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# Preparation of a series of aCTV-based covalent organic frameworks and the substituent effect on their properties

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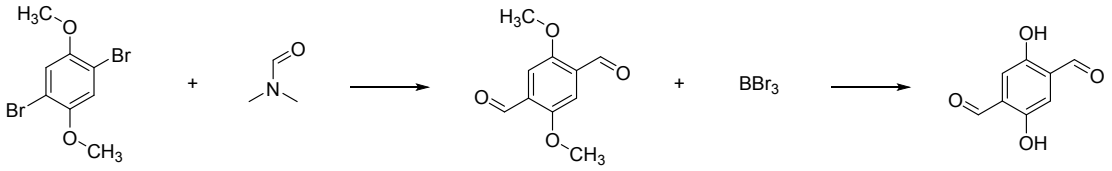
## Experimental section




1 2 3

**2,5-dimethoxyterephthalaldehyde:** n-Butyllithium (2.5 M in hexane) (8.8 ml, 22 mmol) was added to a solution of 2,5-dimethoxyterephthalaldehyde (1) (2.96 g, 10 mmol) in dry THF (50 ml) at -78 °C under an argon atmosphere. The solution was stirred for 3h at -78 °C . DMF (3.0 ml) was added to the mixture and the solution was stirred for 1h, and then was allowed to warm to room temperature for another 1h. Saturated ammonium chloride was added to the mixture to quench the reaction. THF was removed under reduced pressure. The organic layer was separated and the aqueous layer was extracted with 3 × 15 ml dichloromethane. The extract was dried over $Na_2SO_4$, and recrystallized from petrol ether. H-NMR (400 MHz; CDCl3): δ=10.5 (s, 2H), 7.5 (s, 2H), 4.0 (s, 6H); $^{13}C$ NMR (400MHz; CDCl3) 189.6, 156.0, 129.4, 111.1, 56.3; *m/z* (ESI) 195(100%, $M^+$).

**2,5-dihydroxyterephthalaldehyde:** 2,5-dimethoxyterephthalaldehyde (194 mg, 1 mmol) was dissolved in 10 ml DCM at 0 C under an argon atmosphere. 0.5 ml of BBr3 was added dropwise and stirred at room temperature for 4 hours. After complete reaction, the reacted mixture was neutralized with 10 ml H2O and stirred overnight, followed by extraction with water and DCM and recrystallization within DCM and PE to obtain 2, 5-dihydroxyterephthalaldehyde in 70% yield. H-NMR (400 MHz, DMSO): δ=10.30 (s, 2H), 7.20 (s, 2H; aromatic); *m/z* (ESI) 165 (100%, $M^+$).

**FTIR spectra:**

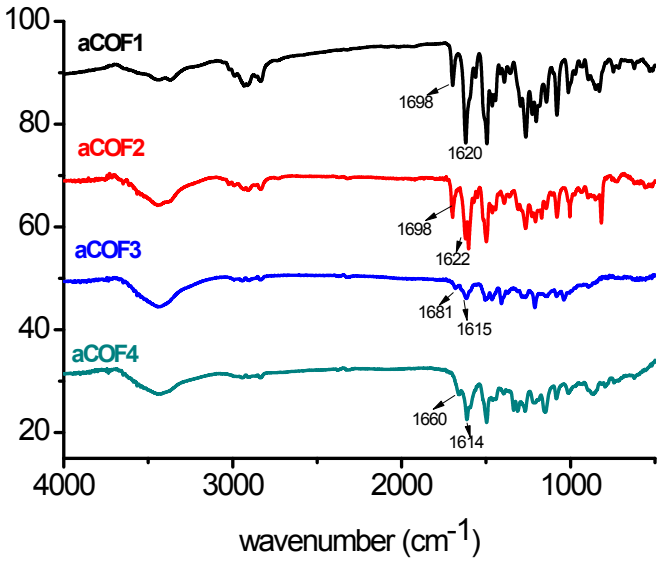



**Fig. S1** FT-IR spectra of aCTV-COF1 (black), aCTV-COF2 (red), aCTV-COF3 (blue) and aCTV-COF4 (green)

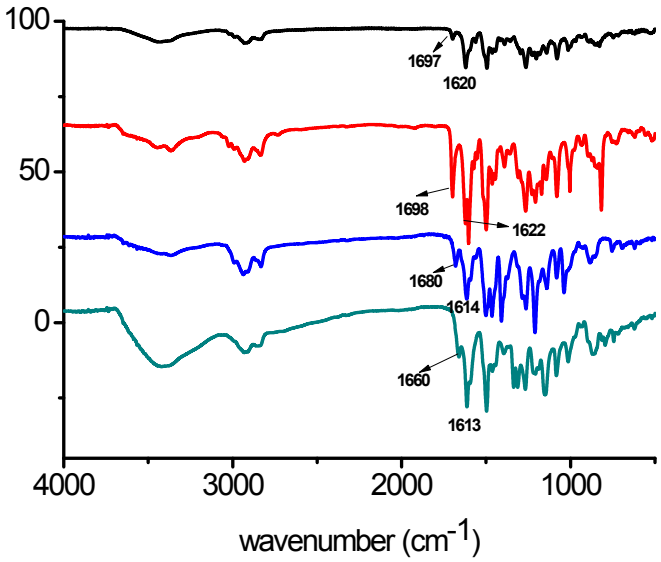



**Fig. S2** FT-IR spectra of aCTV-COF1 (black), aCTV-COF2 (red), aCTV-COF3 (blue) and aCTV-COF4 (green) in water for 10h

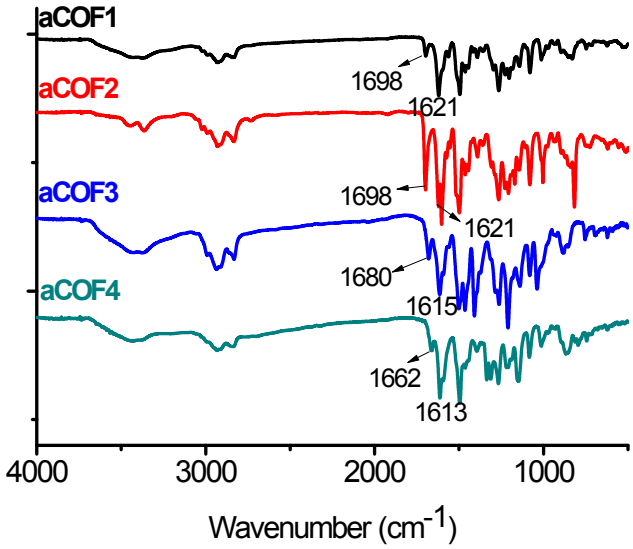



**Fig. S3** FT-IR spectra of aCTV-COF1 (black), aCTV-COF2 (red), aCTV-COF3 (blue) and aCTV-COF4 (green) in water for 24h

**$^{13}$C CP-MAS NMR spectra for aCTV-COFs**

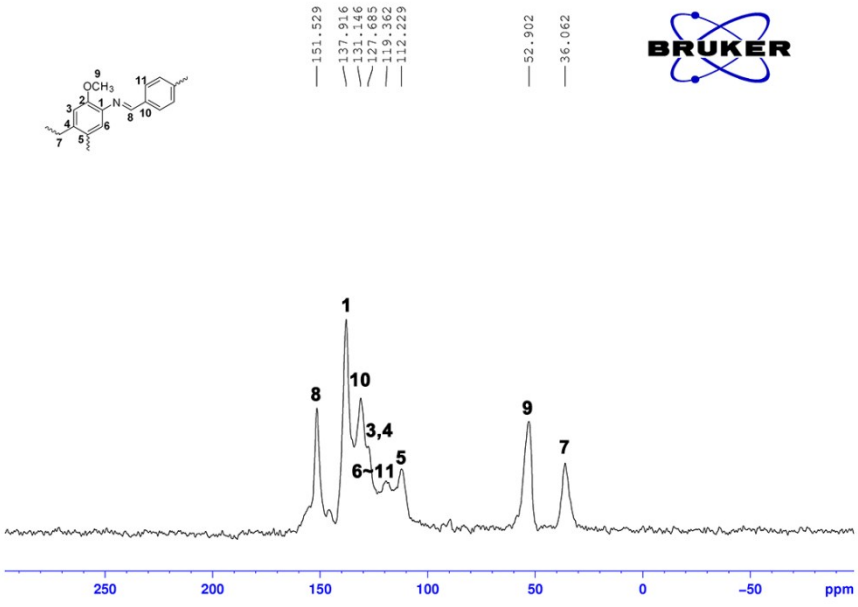



**Fig. S4** $^{13}$C CP-MAS NMR spectra for aCTV-COF1

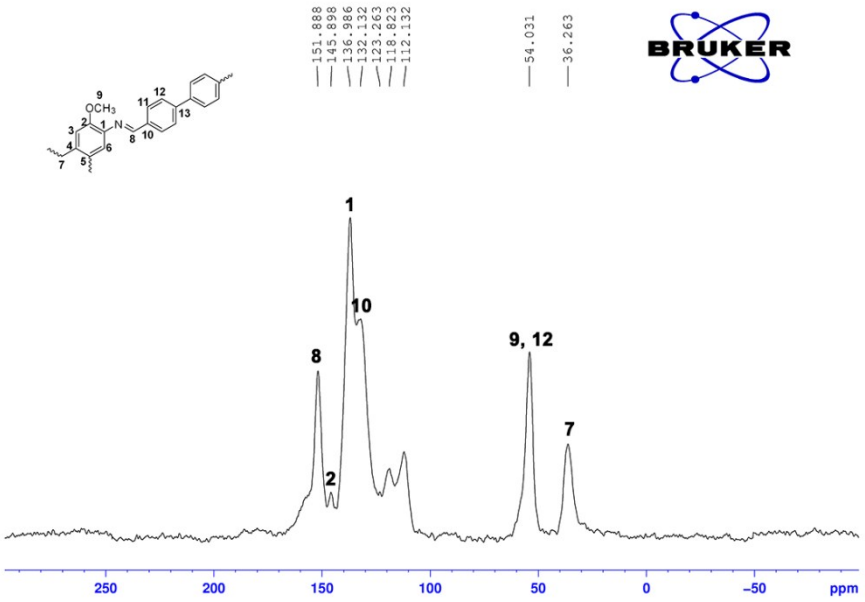



**Fig. S5** $^{13}$C CP-MAS NMR spectra for aCTV-COF2

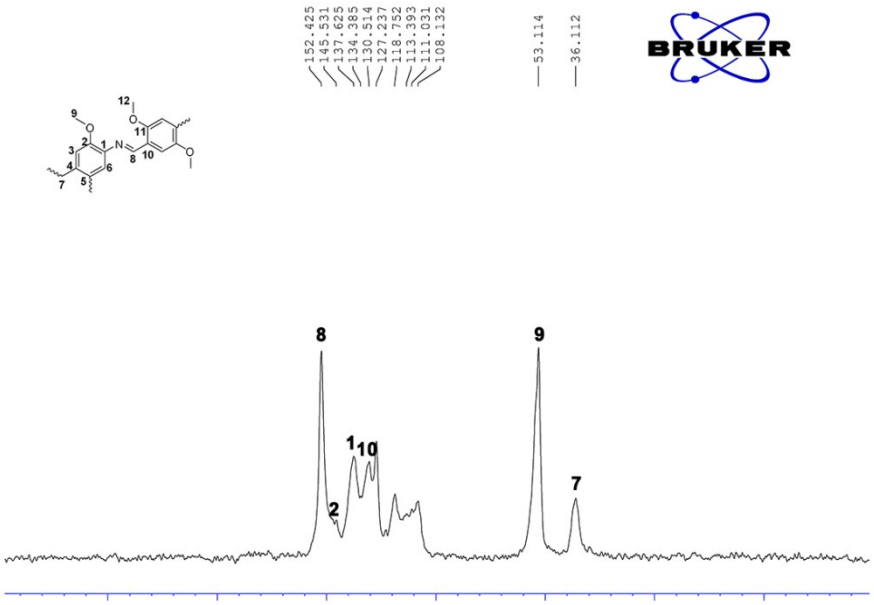



**Fig. S6** $^{13}$C CP-MAS NMR spectra for aCTV-COF3

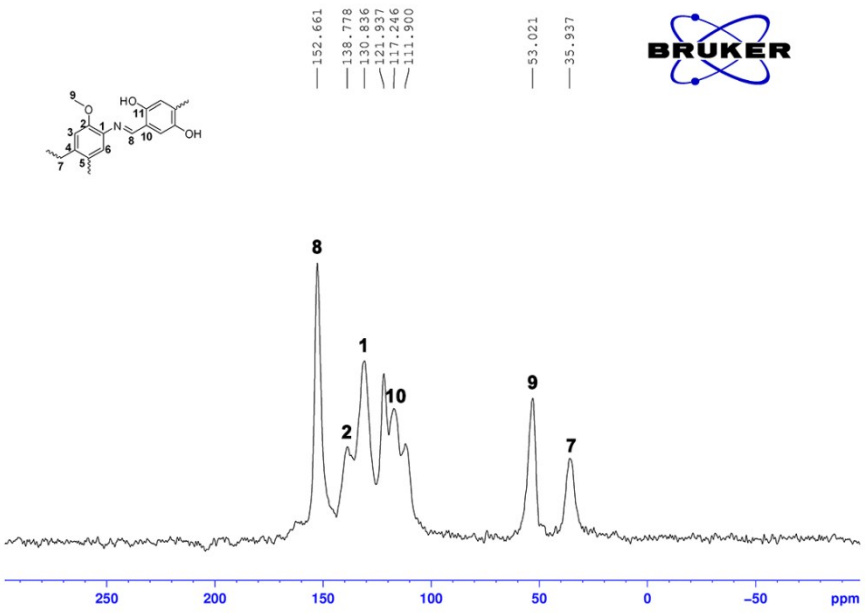



**Fig. S7** $^{13}$C CP-MAS NMR spectra for aCTV-COF4

**TGA measurement for aCTV-COFs:**

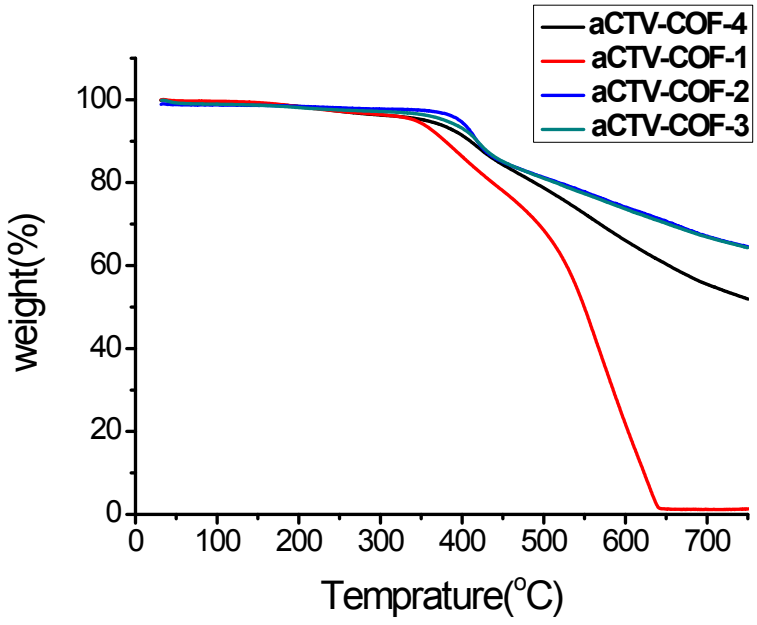



**Fig. S8** TGA measurement for aCTV-COF-1 (red), aCTV-COF-2 (blue), aCTV-COF-3 (green) and aCTV-COF-4 (black).

**PXRD**

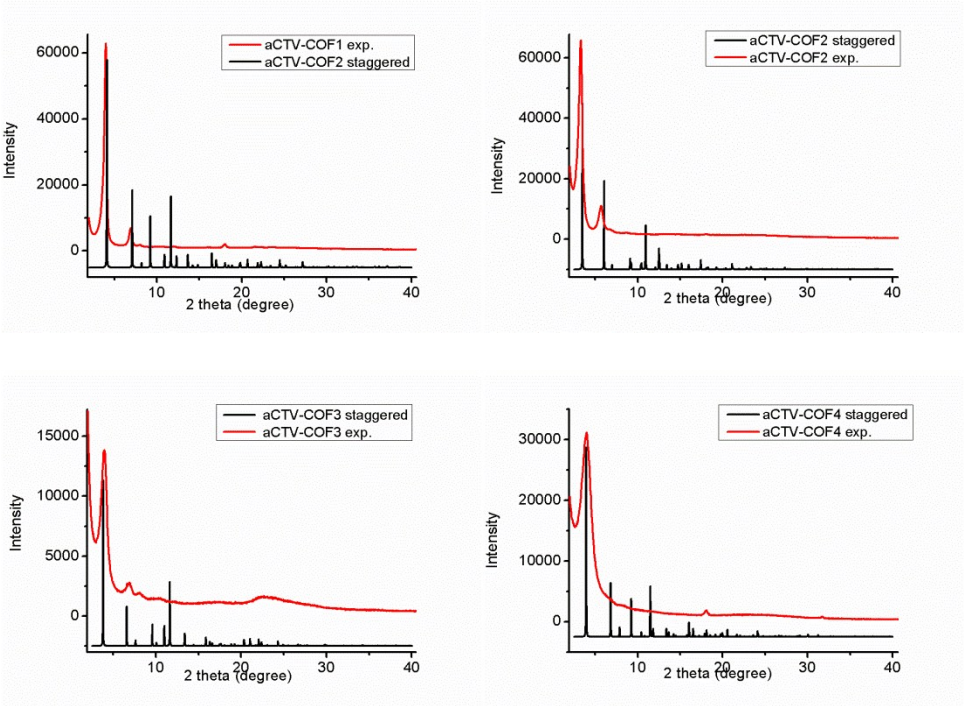



**Fig. S9** Comparison of the experimentally observed PXRD pattern with the simulated staggered pattern for aCTV-COFs

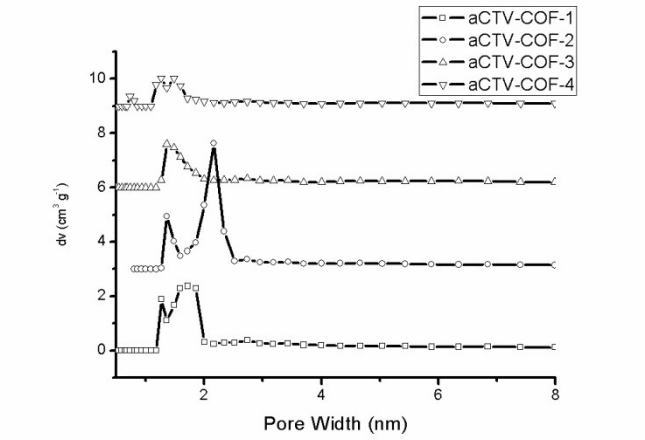



**Fig. S10** Pore size distribution of aCTV-COFs

**Models of CTV-COFs**

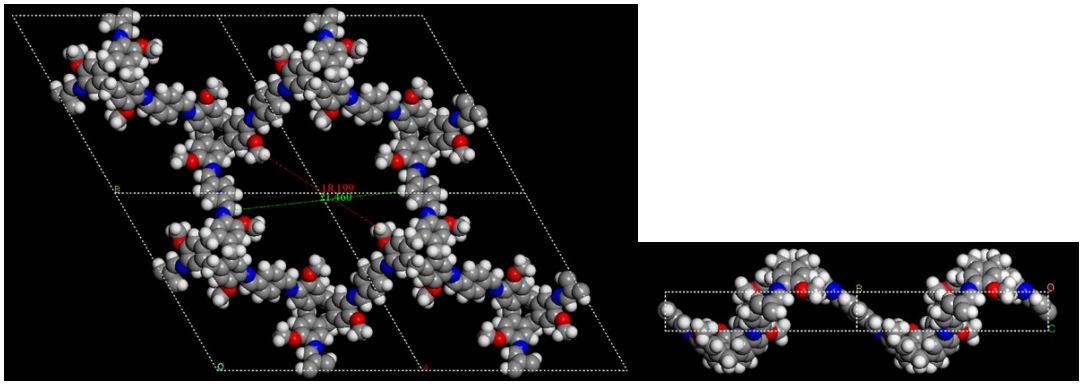


**Fig. S11** Top view (a) and side view (b) of eclipsed aCTV-COF-1. C gray, O red, N blue, H white.

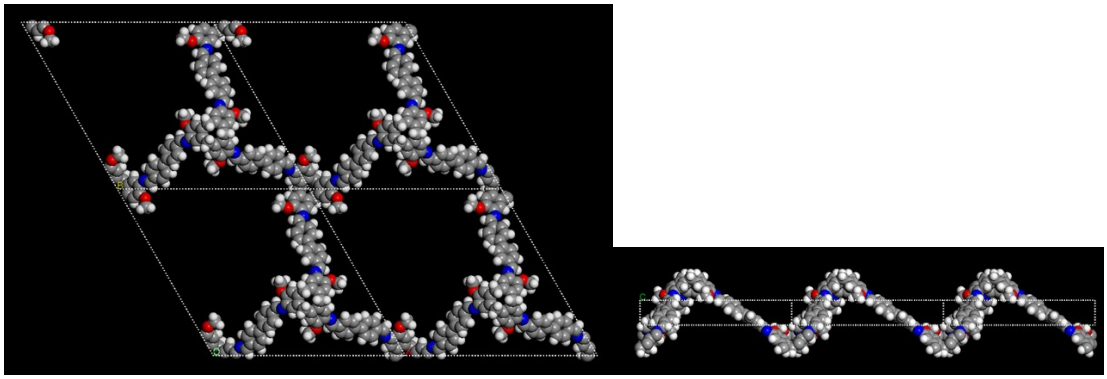


**Fig. S12** Top view (a) and side view (b) of eclipsed aCTV-COF-2. C gray, O red, N blue, H white.

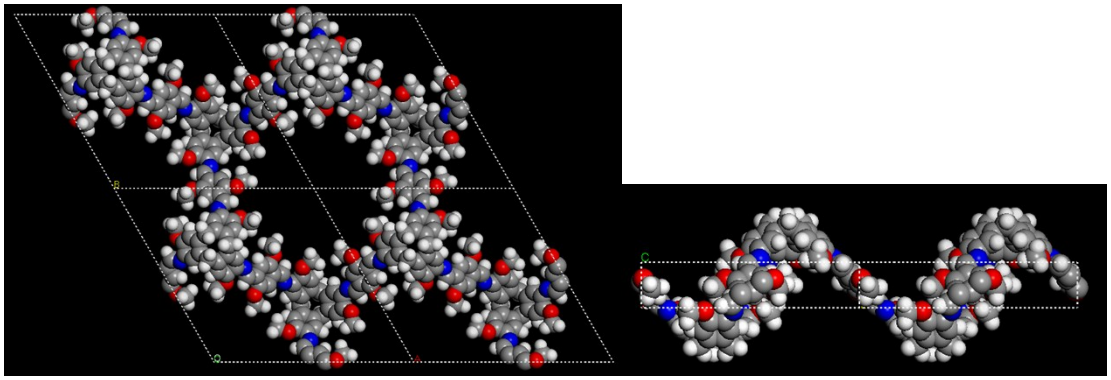


**Fig. S13** Top view (a) and side view (b) of eclipsed aCTV-COF-3. C gray, O red, N blue, H white.

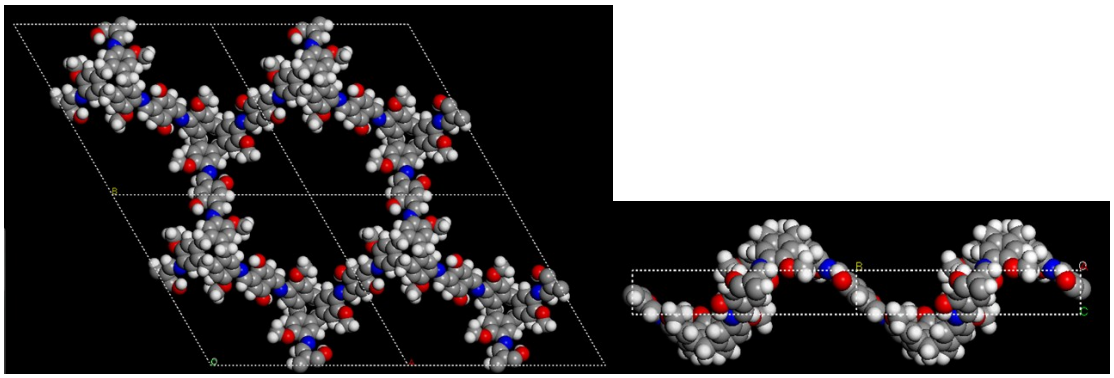


**Fig. S14**Top view (a) and side view (b) of eclipsed aCTV-COF-4. C gray, O red, N blue, H white.

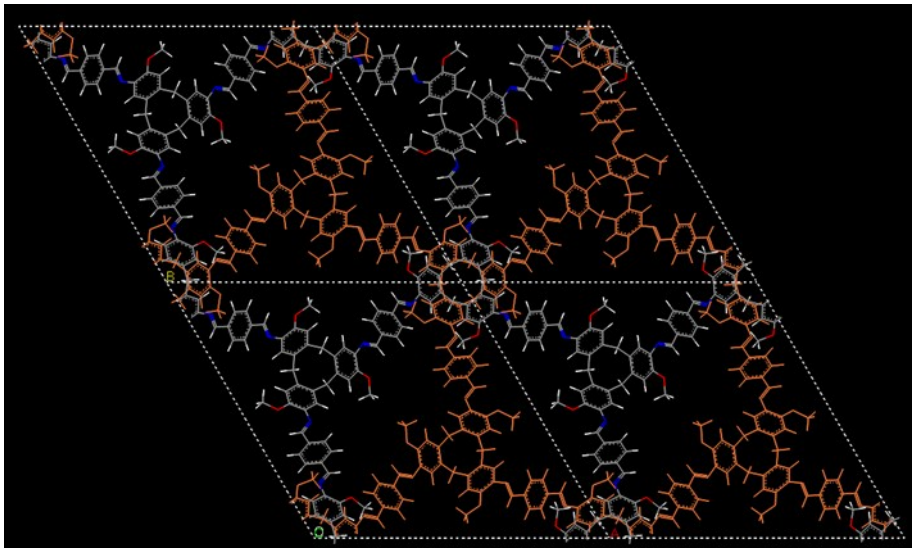


**Fig. S15** Top view staggered aCTV-COF-1. C gray, O red, N blue, H white. Another layer is colored in orange.

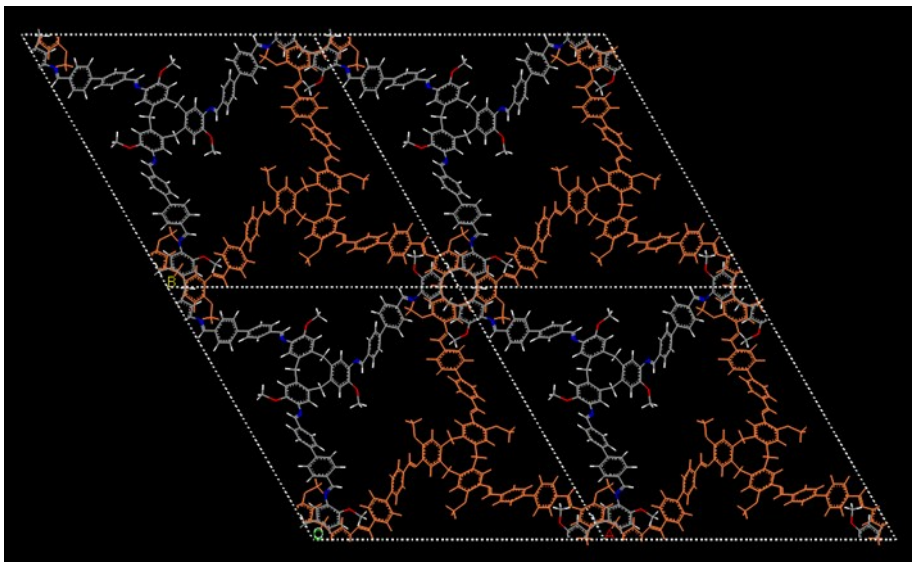


**Fig. S16** Top view staggered aCTV-COF-2. C gray, O red, N blue, H white. Another layer is colored in orange.

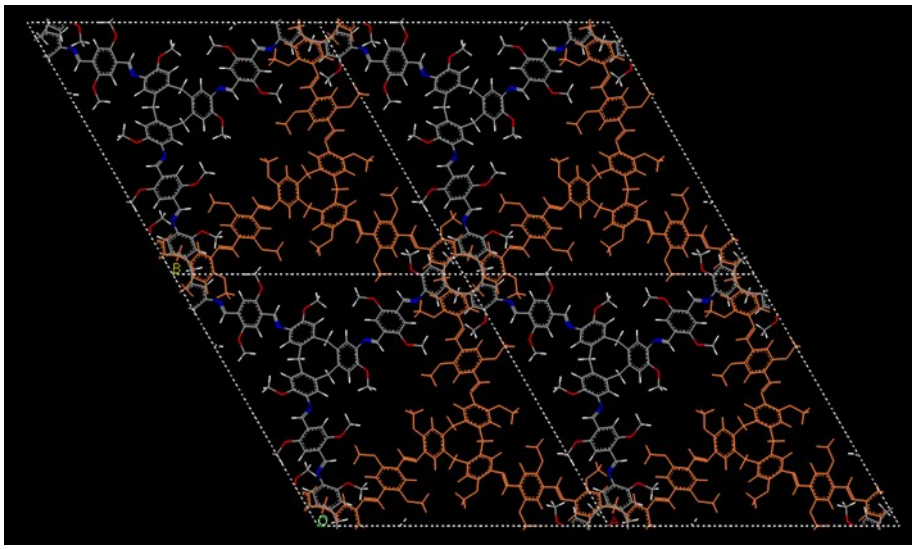


**Fig. S17** Top view staggered aCTV-COF-3. C gray, O red, N blue, H white. Another layer is colored in orange.

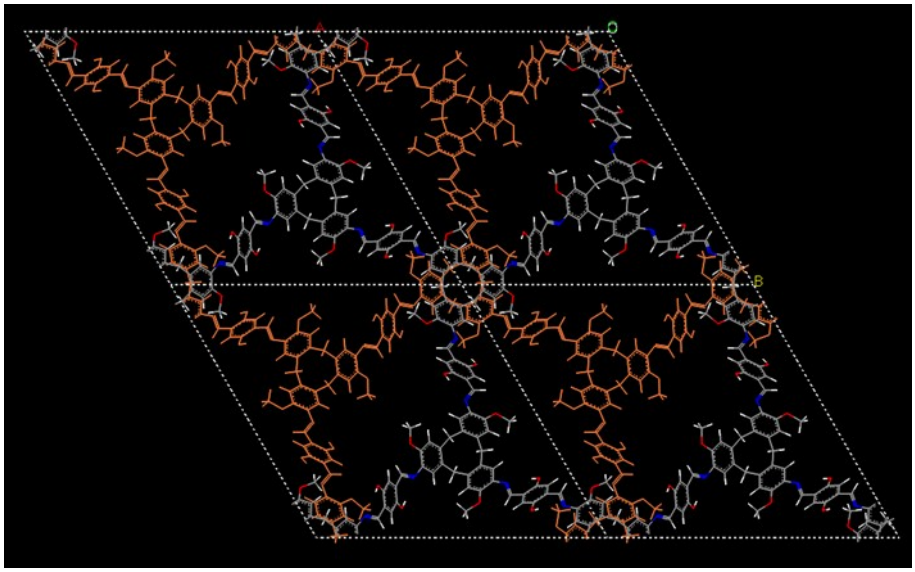


**Fig. S18** Top view staggered aCTV-COF-4. C gray, O red, N blue, H white. Another layer is colored in orange.