

Supplementary Information

***In silico* screening of nanoporous materials for urea removal in
hemodialysis applications**

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Section S1. Simulation Equations and parameters

Molecular energy U , due to the rigidity of the adsorbates and the structures, is computed as the sum of the non-bonded interactions, namely the Van der Waals and the electrostatic terms.

$$U = \sum_{non-bonded} U_{nb}(r) \quad (S1)$$

Van der Waals intermolecular interactions were described through a Lennard Jones potential, reported in **Equation S2** (Equation 3.78 in RASPA documentation) where ε (in K), while σ (in Å) are two parameters.

$$U_{vdW} = 4 \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (S2)$$

Ewald summation, in **Equation S3**, was used for electrostatics interactions (Equation 3.105 in RASPA documentation)

$$U_{electrostatic} = \sum_{i < j} q_i q_j \frac{erfc(\alpha r_{ij})}{r_{ij}} + \frac{2\pi}{V} \sum_{k \neq 0} \frac{1}{k^2} e^{-\frac{k^2}{4\alpha^2}} \left(\left| \sum_{i=1}^N q_i \cos(k \cdot r_i) \right|^2 + \dots \right) \quad (S3)$$

where q_i and q_j are the charges of particle i and j , respectively, r_i the position of atom i . The volume of the cell is V , α is damping factor, k the wavelength, and $erfc$ the complementary error function.

The parameters used for water come from the TIP5P-E [1] model, five-sites rigid model extension of the TIP5P, accounting for the Ewald summation reported in Table xxxx. A 5-site model is more accurate

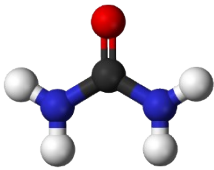
than a three-site one like the TIP3P model, due to the two additional massless sites for negative charges. The choice of TIP5P-E versus the TIP5P was justified by the results of Castillo et al., which show that this model has the best performance in predicting the water adsorption of zeolites, nanoporous materials in which electrostatics play an important role. [2]

Unfortunately, for urea a similar work reporting parameters optimised on adsorption in porous materials is not available in the literature. Therefore, urea parameters were retrieved from the work of Weerasinghe and Smith [2] who fitted them on experimental data relative to the urea-water mixture.

Table S1. Water model parametrization (TIP5P) [1]

TIP5P	ϵ	σ	q
	K	Å	-
O	89.57	3.0970	0
L	0	0	-0.241
H	1	1	0.241
Bond length			
	Å		Bond Angle
			degrees
O-L	0.70	L-O-L	109.47
O-H	0.9572	H-O-H	104.52

Table S2. Urea model parametrization [1]

	ϵ	σ	q
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	K	Å	-
O	67.35	3.10	-0.675
C	50.15	3.77	0.921
H	10.58	1.58	0.285
N	66.15	3.11	-0.693
	Bond length		Bond Angle
	Å		degrees
C-N	1.350	C-N-H	120.0
C-O	1.265	O-C-N	121.4
C-H	1.000	N-C-N	117.2
		H-N-H	120.0
	Dihedrals		
	degrees		
O-C-N-H	-180		

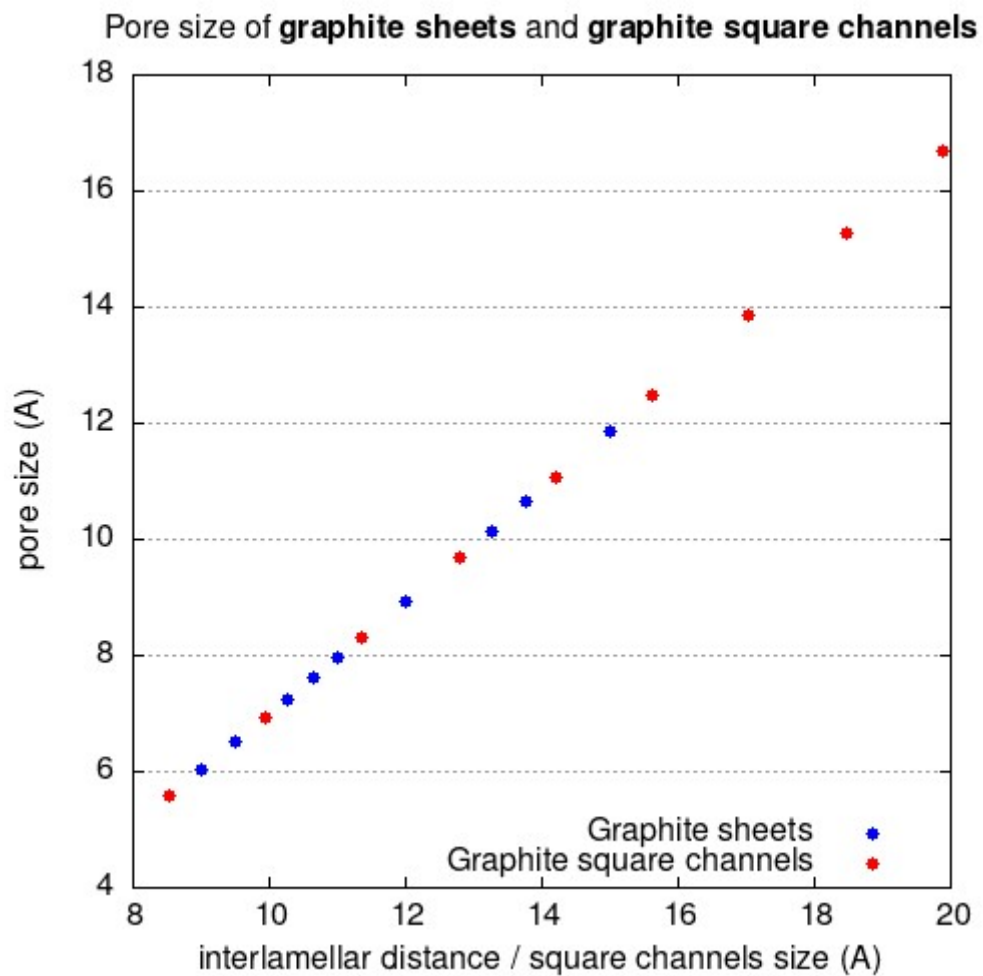


Figure S1. Pore size of graphite sheets and graphite square channels calculated with Zeo++ versus the interlamellar distance for graphite sheets and the channel size for graphite square channels.

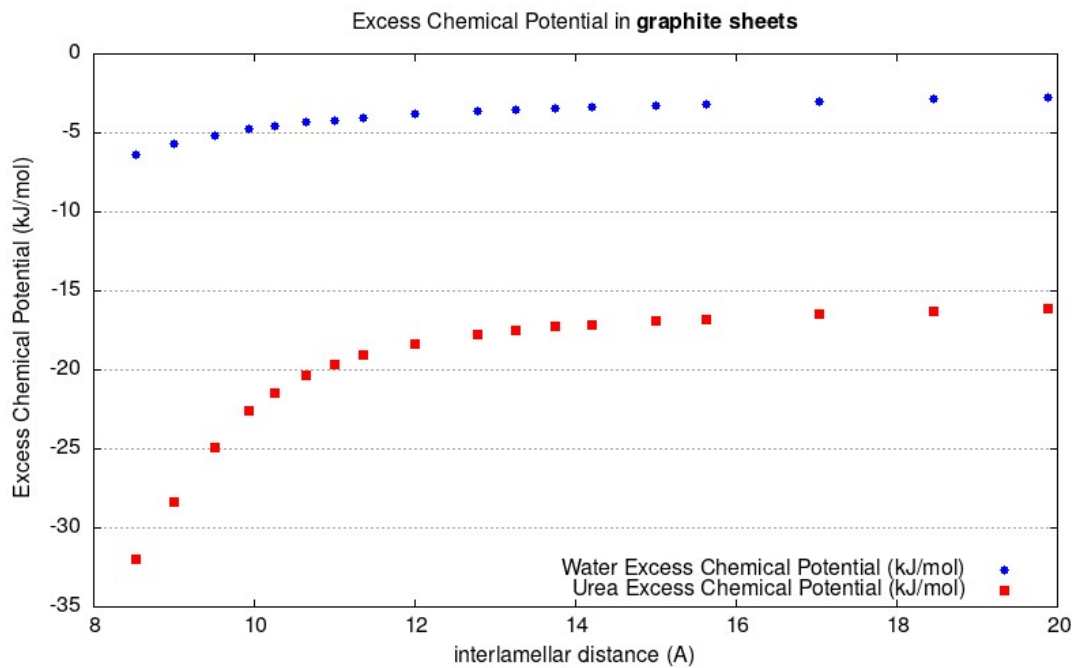


Figure S2. Inter-lamellar distance influence on excess chemical potential of urea and water in graphite sheets.

Table S3. Henry's law constant values of urea in MOFs and urea/water selectivity evaluated as $K_{H,u}/K_{H,w}$.¹ considering density of the framework equal to 1 g cm³.

	$K_{H,u}$ (mol kg ⁻¹ Pa ⁻¹)	$K_{H,u}/K_{H,w}$	μ_u^{ex} (kJ/mol)	$\mu_u^{ex} - \mu_w^{ex}$ (kJ/mol)	Ref.
ZIF-7	3.33 · 10 ⁻¹	2637	-35.79	-30.58	This work
UIO-66	2.58 · 10 ⁻³	1073	-23.20	-17.65	This work
A list of 66 Bio-MOFs	1.81 · 10 ⁻⁶	12.1	-3.97	-6.43	[2]
	÷ 9.63 · 10 ⁻³	÷ 1366	÷ -26.08 ¹	÷ -18.61	
MIL-100	1.35 · 10 ⁻⁴	78.5	-15.29	-11.25	[2], [3]

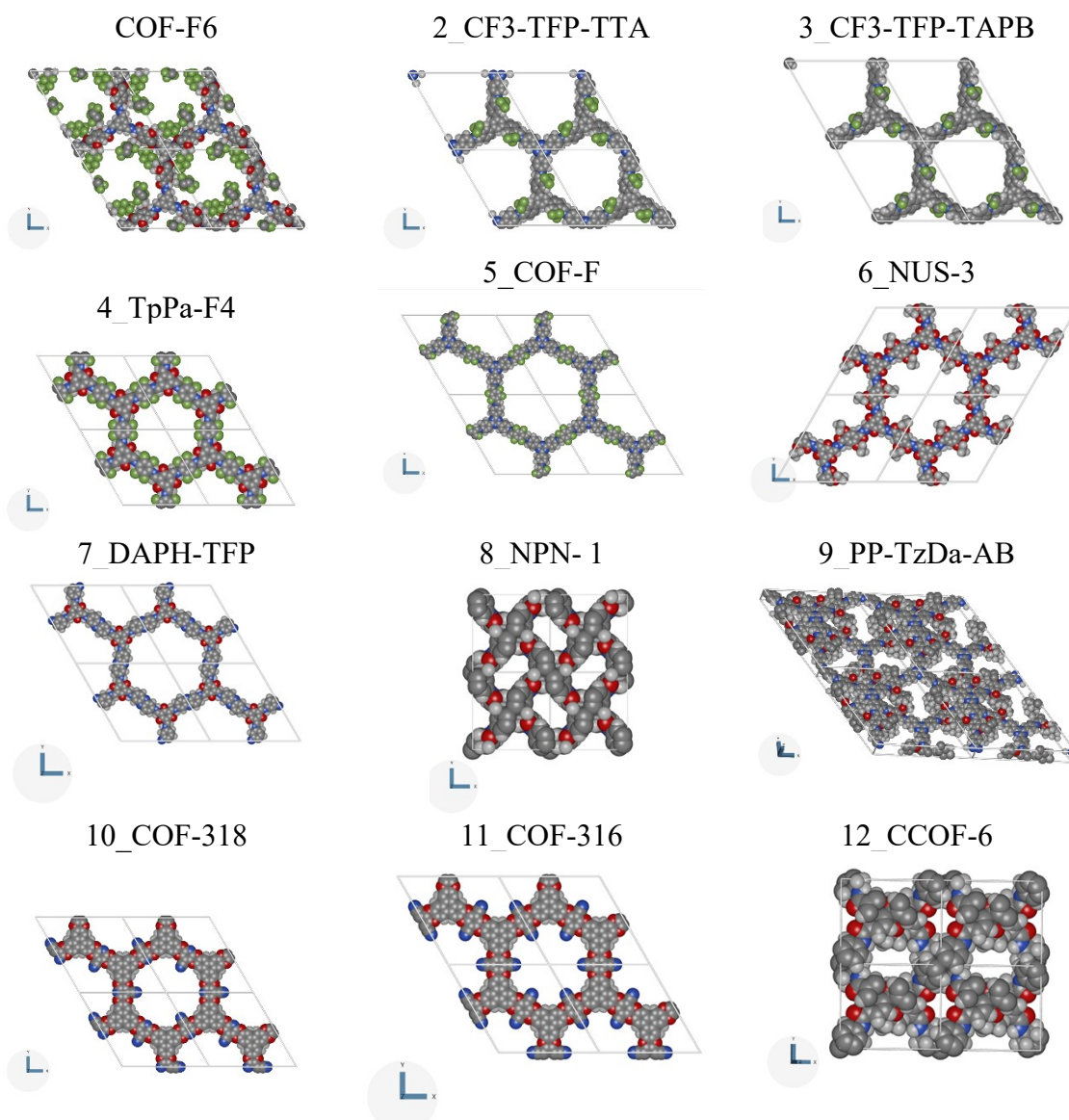


Figure S4. Structures of the 12 COFs listed in **Table 2**.

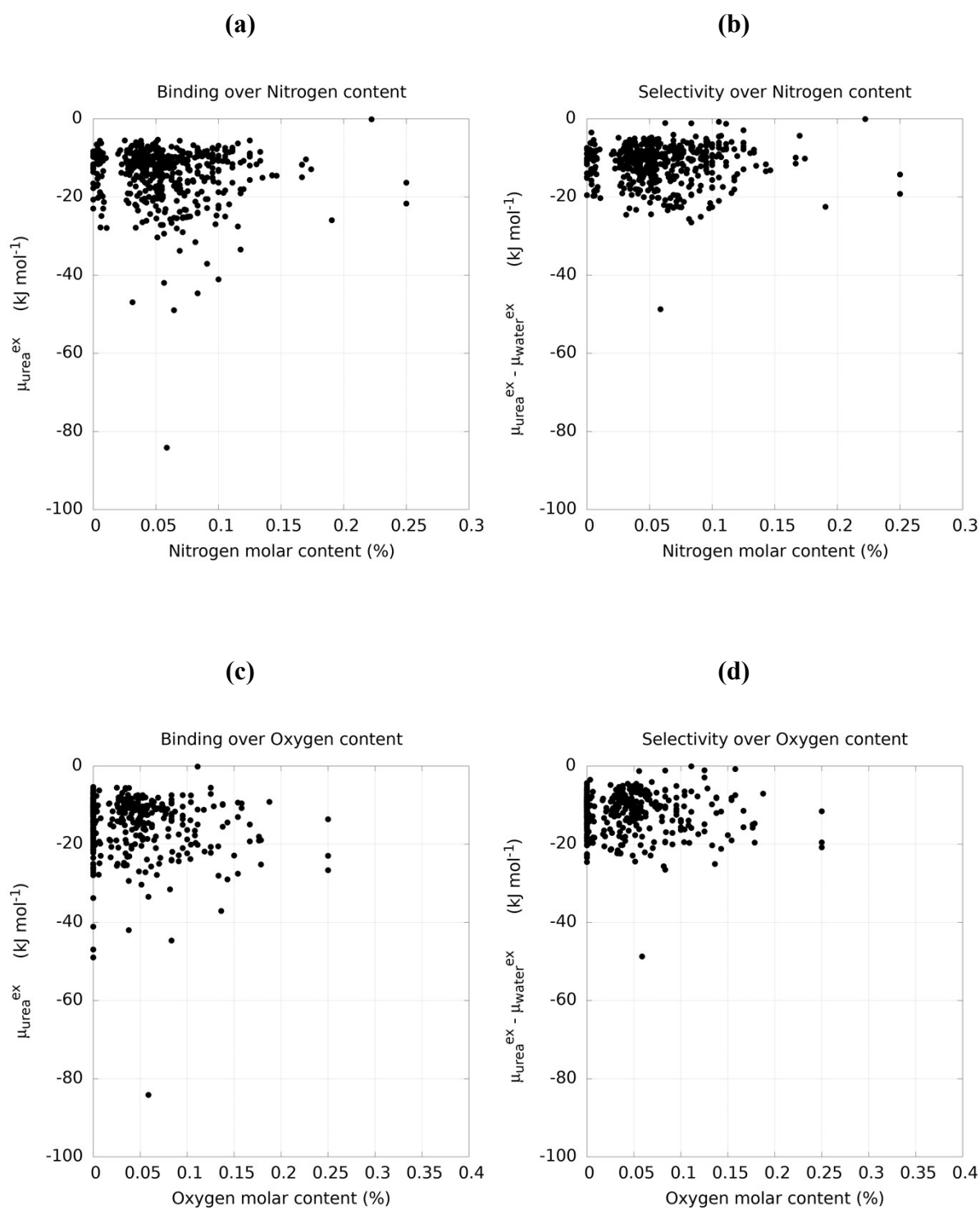


Figure S4: Urea binding strength and urea/water selectivity of COFs versus elemental composition. a) Urea binding and b) urea/water selectivity vs. N content. c) Urea binding and d) urea/water selectivity vs. O content.

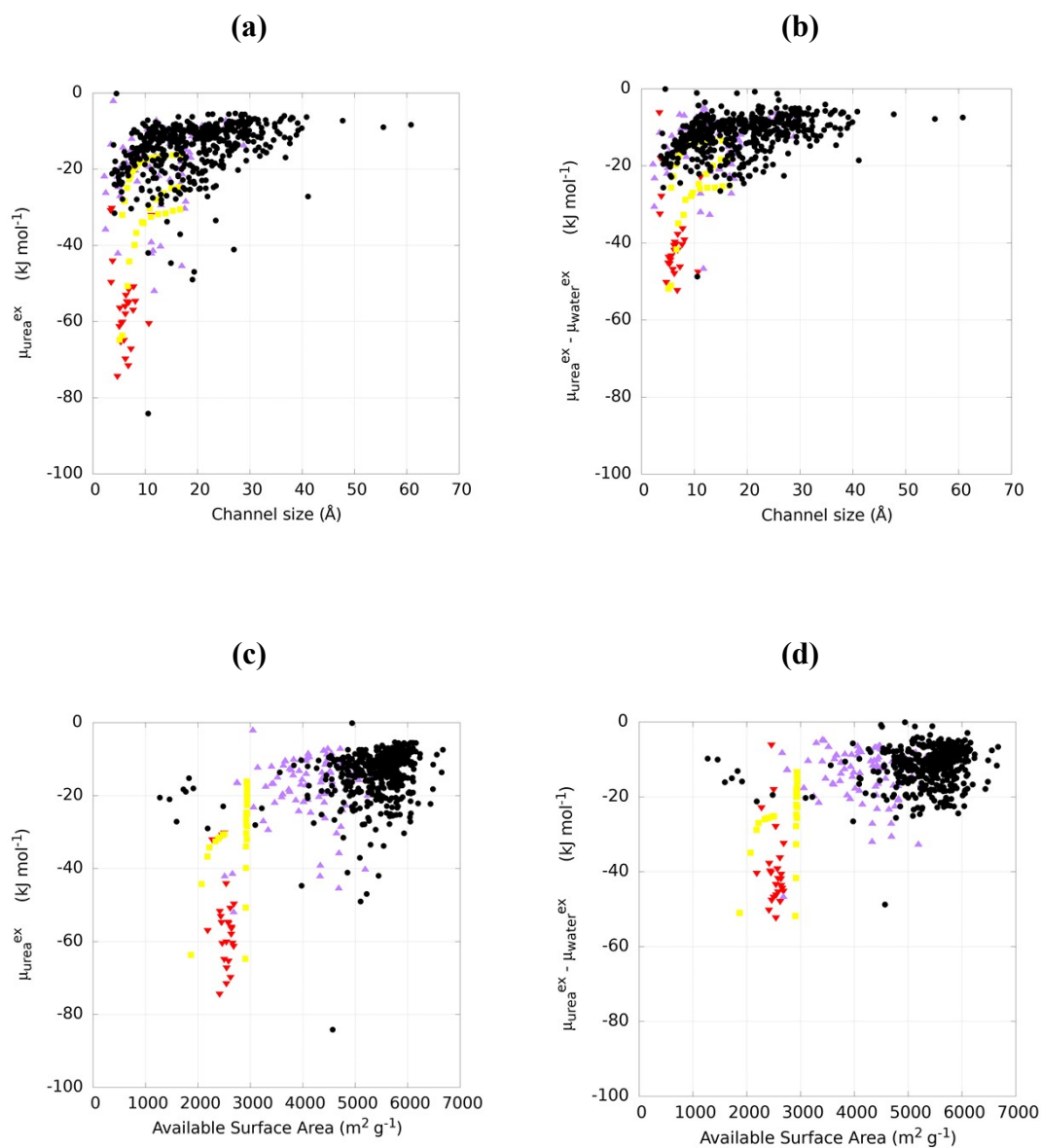


Figure S5: Urea binding strength and urea/water selectivity of COFs materials versus pore size and ASA. a) Urea binding and b) urea/water selectivity vs. pore size. c) Urea binding and d) urea/water selectivity vs. ASA.

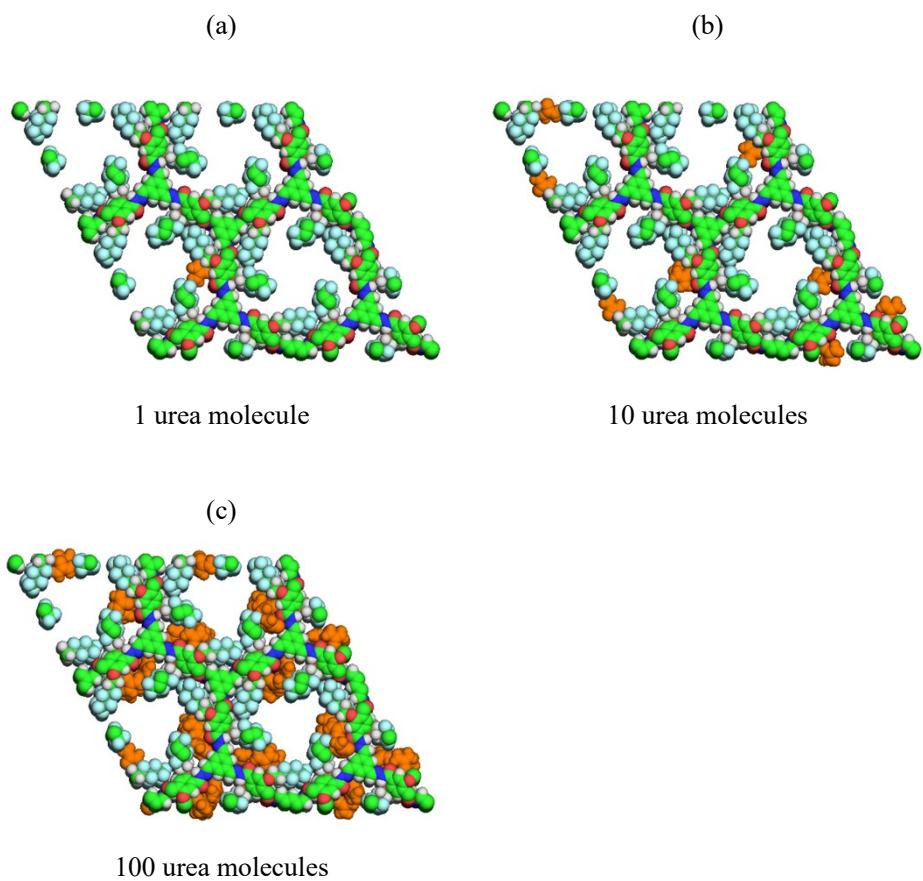


Figure S6: Snapshots of MD simulations of urea in COF-F6 with increasing number of urea molecules (in orange) a) 1 molecule; b) 10 molecules; c) 100 molecules;

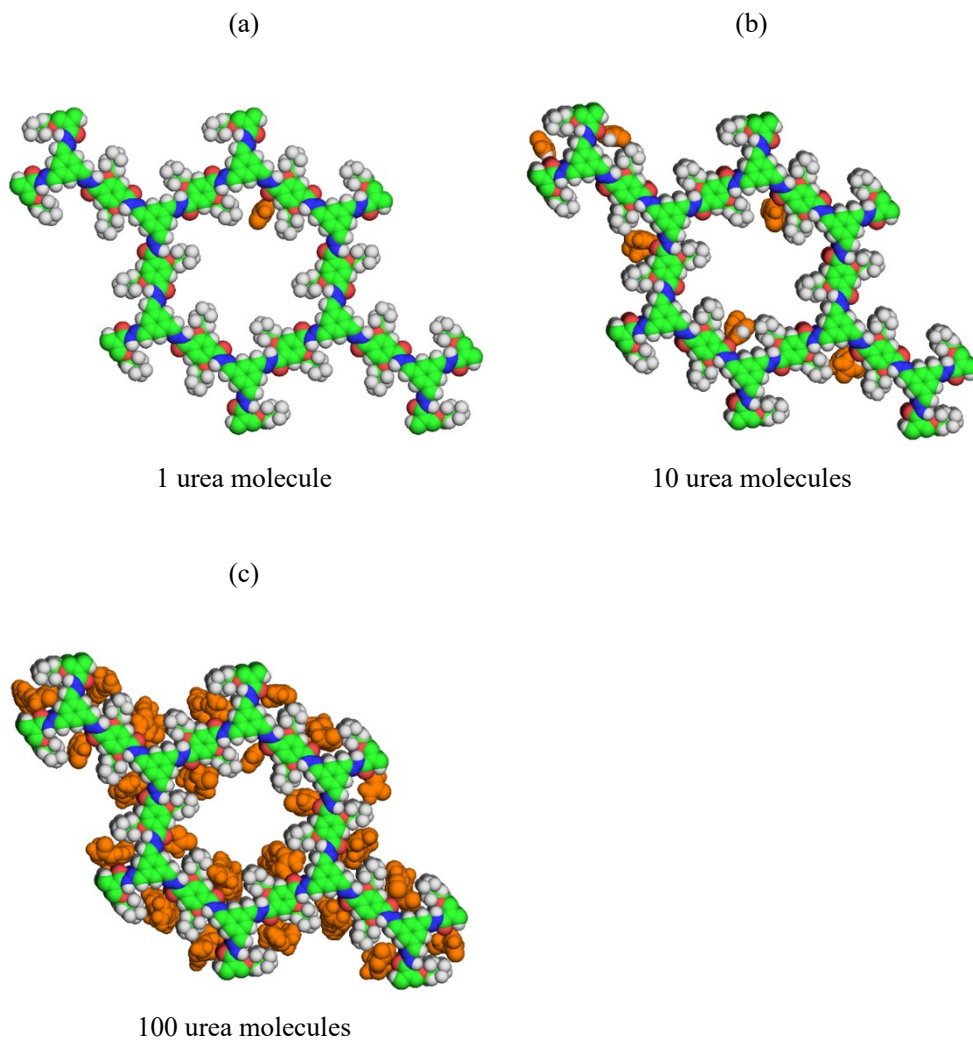
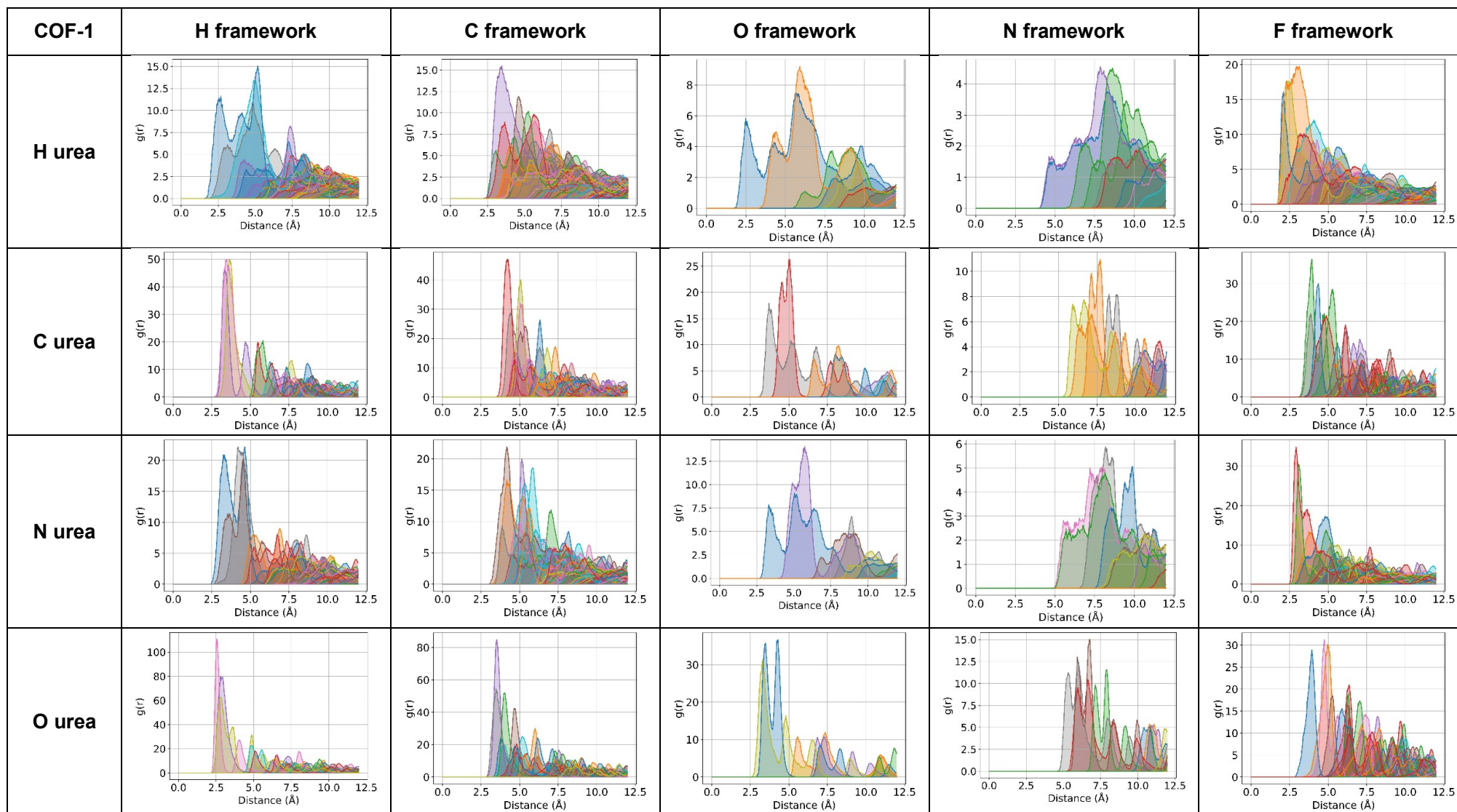
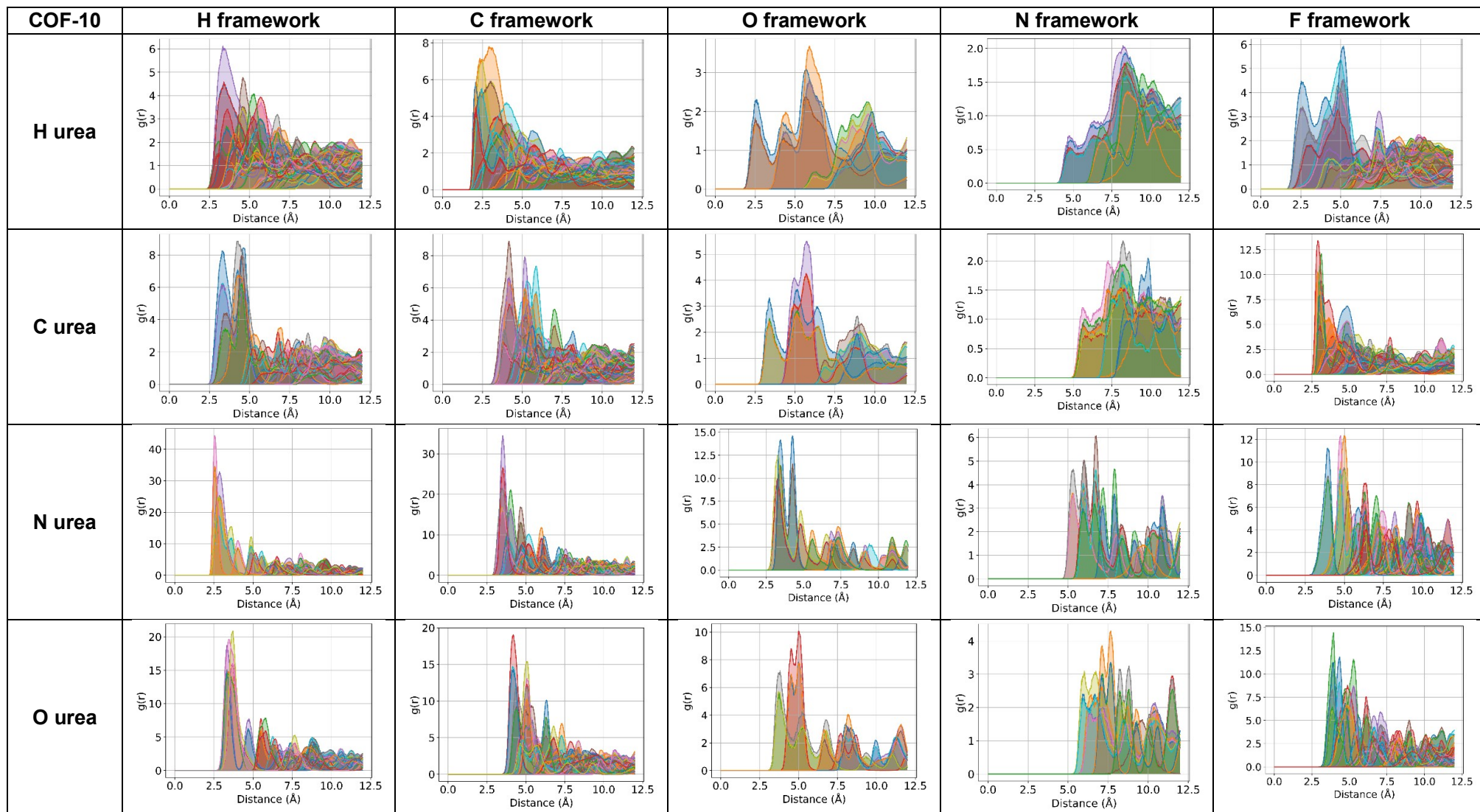


Figure S7: Snapshots of MD simulations of urea in Tf-DHzDPr with increasing number of urea molecules (in orange): a) 1 molecule; b) 10 molecules ; c) 100 molecules;





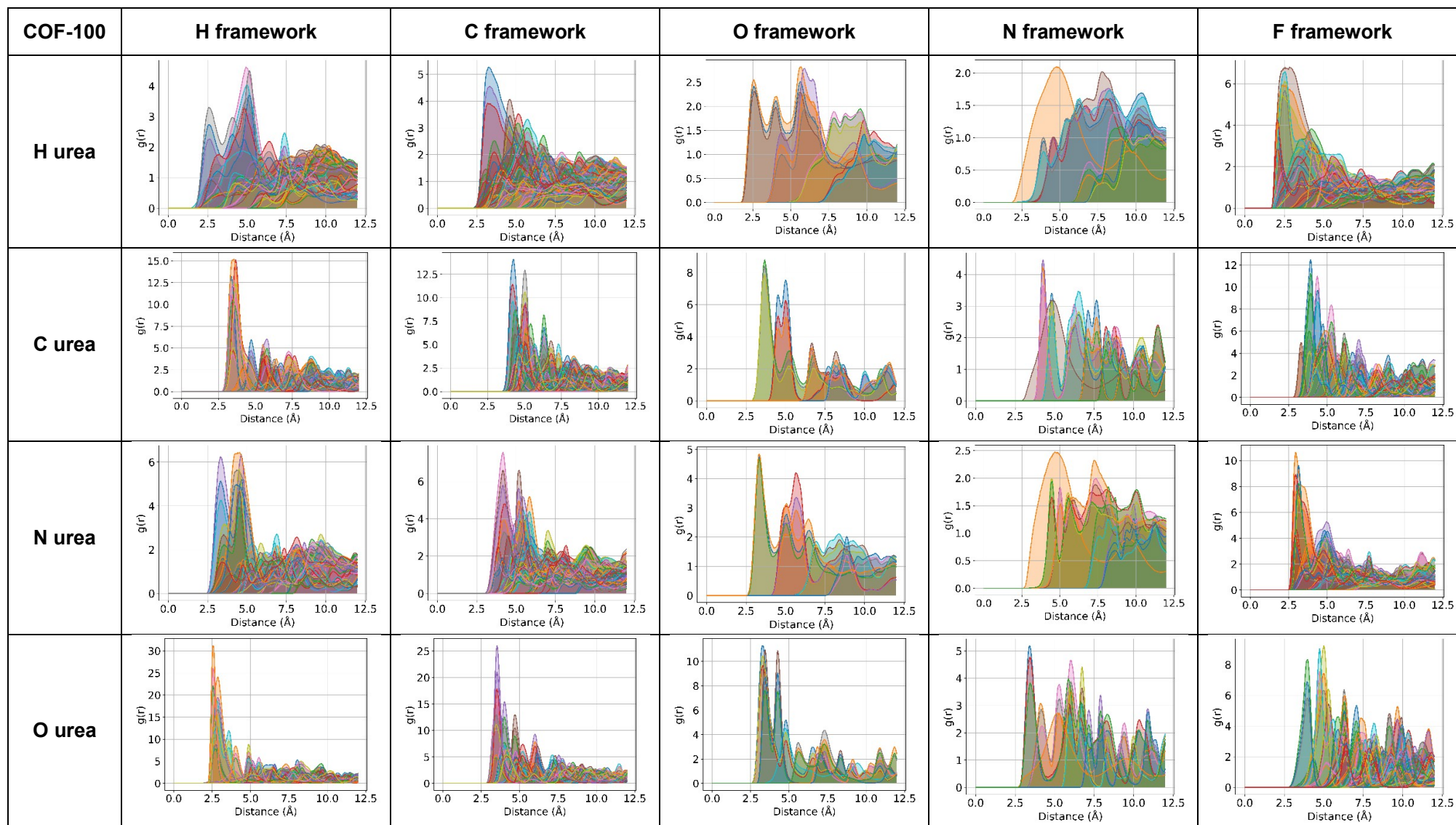
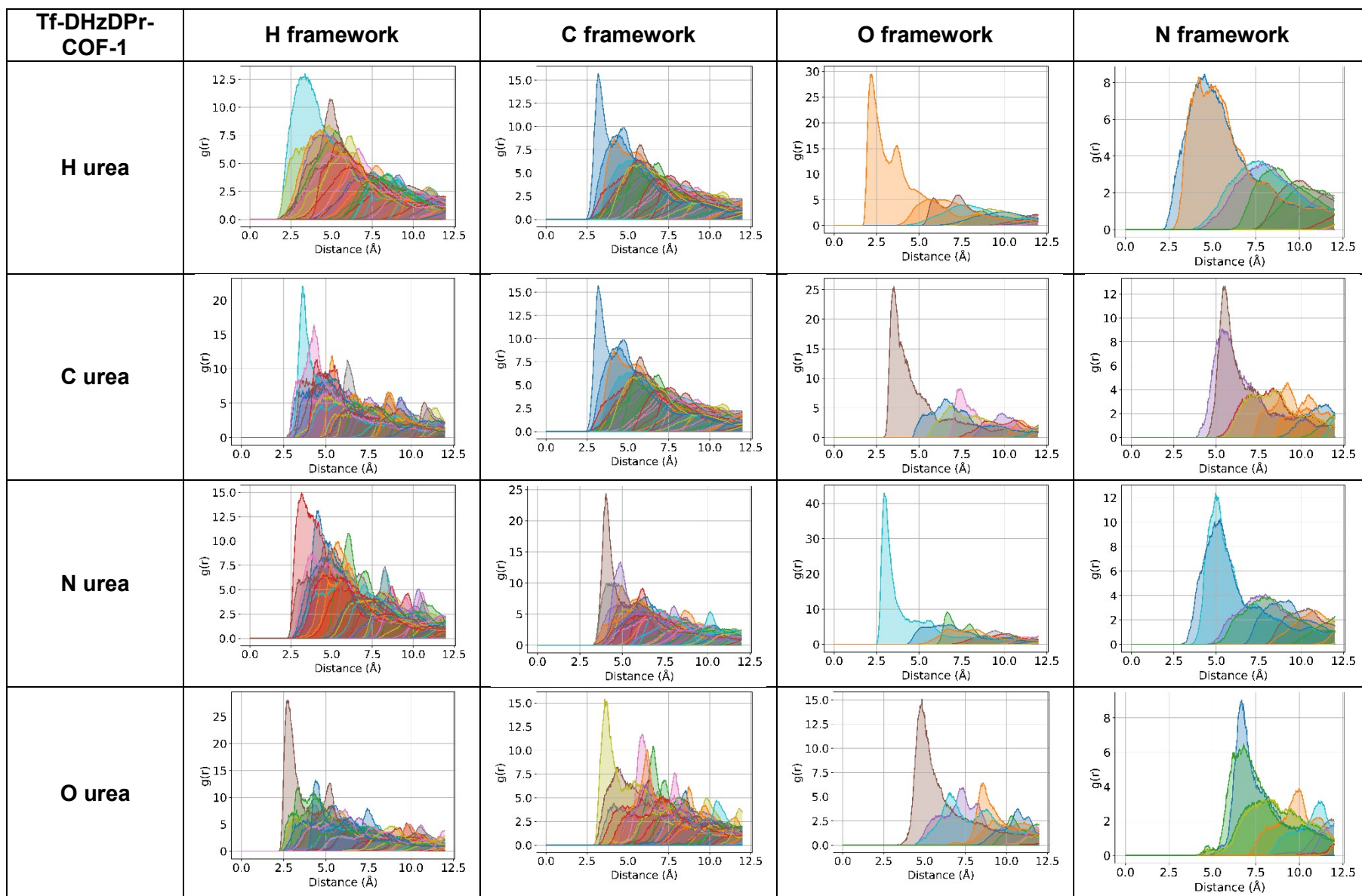
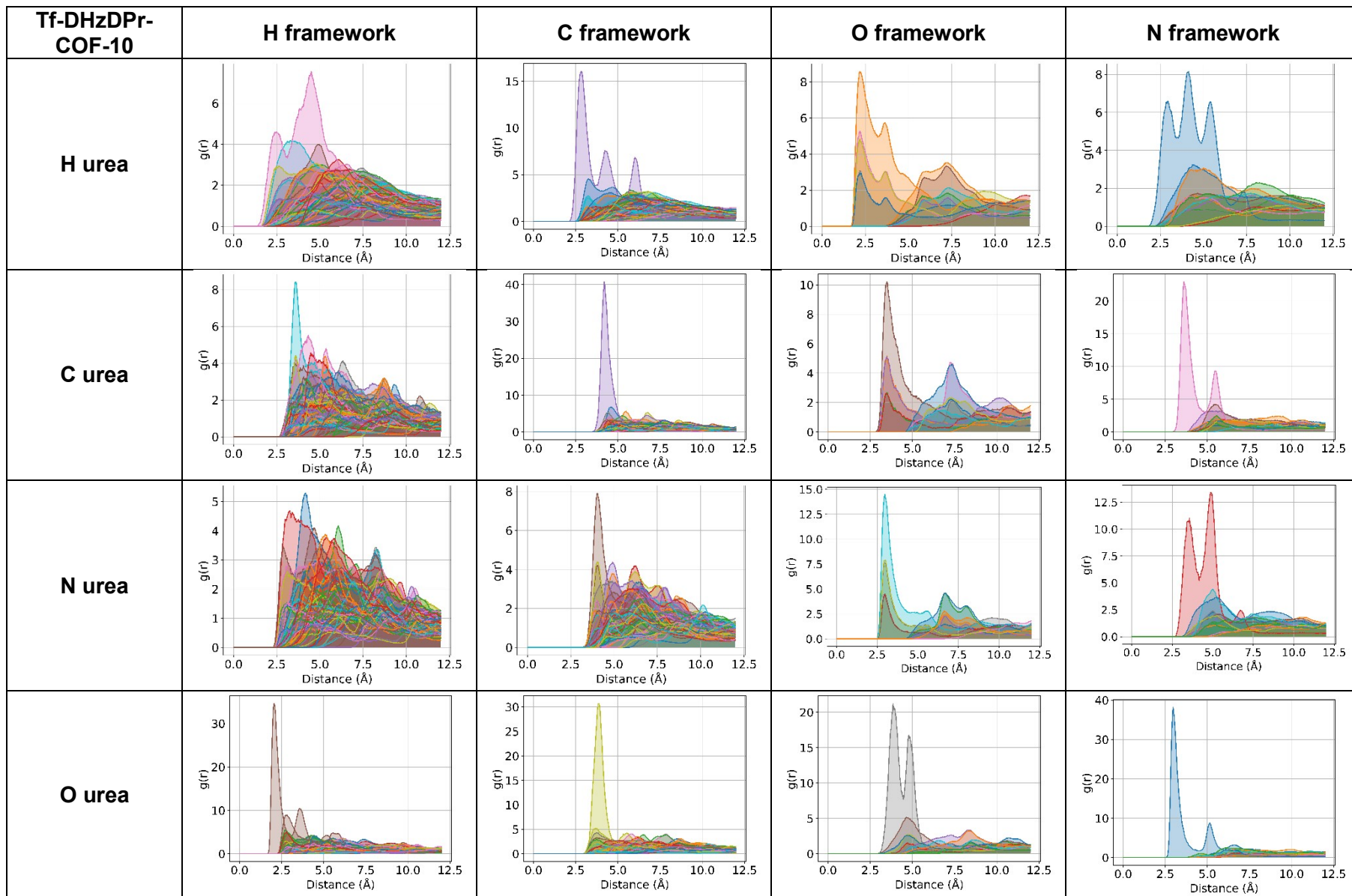


Figure S8. Interaction of electropositive atoms (C, H) and electronegative atoms (O, N) in the single urea molecule with the COF-F6 framework atoms (from left to right H, C, O, N, F)





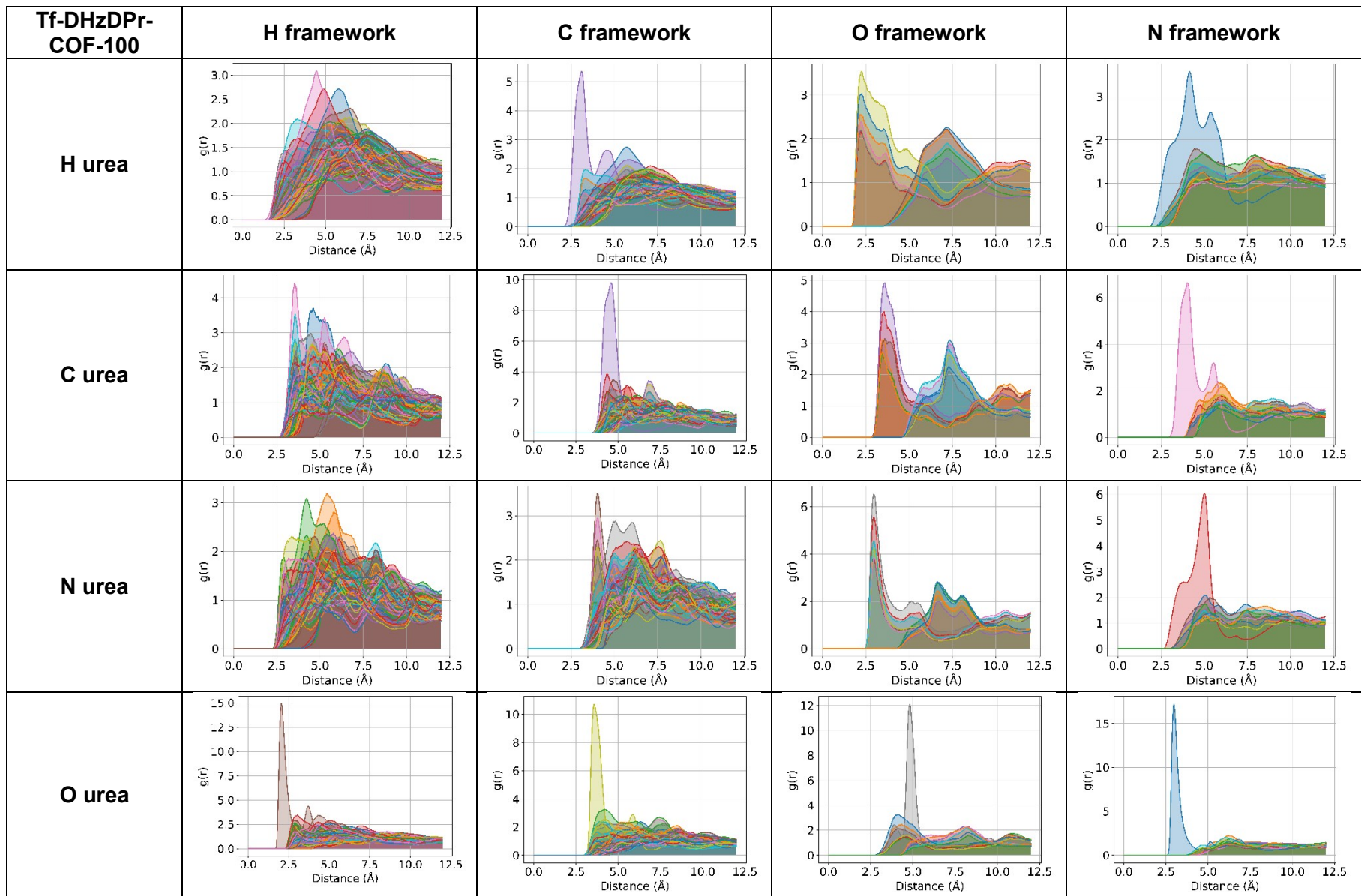


Figure S9. Interaction of electropositive atoms (C, H) and electronegative atoms (O, N) in the single urea molecule with the Tf-DHzDPr-COF framework atoms (from left to right H, C, O, N)

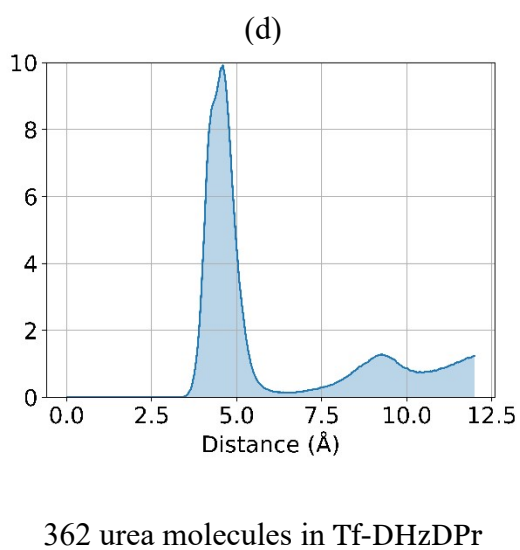
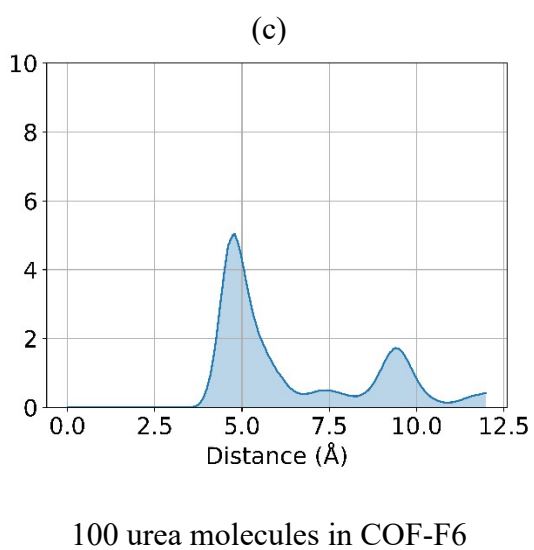
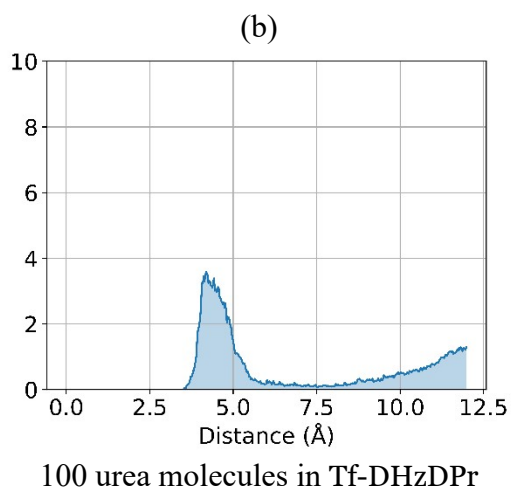
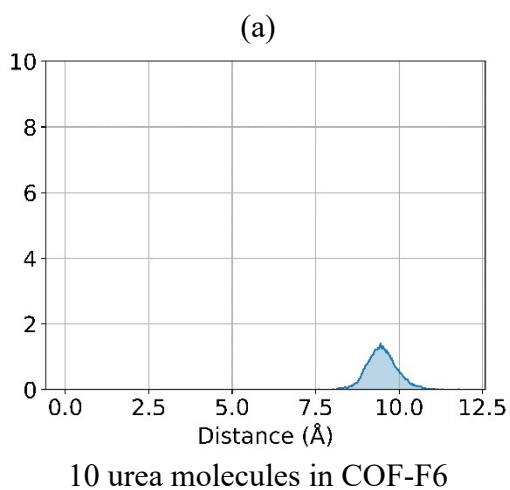


Figure S10: Radial Distribution Function for urea carbons in COF-F6 and Tf-DHzDPr

References

- [1] H. Kokubo, J. Rösger, D. W. Bolen, and B. M. Pettitt, “Molecular Basis of the Apparent Near Ideality of Urea Solutions,” *Biophys. J.*, vol. 93, no. 10, pp. 3392–3407, Nov. 2007, doi: 10.1529/biophysj.107.114181.
- [2] B. Akkoca Palabıyık, M. Batyrow, and I. Erucar, “Computational investigations of Bio-MOF membranes for uremic toxin separation,” *Sep. Purif. Technol.*, vol. 281, p. 119852, Jan. 2022, doi: 10.1016/j.seppur.2021.119852.
- [3] T. Yıldız and I. Erucar, “Revealing the performance of bio-MOFs for adsorption-based uremic toxin separation using molecular simulations,” *Chem. Eng. J.*, vol. 431, p. 134263, Mar. 2022, doi: 10.1016/j.cej.2021.134263.