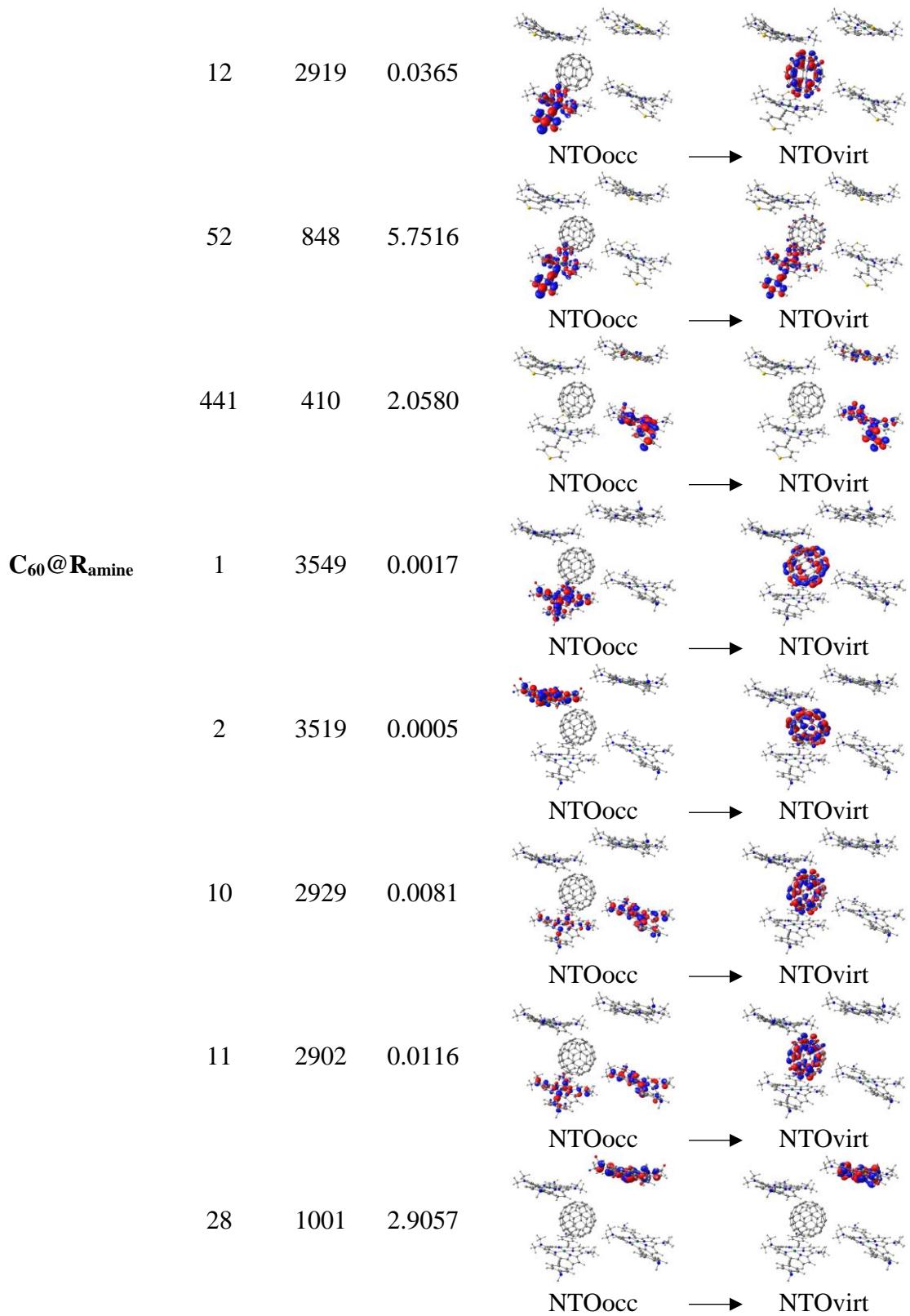


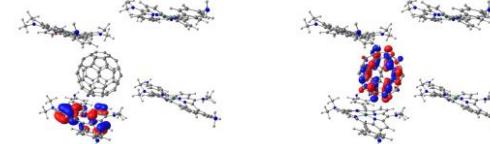
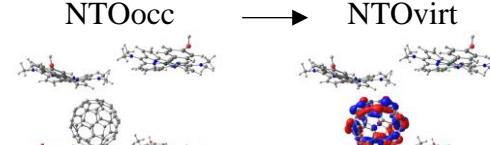
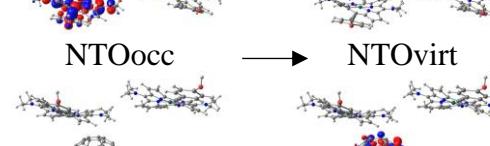
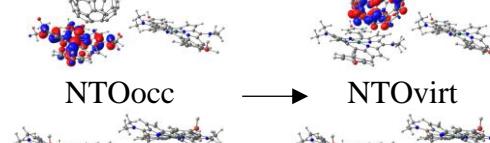
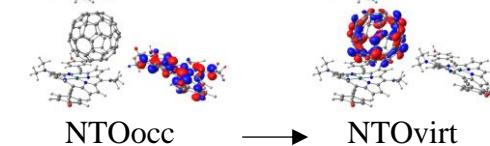
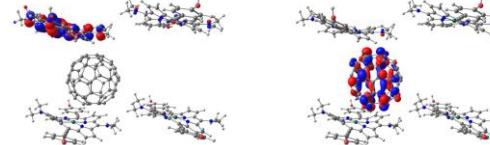
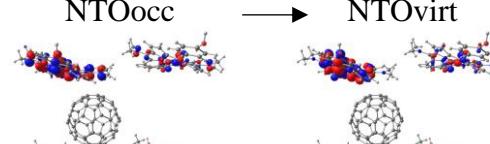
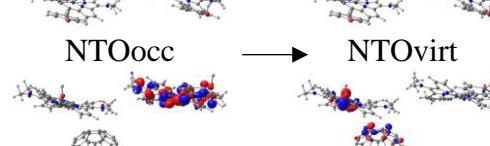
**Figure S6.** Electronic absorption spectra of MOFs clusters calculated at the TPSSh/6–31G level of theory. <sup>a</sup> MOF cluster without  $C_{60}$ . <sup>b</sup> Porphyrin unit.

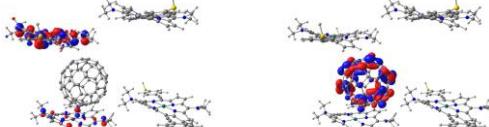
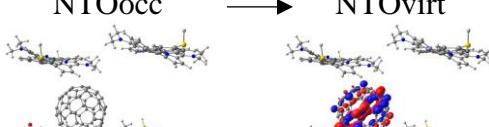
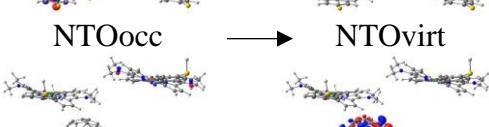
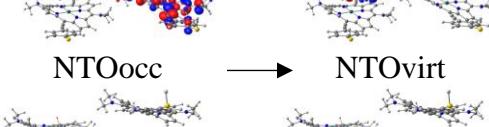
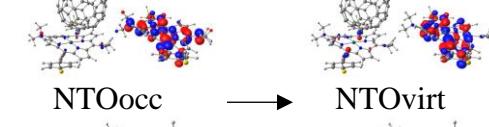
**Table S2.** Excited states, excitation wavelength ( $\lambda$ ), oscillator strengths ( $f$ ) for model C<sub>60</sub>@MOFs clusters obtained from TD-DFT calculations (TPSSh/6-31G).

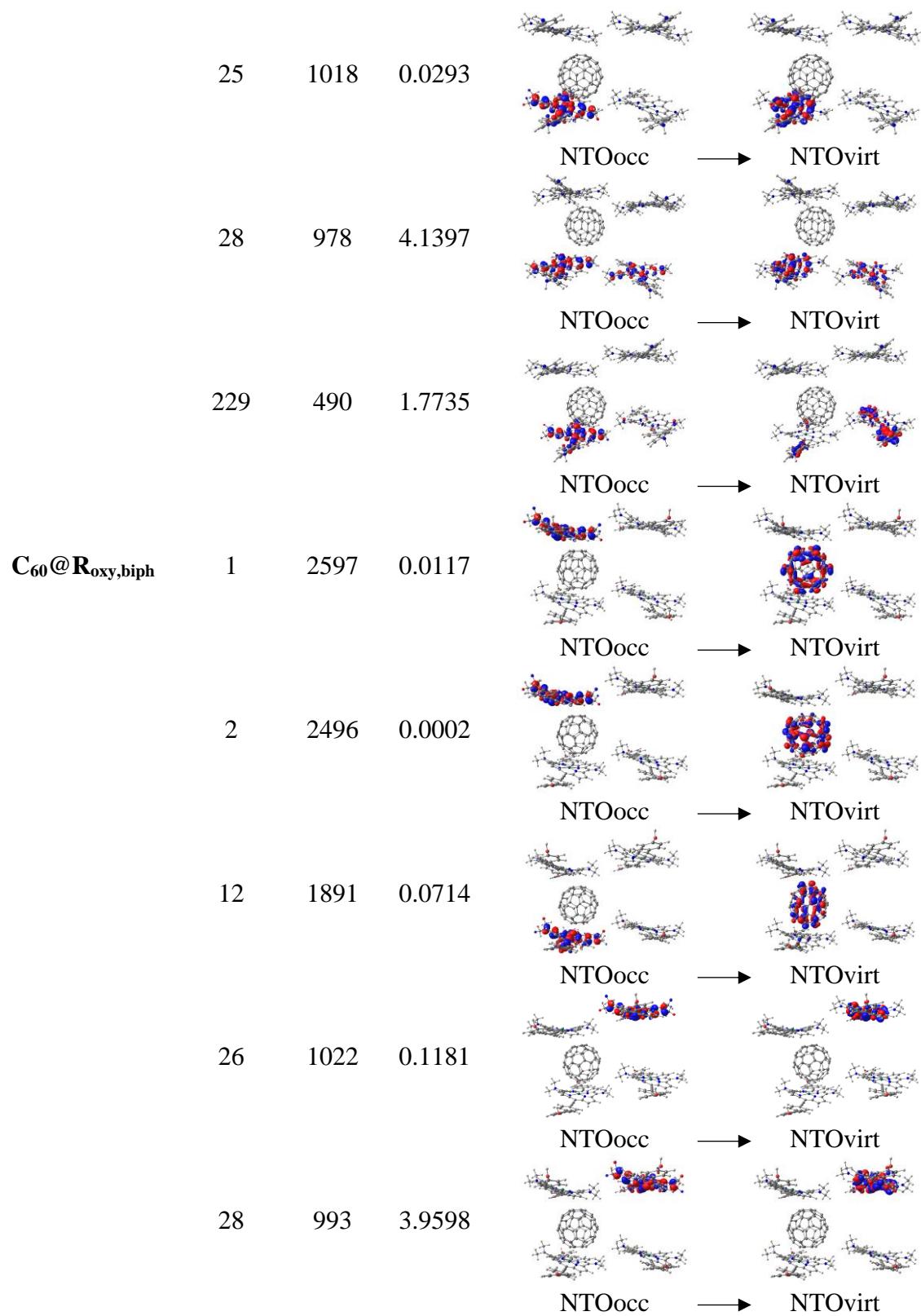
MOF	Excited State	$\lambda$ (nm)	$f$	Transition Involved
C <sub>60</sub> @R <sub>py</sub>	1	2139	0.0001	
	2	2064	0.0082	
	6	1952	0.0284	
	8	1910	0.0378	
	28	889	2.6075	
	346	413	2.2285	
	1	7161	0.0015	

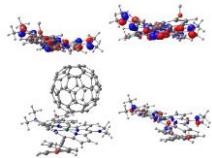
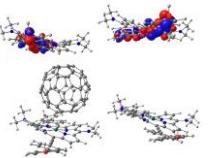
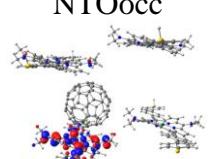
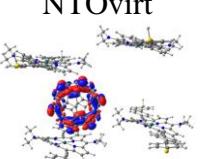
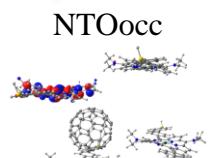
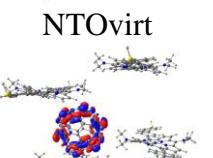
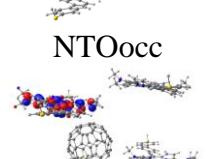
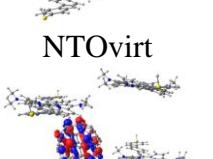
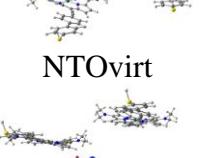
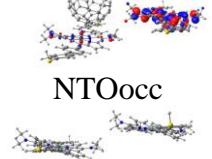
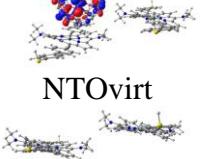
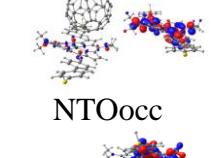
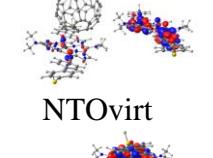




	357	421	1.4103	
			NTOocc → NTOvirt	
<b>C<sub>60</sub>@R<sub>phen</sub></b>	1	4053	0.0001	
			NTOocc → NTOvirt	
	2	3839	0.0045	
			NTOocc → NTOvirt	
	9	3131	0.0521	
			NTOocc → NTOvirt	
	12	2735	0.0294	
			NTOocc → NTOvirt	
	28	1016	2.8760	
			NTOocc → NTOvirt	
	337	424	1.2110	
			NTOocc → NTOvirt	
<b>C<sub>60</sub>@R<sub>sulf</sub></b>	1	2809	0.0042	
			NTOocc → NTOvirt	

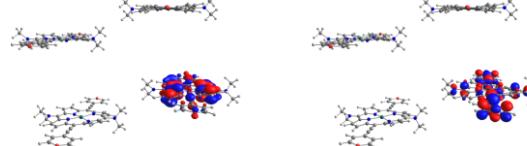
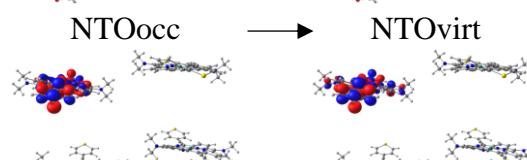
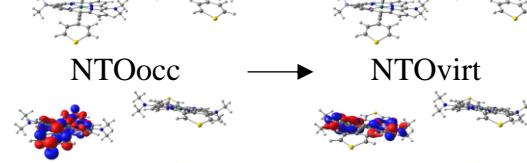
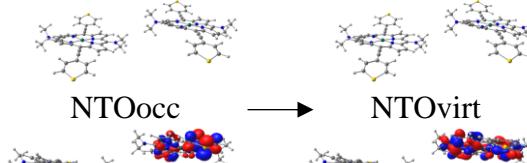
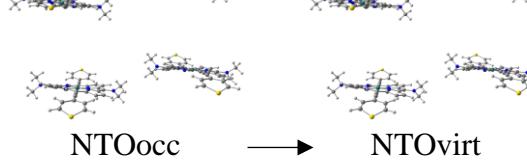
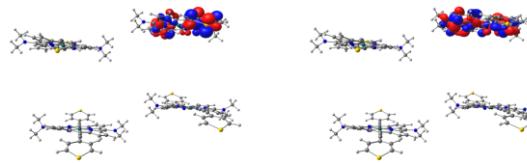
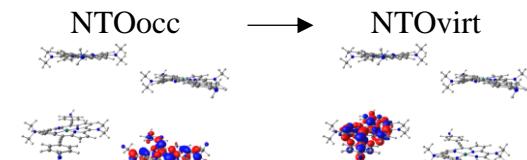
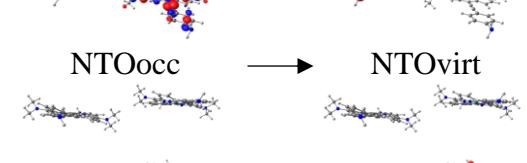
2	2797	0.0026		NTOocc → NTOvirt
4	2641	0.0116		NTOocc → NTOvirt
9	2417	0.0308		NTOocc → NTOvirt
28	1009	3.0878		NTOocc → NTOvirt
295	448	3.0212		NTOocc → NTOvirt
<b>C<sub>60</sub>@R<sub>amine,biph</sub></b>		1	2780	0.0006
		2	2769	0.0011
		19	1231	0.0012



225	493	1.2715		
<b>C<sub>60</sub>@R<sub>sulf,biph</sub></b>	<b>1</b>	<b>2706</b>	<b>0.0005</b>	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	

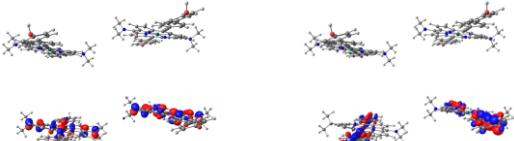
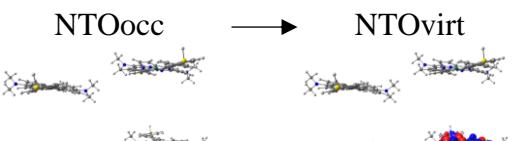
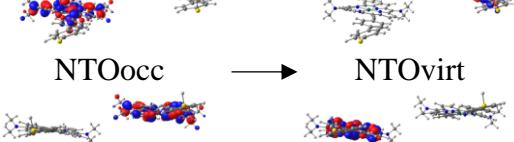
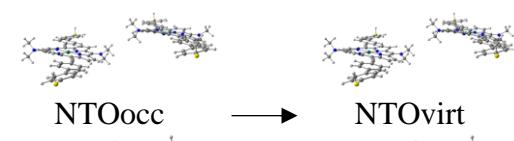
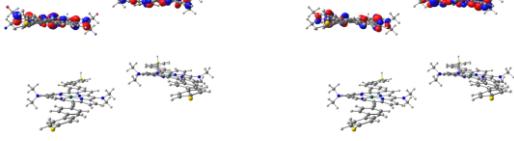
**Table S3.** Excited states, excitation wavelength ( $\lambda$ ), oscillator strengths ( $f$ ) for model MOFs without C<sub>60</sub> clusters obtained from TD-DFT calculations (TPSSh/6-31G).

MOF	Excited		$\lambda$ (nm)	$f$	Transition Involved	
	State					
<b>R<sub>pyr</sub></b>	5	1009	0.0003			
					NTOocc	→ NTOvirt
	6	1008	0.0003			
					NTOocc	→ NTOvirt
	94	474	3.5877			
					NTOocc	→ NTOvirt
	136	420	2.6265			
					NTOocc	→ NTOvirt
<b>R<sub>pyr</sub></b>	15	819	0.0004			
					NTOocc	→ NTOvirt
	16	818	0.0029			
					NTOocc	→ NTOvirt
<b>R<sub>pyr</sub></b>	20	794	7.7422			
					NTOocc	→ NTOvirt

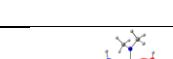
	208	403	2.9409	
<b>Rthiopyr</b>	16	849	8.2807	
	18	807	0.0753	
	20	806	0.1775	
	196	419	2.8305	
<b>Ramine</b>	5	1157	0.0002	
	6	1156	0.0002	
	16	926	3.1380	

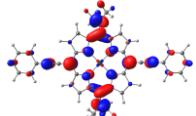
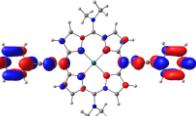
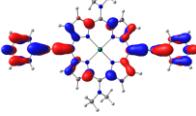
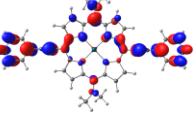
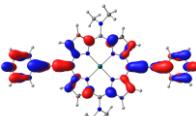
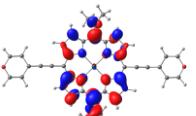
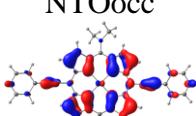
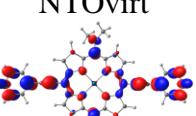
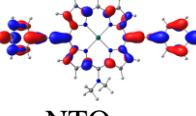
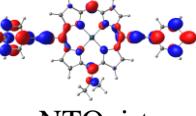
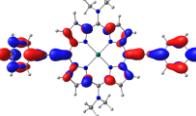
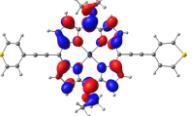
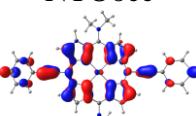
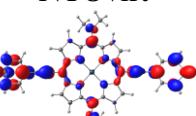
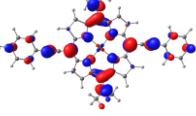
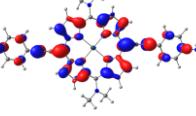
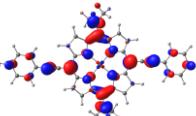
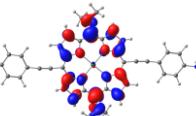
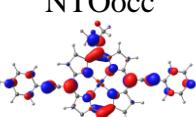
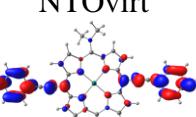


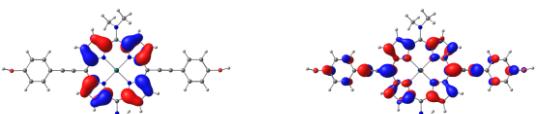
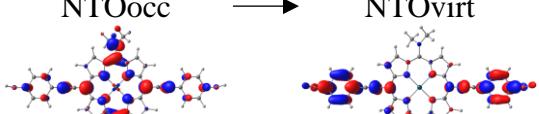
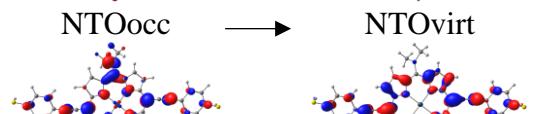
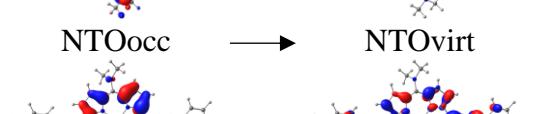
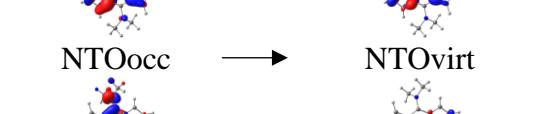
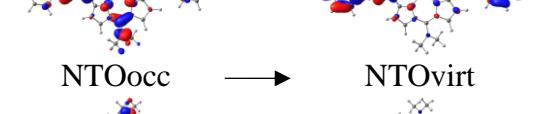
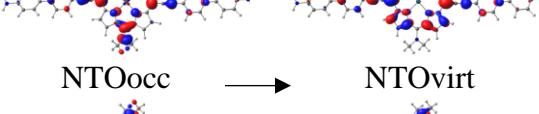
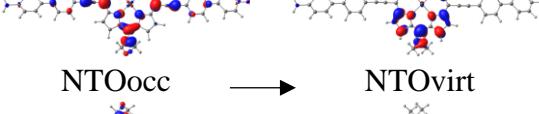
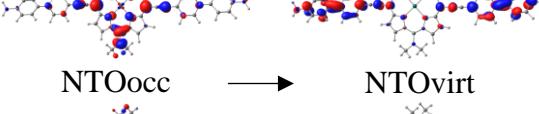


116	480	3.3545	
<b>R<sub>sulf,biph</sub></b>			NTOccupied → NTOrandom
5	1082	0.0003	
6	1081	0.0003	
30	642	0.4228	
105	498	3.2969	

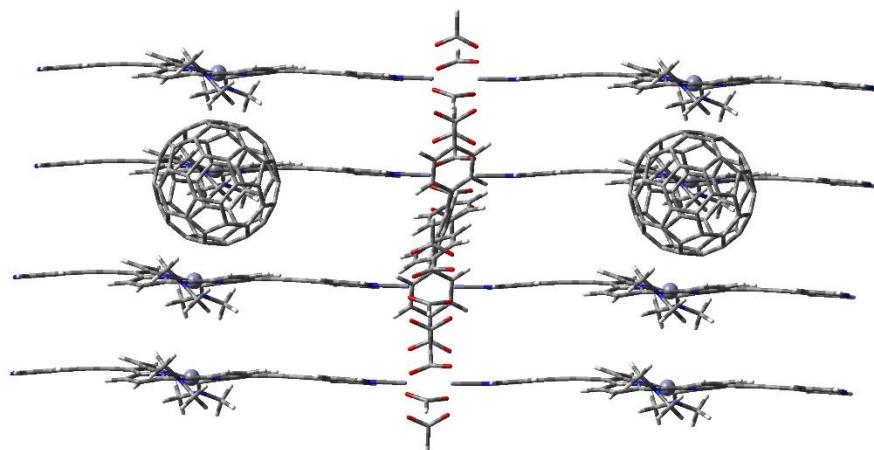
**Table S4.** Excited states, excitation wavelength ( $\lambda$ ), oscillator strengths ( $f$ ) for porphyrin unit of MOFs obtained from TD-DFT calculations (TPSSh/6-31G).

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

	9	422	0.8383		
<b>R<sub>pyr</sub></b>	1	820	2.0541		
	2	818	0.0675		
	13	405	0.7184		
<b>R<sub>thiopyr</sub></b>	1	883	2.3060		
	2	807	0.0253		
	13	420	0.6956		
<b>R<sub>amine</sub></b>	1	945	0.8701		
	2	654	0.1109		
	9	413	0.8640		

<b>R<sub>phen</sub></b>	1	924	0.8461	
				NTOocc → NTOvirt
	7	469	0.8629	
				NTOocc → NTOvirt
	9	411	1.3622	
				NTOocc → NTOvirt
<b>R<sub>sulf</sub></b>	1	955	0.8722	
				NTOocc → NTOvirt
	7	478	0.9062	
				NTOocc → NTOvirt
	9	438	0.9529	
				NTOocc → NTOvirt
<b>R<sub>amine,biph</sub></b>	1	930	1.2742	
				NTOocc → NTOvirt
	2	653	0.1224	
				NTOocc → NTOvirt
	9	458	0.9318	
				NTOocc → NTOvirt
<b>R<sub>oxy,biph</sub></b>	1	936	1.2366	
				NTOocc → NTOvirt

5	540	0.9029	NTOocc	NTOvirt	
19	392	0.9836	NTOocc	NTOvirt	
<b>R<sub>sulf,biph</sub></b>	1	937	1.1446	NTOocc	NTOvirt
7	502	1.6084	NTOocc	NTOvirt	
9	475	0.8566	NTOocc	NTOvirt	



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