

Theoretical investigation of CO₂ capture in MIL-88 series: Effects of organic linker modification

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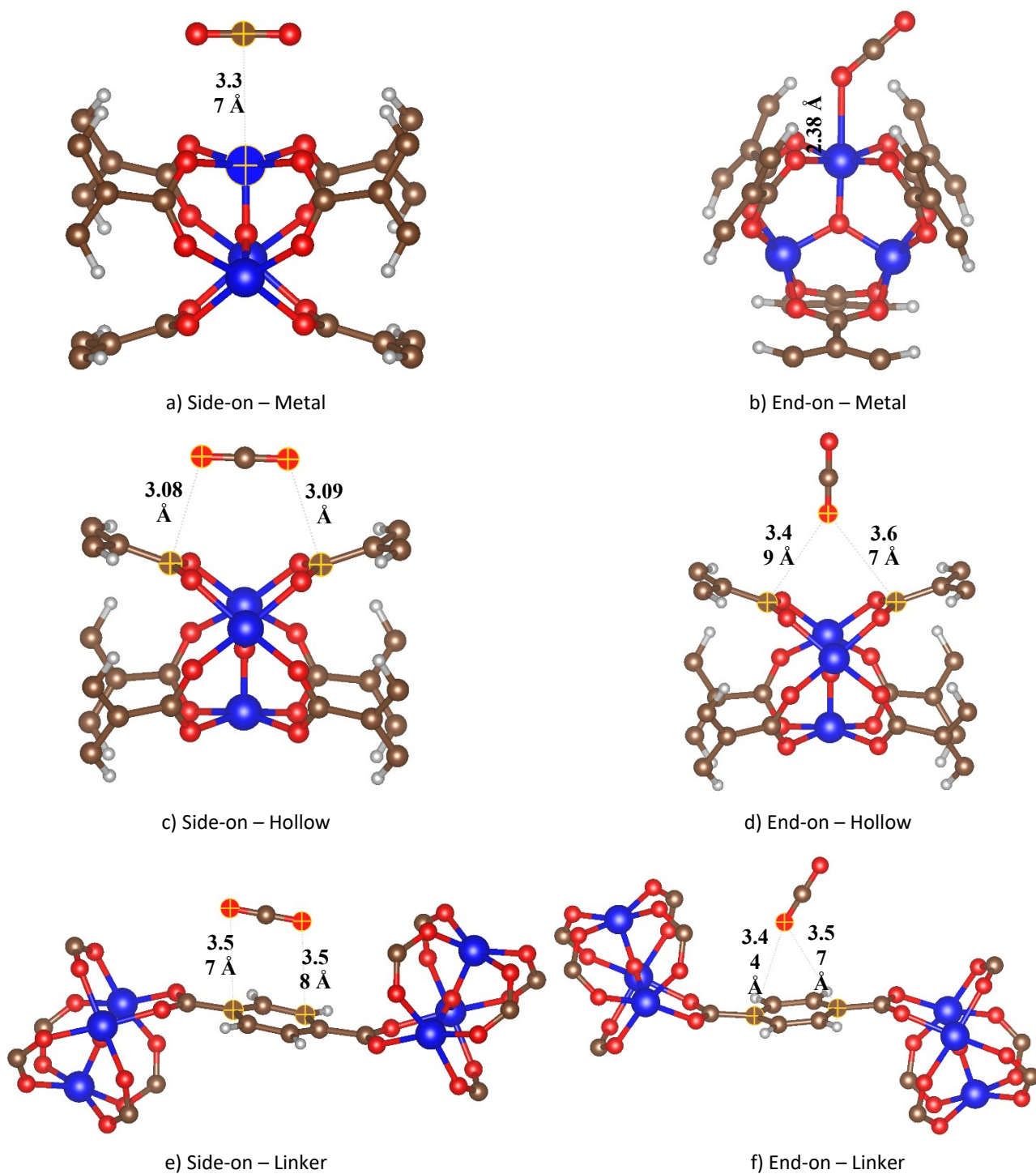
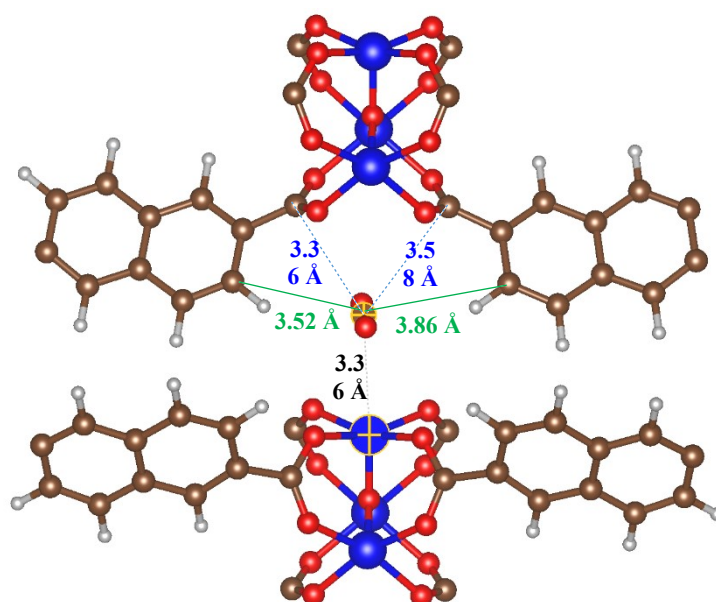
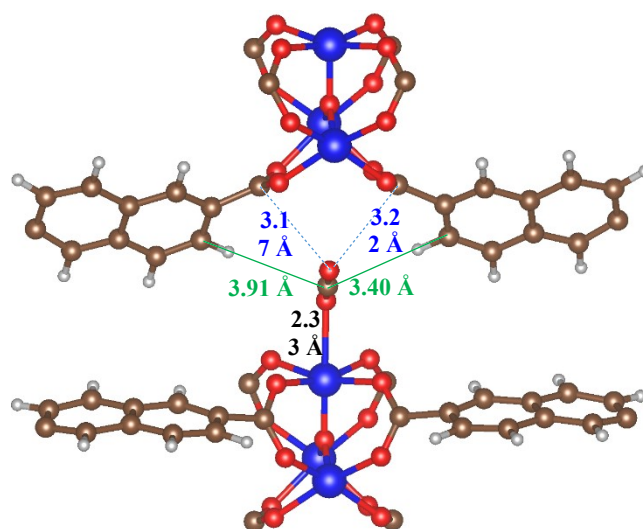


Figure S1. The favourable CO₂ adsorption sites in MIL-88B. Fe (blue), O (red), and C (brown), and H (light-grey).



a) Side-on – Metal/ Side-on – Hollow



b) End-on – Metal/ End-on – Hollow

Figure S2. The favorable CO₂ adsorption sites in MIL-88C. Fe (blue), O (red), and C (brown), and H (light-gray).

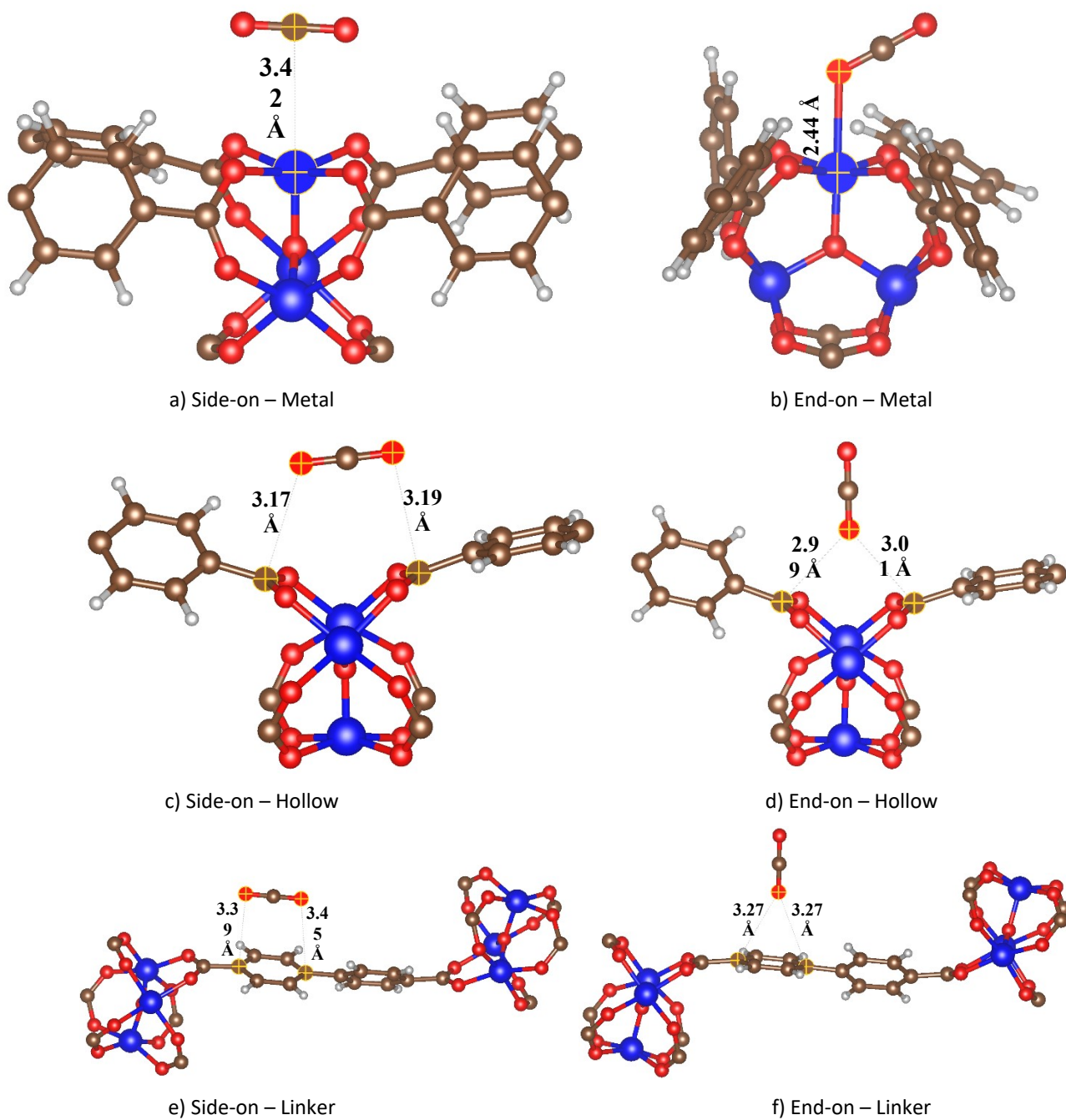


Figure S3. The favorable CO₂ adsorption sites in MIL-88D. Fe (blue), O (red), and C (brown), and H (light-gray).

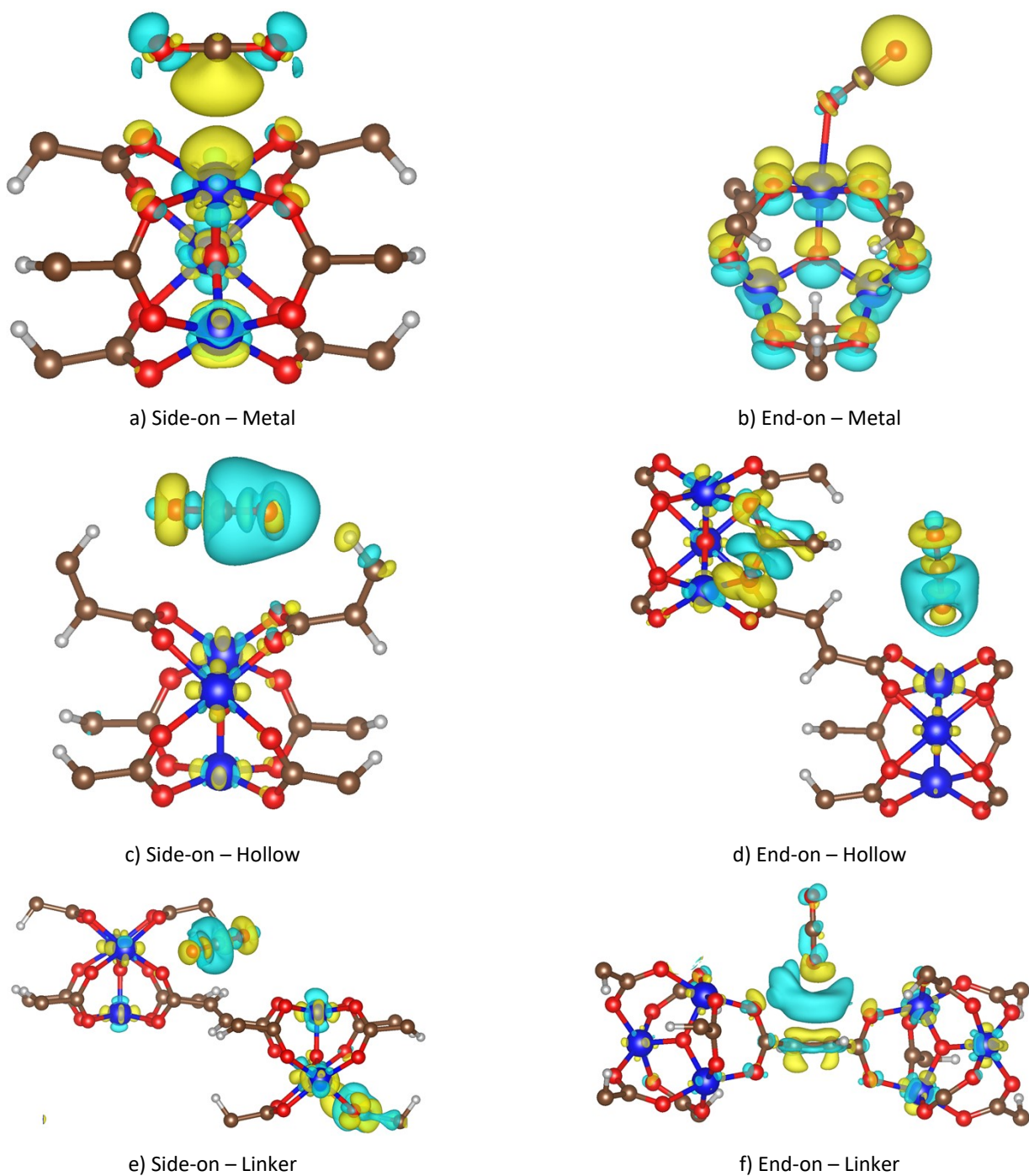


Figure S4. The charge density difference of the CO₂@MIL-88A system with the different adsorption configurations and sites. Negative charge accumulation (yellow) and donation (cyan). Isosurface values (e^-/bohr^3) for the charge density difference of the MIL-88A@CO₂ system at different sites are listed in Table S1.

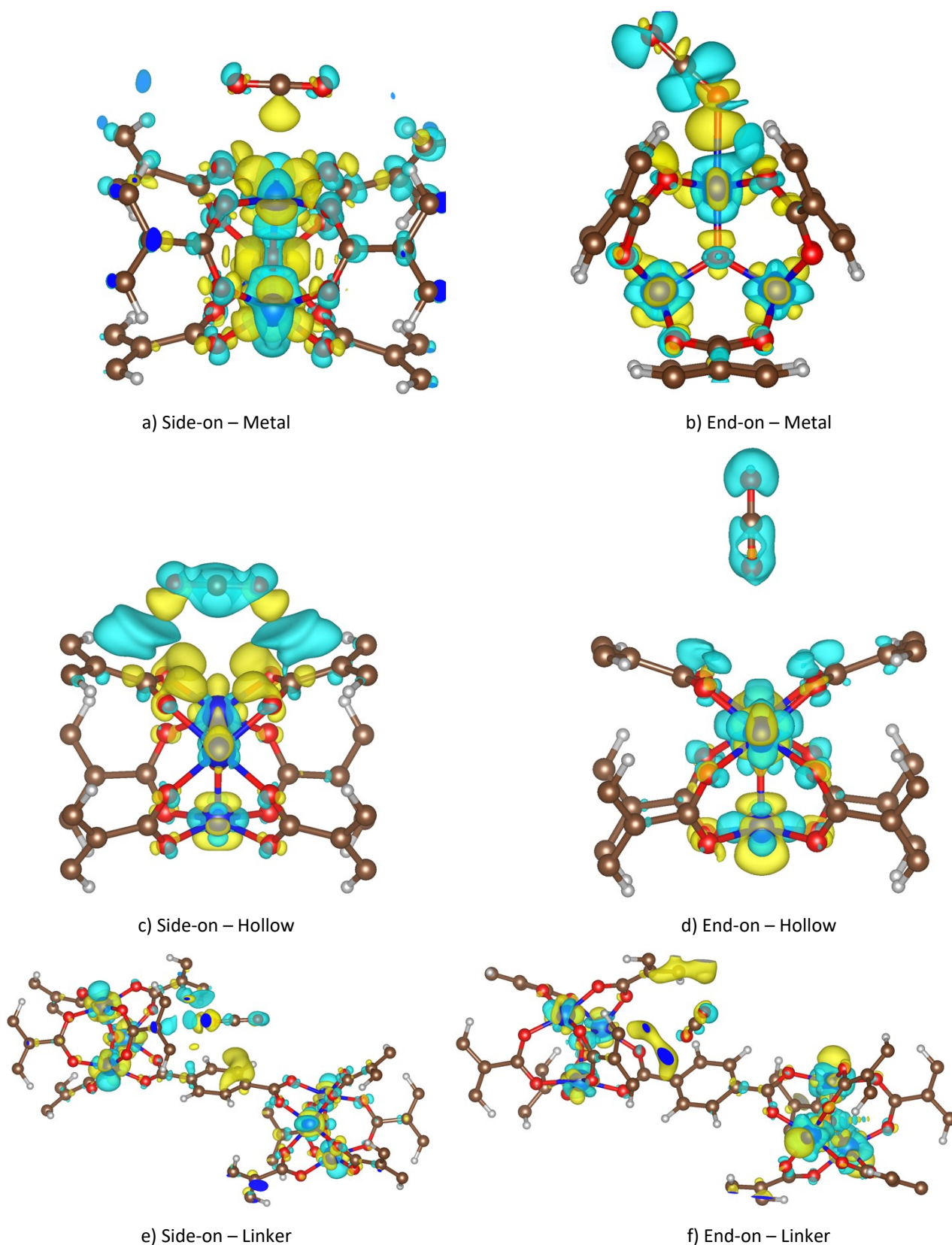


Figure S5. The charge density difference of the CO₂@MIL-88B system with the different adsorption configurations and sites. Negative charge accumulation (yellow) and donation (cyan). Isosurface values (e^-/bohr^3) for the charge density difference of the MIL-88B@CO₂ system at different sites are listed in Table S1.

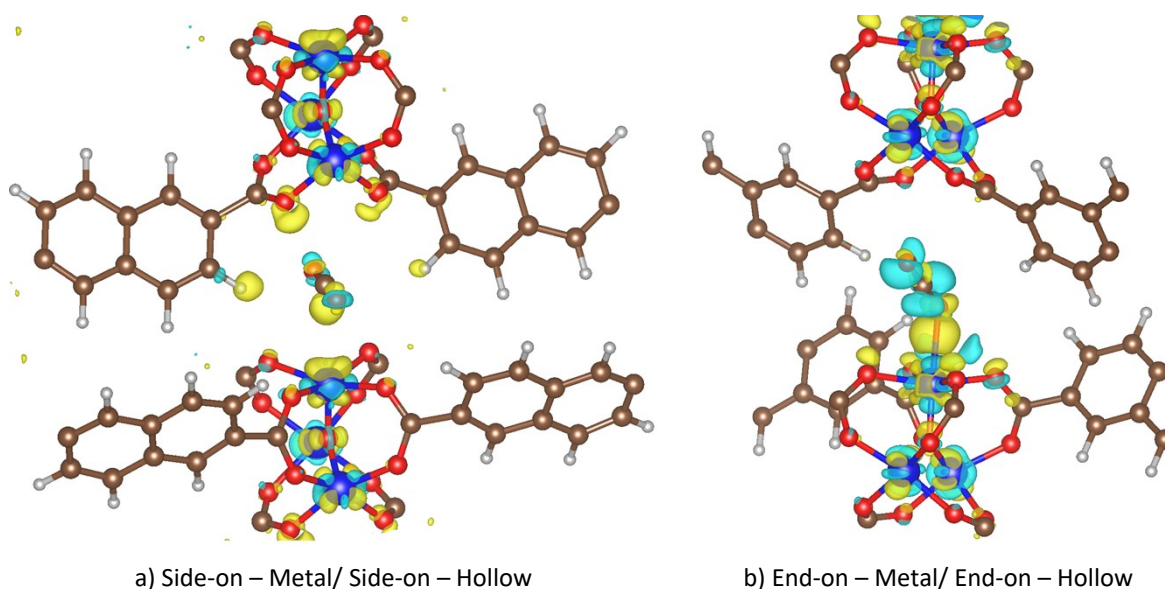


Figure S6. The charge density difference of the CO₂@MIL-88C system with the different adsorption configurations and sites. Negative charge accumulation (yellow) and donation (cyan). Isosurface values (e^-/bohr^3) for the charge density difference of the MIL-88C@CO₂ system at different sites are listed in Table S1.

Table S1. Isosurface values (e^-/bohr^3) for the charge density difference of the MIL-88s@CO₂ systems.

Site	Configuration	MIL – 88A	MIL – 88B	MIL – 88C	MIL – 88D
Metal	Side-on	0.0004	0.0005	0.0007	0.0003
	End-on	0.0350	0.0006	0.0010	0.0070
Hollow	Side-on	0.0030	0.0002	-	0.0080
	End-on	0.0050	0.0002	-	0.0090
Linker	Side-on	0.0050	0.0003	-	0.0080
	End-on	0.0003	0.0004	-	0.0050

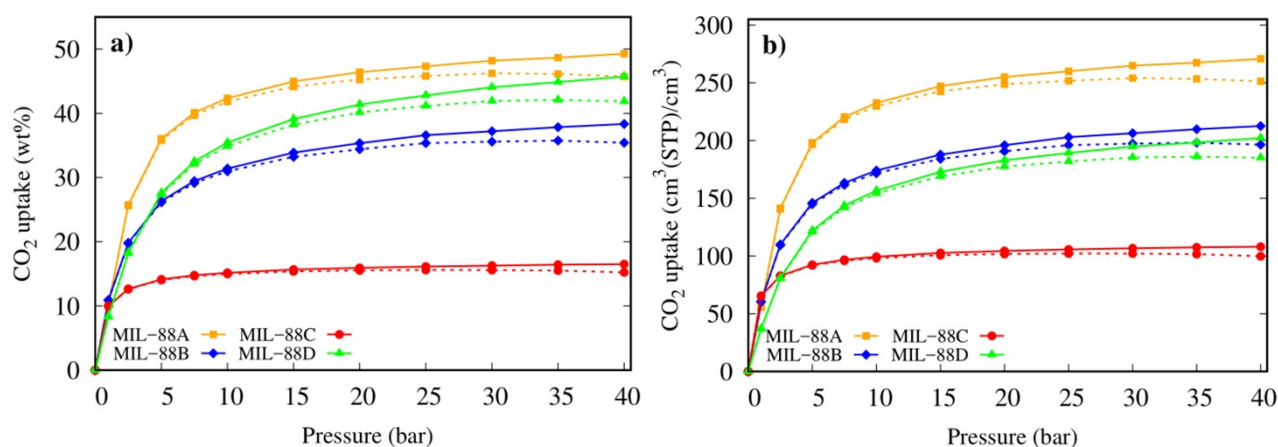


Figure S7. The excess (dashed line) and total (solid line) CO₂ adsorption isotherms of MIL-88A, B, C, and D in the presence of H₂O at 298 K: a) gravimetric capacity and b) volumetric capacity.

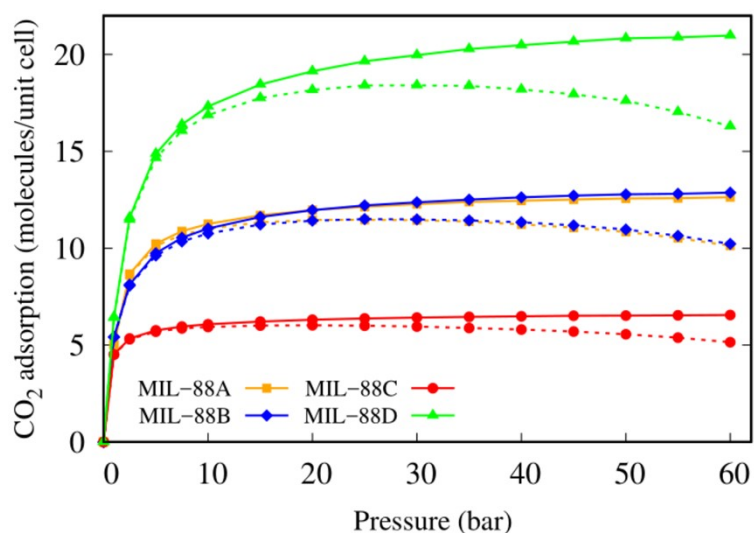


Figure S8. The excess (dashed line) and total (solid line) CO₂ adsorption isotherms of MIL-88A, B, C, and D in the unit of CO₂ molecules per unit cell.

Table S2. The excess and absolute capture capacities of CO₂ in MIL-88A, B, C, and D with and without H₂O at 298 K.

Adsorbent	Without H ₂ O				With H ₂ O			
	wt%		cm ³ (STP)/cm ³		wt%		cm ³ (STP)/cm ³	
	Total	Excess	Total	Excess	Total	Excess	Total	Excess
MIL-88A	52.10	47.98 (25 bar)	286.27	263.61	49.28	46.25 (30 bar)	270.79	254.10
MIL-88B	41.10	37.45 (25 bar)	227.85	207.60	38.34	35.76 (35 bar)	212.53	198.22
MIL-88C	17.27	16.04 (20 bar)	113.05	104.98	16.50	15.61 (25 bar)	108.02	102.18
MIL-88D	49.83	44.79 (30 bar)	220.25	197.97	45.73	42.08 (35 bar)	202.14	186.03

Total uptakes were taken at 40 bar, while excess uptakes were taken at the pressure 25 bar.

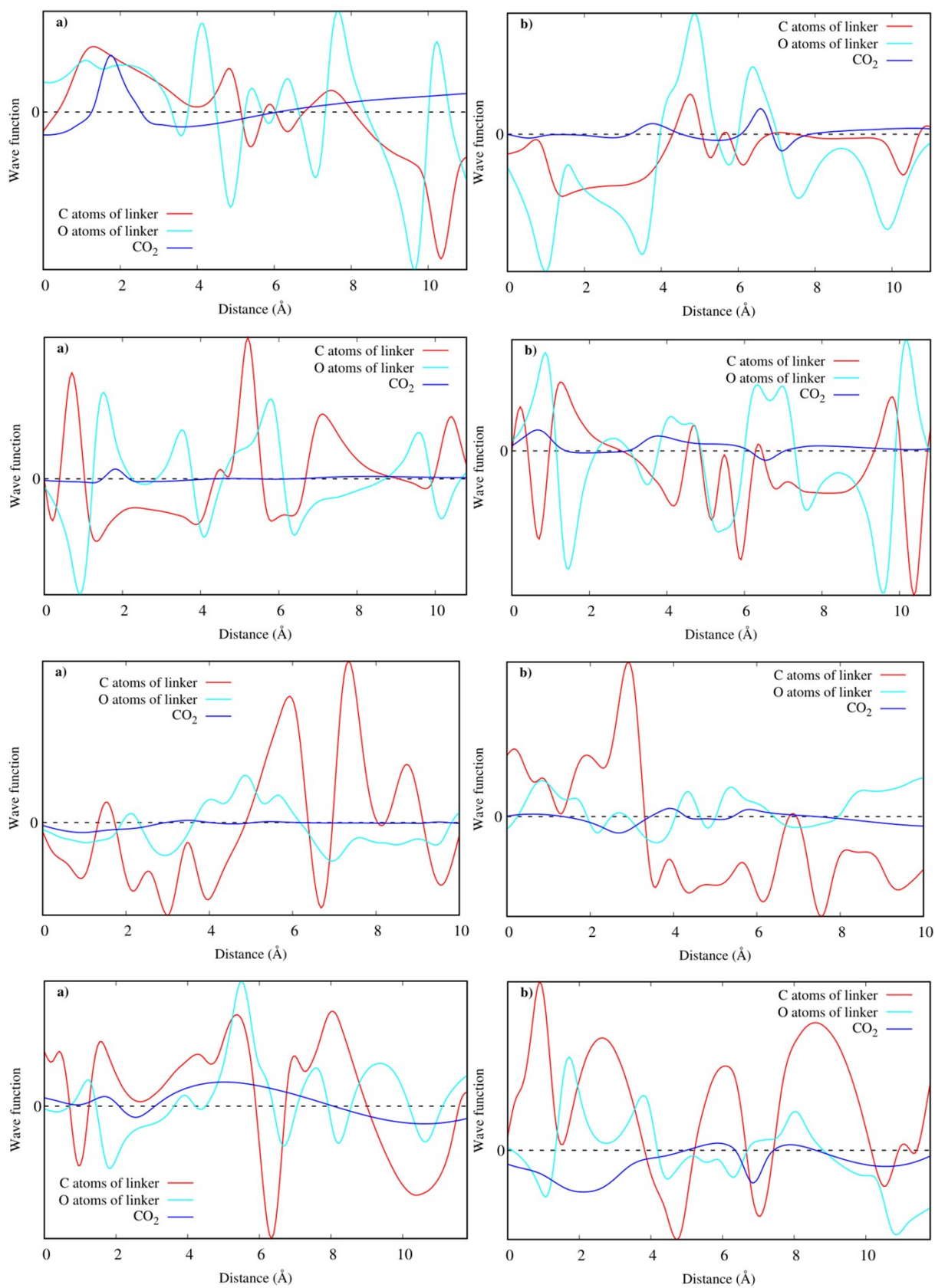


Figure S9. The real parts of the wavefunctions of the CO_2 molecule and the C and O atoms of the organic linker of MIL-88A (first row), MIL-88B (second row), MIL-88C (third row), and MIL-88D (last row) along the x direction: a) metal site (end-on configuration) and b) hollow site (side-on configuration).