Supporting Information for:

Enhancing of NO uptake in Metal-Organic Frameworks by linker functionalization. A Multi-scale theoretical study.

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DFT results

Numerous geometry configurations were optimized at the DSD-BLYP/def2-TZVPP level of theory for each system under study i.e. NO···C_6H_5–X. The configuration with the most favorable energy was found and corrected for the Basis Set Superposition Error (BSSE) with the Counterpoise method [30]. The final equation used to calculate the binding energy between the two monomers is:

$$BE = E_{dimer} - E_{linker}^{ghost} - E_{CO}^{ghost} + \Delta E_{deform} \quad (1)$$

where E_{dimer} is the total energy of the dimer, E_{linker}^{ghost} is the energy of the Benzene linker calculated at the dimer geometry in the presence of the ghost basis of NO molecule, E_{NO}^{ghost} is the energy of NO calculated at the dimer geometry in the presence of the ghost basis of the benzene modified linker, and ΔE_{deform} is the deformation energy, defined as the difference between the isolated interacting molecules (NO and the Benzene modified linker) in the dimer geometry and their optimized structures. The binding energies and the optimized structures are shown in **Figure S1** and **Figure S2** respectively.

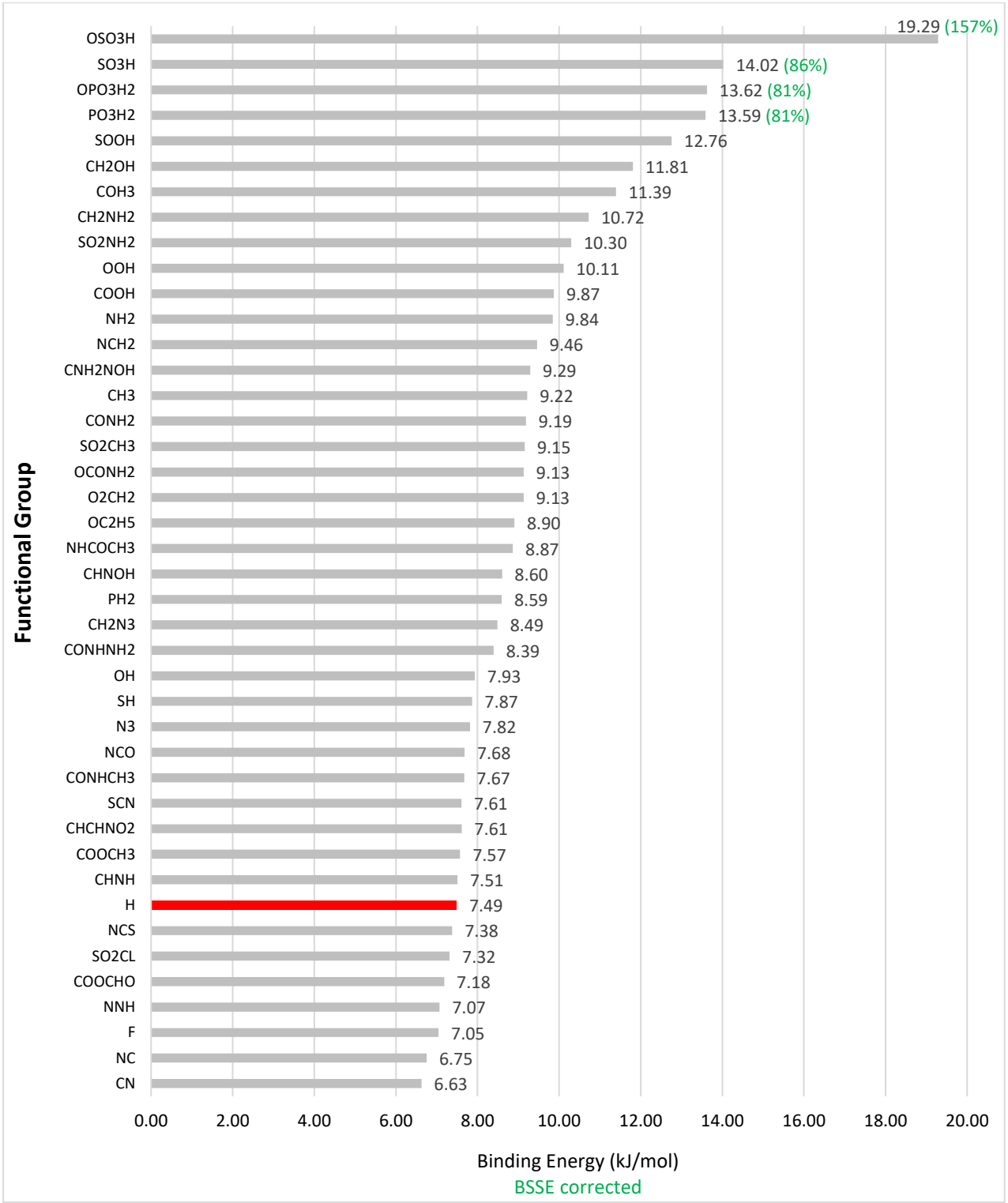
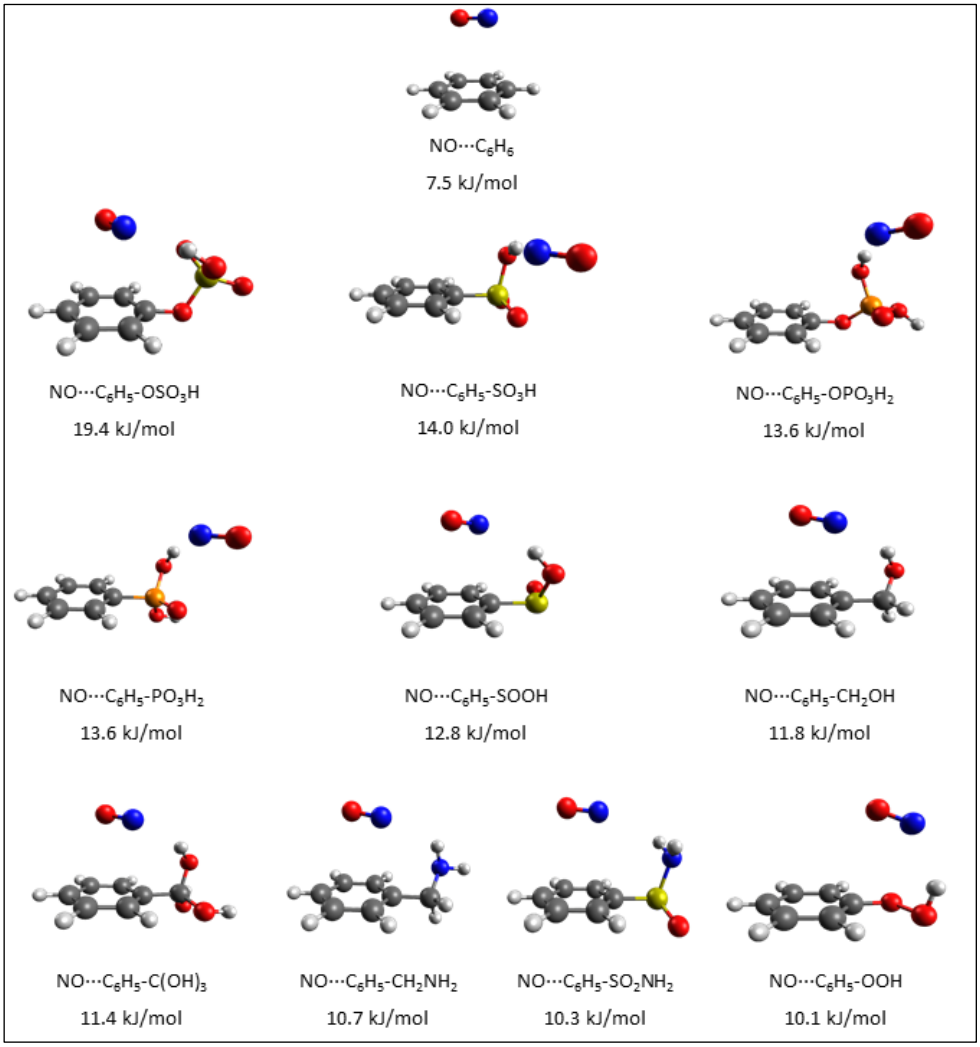
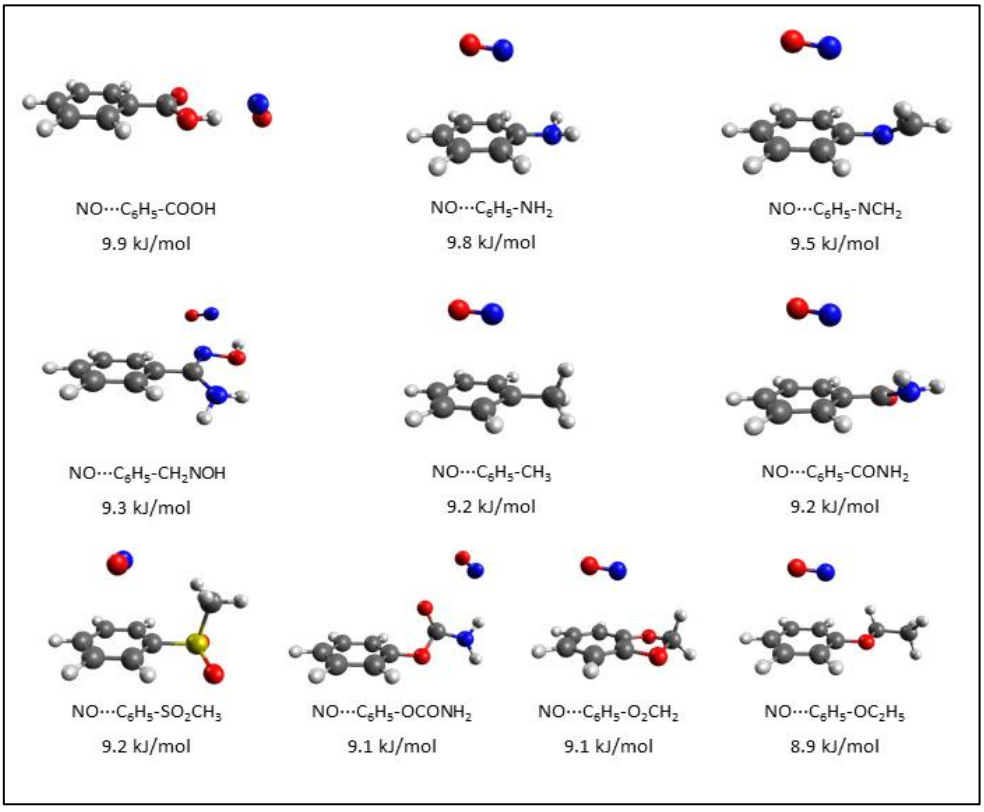


Figure S1: Binding energies (kJ/mol) of the NO···C_6H_5-X dimers, calculated at the DSD-BLYP/def2-TZVPP level of theory. Basis Set Superposition Error (BSSE) was taken into consideration by the full counterpoise method [30].


NO···C6H6
7.5 kJ/mol
NO···C6H5-OSO3H
19.4 kJ/mol
NO···C6H5-SO3H
14.0 kJ/mol
NO···C6H5-OPO3H2
13.6 kJ/mol
NO···C6H5-PO3H2
13.6 kJ/mol
NO···C6H5-SOOH
12.8 kJ/mol
NO···C6H5-CH2OH
11.8 kJ/mol
NO···C6H5-C(OH)3
11.4 kJ/mol
NO···C6H5-CH2NH2
10.7 kJ/mol
NO···C6H5-SO2NH2
10.3 kJ/mol
NO···C6H5-OOH
10.1 kJ/mol


NO···C6H5-COOH
9.9 kJ/mol
NO···C6H5-NH2
9.8 kJ/mol
NO···C6H5-NCH2
9.5 kJ/mol
NO···C6H5-CH2NOH
9.3 kJ/mol
NO···C6H5-CH3
9.2 kJ/mol
NO···C6H5-CONH2
9.2 kJ/mol
NO···C6H5-SO2CH3
9.2 kJ/mol
NO···C6H5-OCONH2
9.1 kJ/mol
NO···C6H5-O2CH2
9.1 kJ/mol
NO···C6H5-OC2H5
8.9 kJ/mol

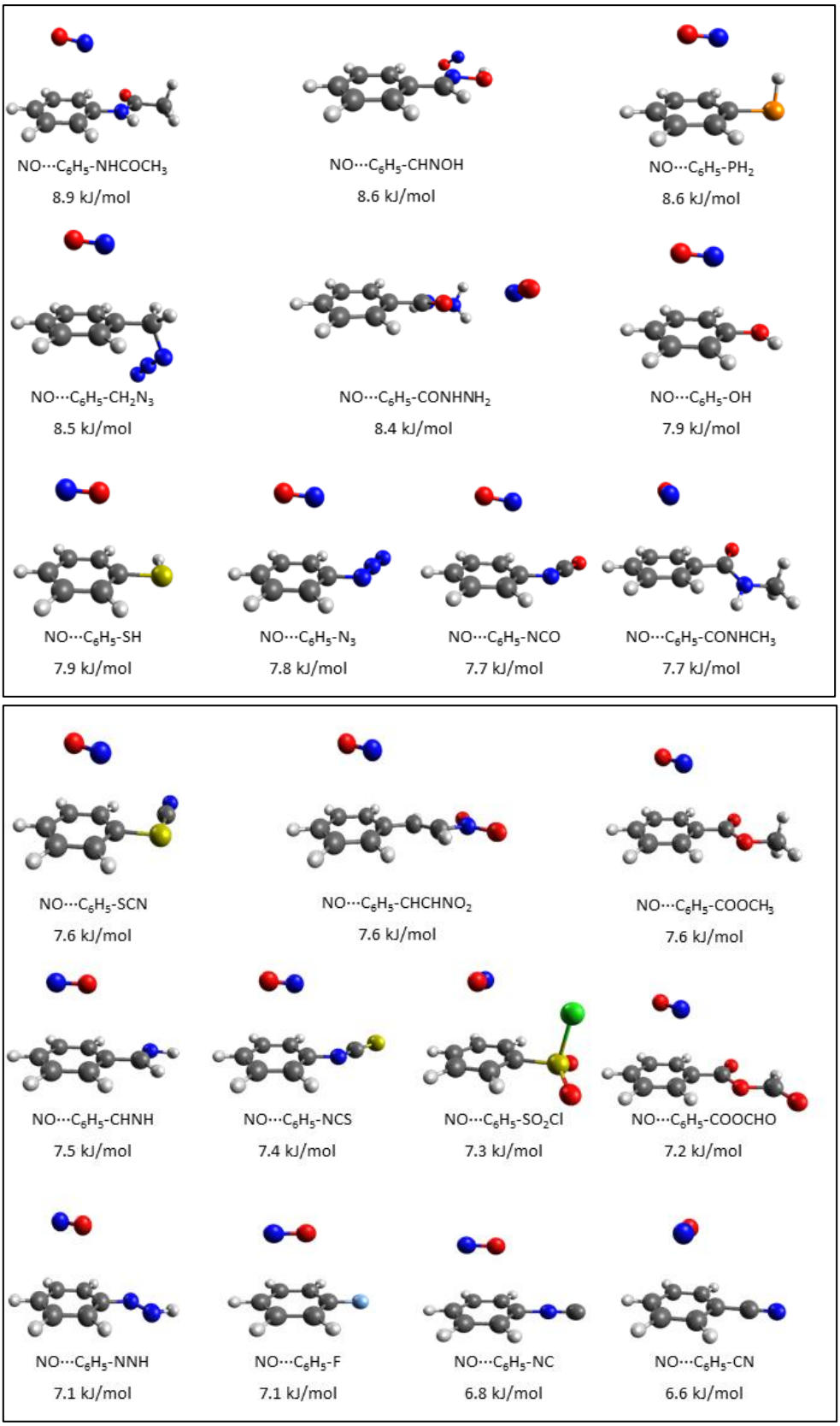
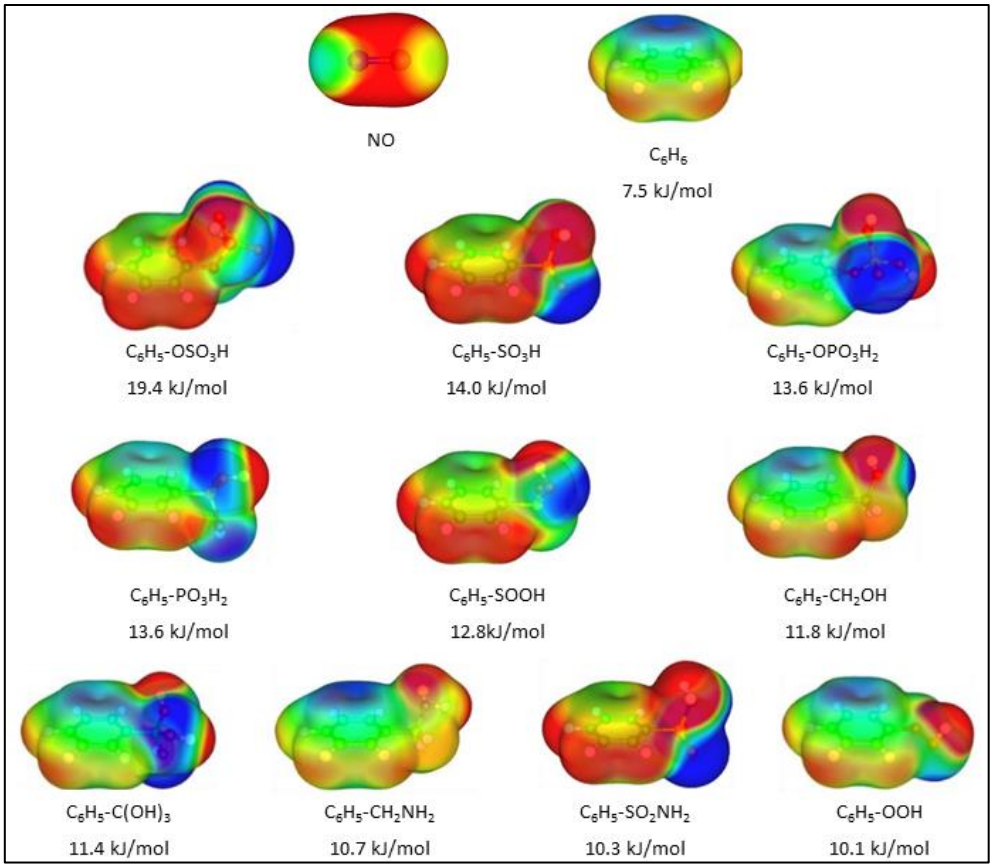
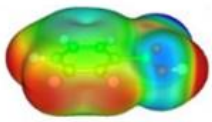


Figure S2: More energy-favorable configurations for the systems in this work.

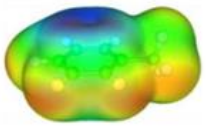
Colored electrostatic potential maps for all functionalized benzene molecules were constructed by mapping the electrostatic potentials onto the 0.001 au electron density isosurface with gOpenMol [31, 32].





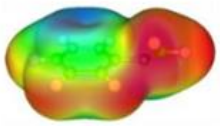
C_6H_5-COOH

9.9 kJ/mol



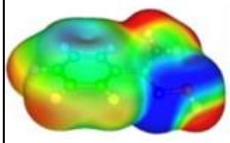
C_6H_5-NH_2

9.8 kJ/mol



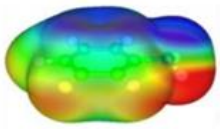
C_6H_5-NCH_2

9.5 kJ/mol



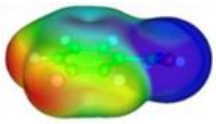
C_6H_5-CH_2NOH

9.3 kJ/mol



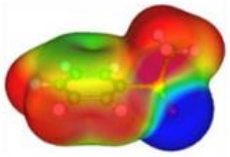
C_6H_5-CH_3

9.2 kJ/mol



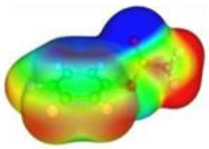
C_6H_5-$CONH_2$

9.2 kJ/mol



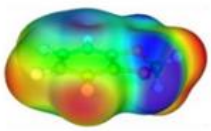
C_6H_5-SO_2CH_3

9.2 kJ/mol



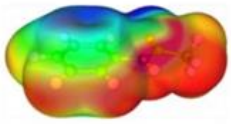
C_6H_5-$OCONH_2$

9.1 kJ/mol



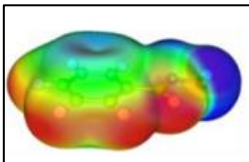
C_6H_5-O_2CH_2

9.1 kJ/mol



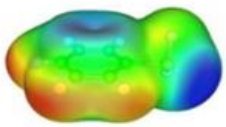
C_6H_5-$NHCOCH_3$

8.9 kJ/mol



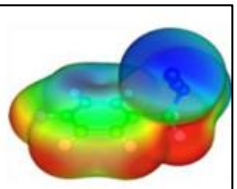
C_6H_5-CHNOH

8.6 kJ/mol



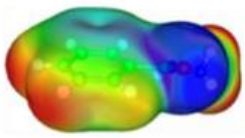
C_6H_5-PH_2

8.6 kJ/mol



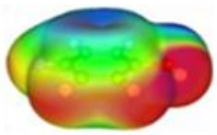
C_6H_5-CH_2N_3

8.5 kJ/mol



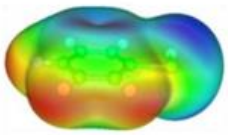
C_6H_5-$CONHNH_2$

8.4 kJ/mol



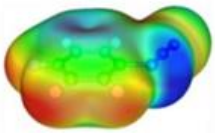
C_6H_5-OH

7.9 kJ/mol



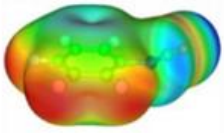
C_6H_5-SH

7.9 kJ/mol



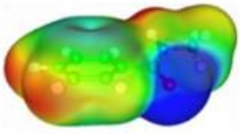
C_6H_5-N_3

7.8 kJ/mol



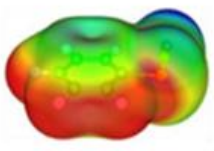
C_6H_5-NCO

7.7 kJ/mol



C_6H_5-$CONHCH_3$

7.7 kJ/mol



C_6H_5-SCN

7.6 kJ/mol

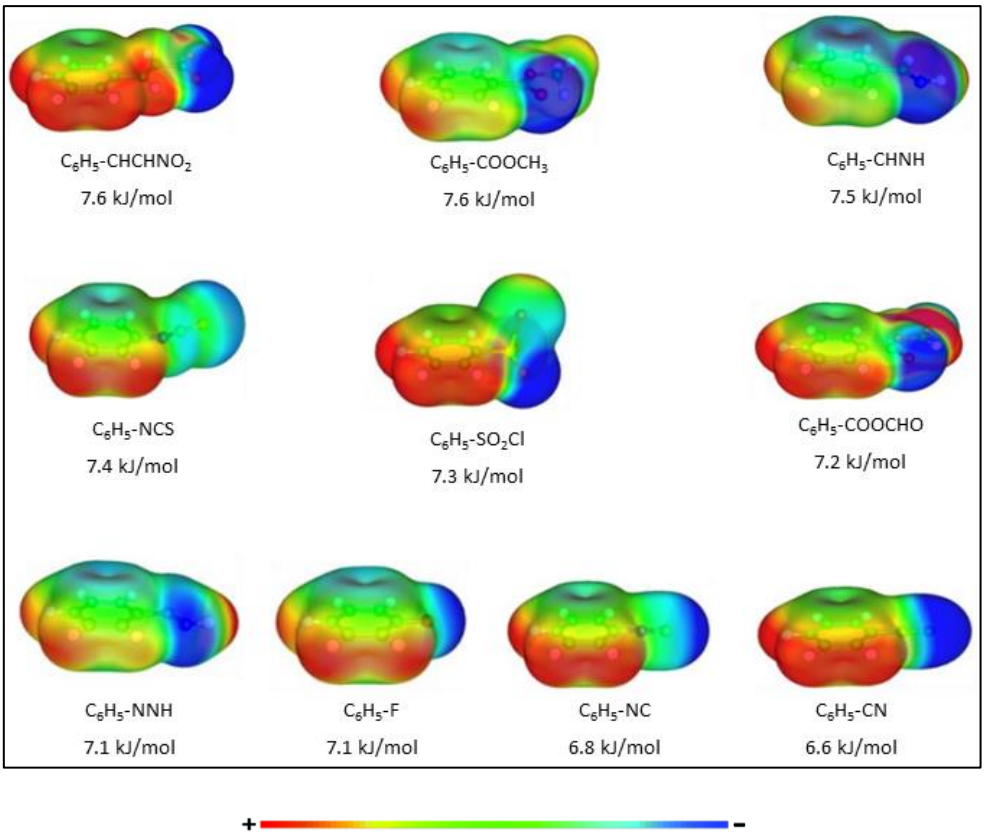


Figure S3: Electrostatic potential maps of all substituted monomers C_6H_5-X. Calculated using the DSD-BLYP/def2-TZVPP method with ORCA 4.2 [24, 25] and visualized with gOpenMol. The varying intensities are ranging from -0.03 to +0.03 Hartree·e^{-1}. Red: Electron-poor regions - high potential value, Blue: electron-rich regions - low potential.

DFT derived interatomic potential fitting

The interaction energies between the Nitric Oxide molecule and the C_6H_5-X monomer at certain distances around the global minimum were determined by employing rigid scans at the DSD-BLYP/def2-TZVPP level of theory. The ε/k_b, σ parameters of the interatomic potential were fitted using an in-home python algorithm in order to correctly describe the DFT derived energies. All parameters were mixed during the Lorentz-Berthelot mixing rules [37].

The significant disparity between UFF [36] and the DFT points seen in **Figure S4** and **Figure S5** proves the significance of the stated fitting procedure and highlights the importance of ensuring the validity of classical Force Fields on the system under study.

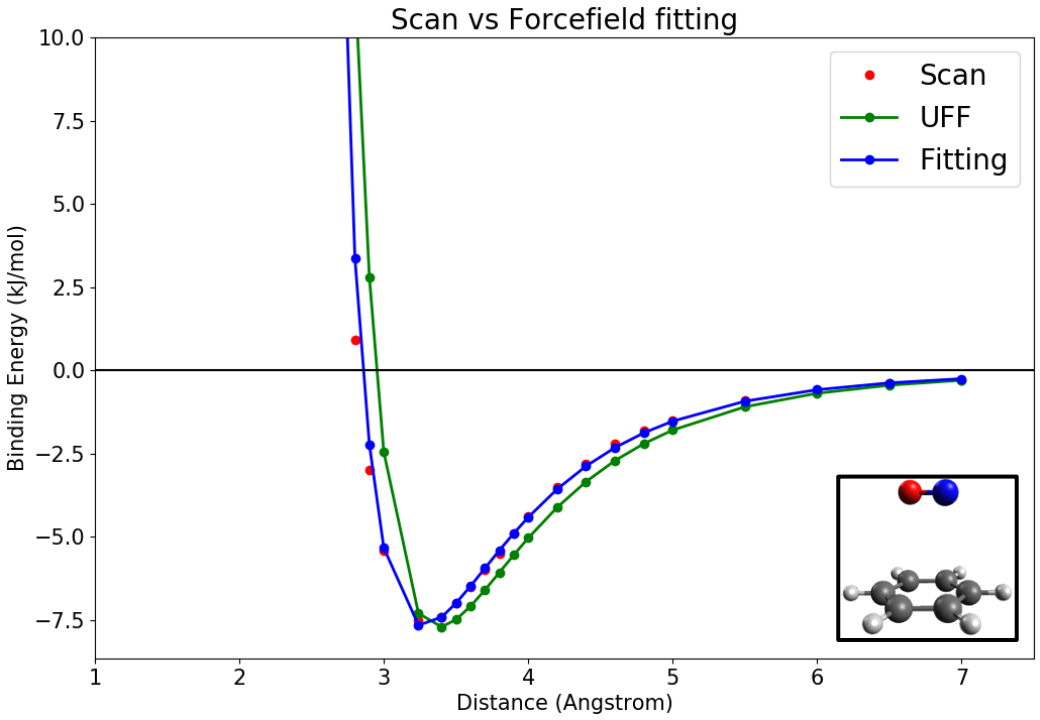
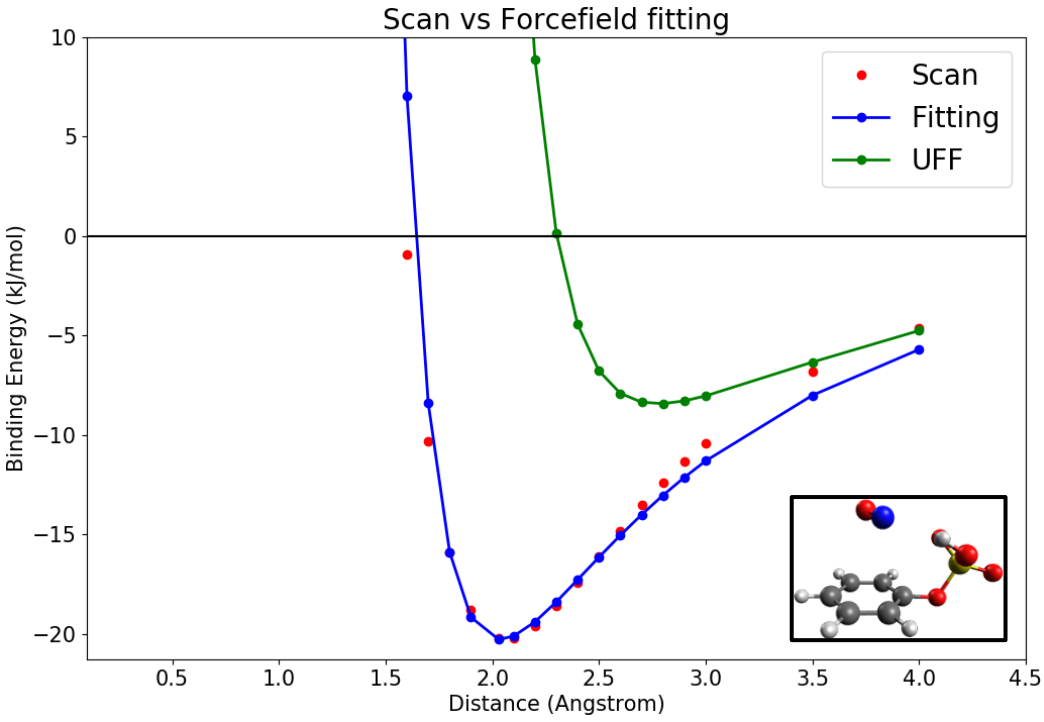
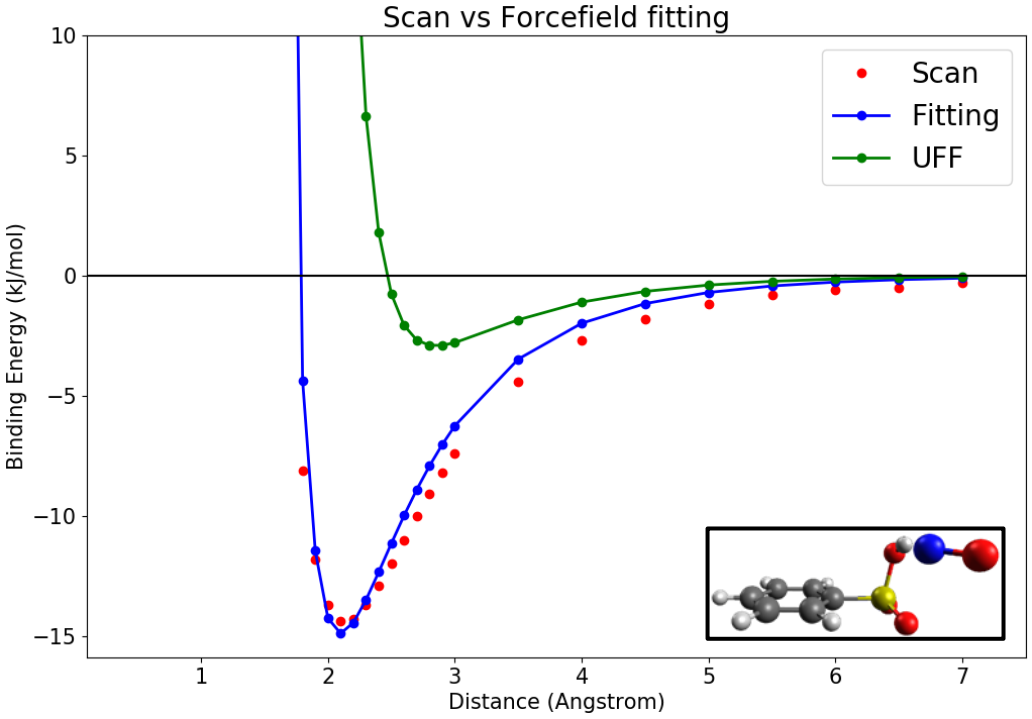


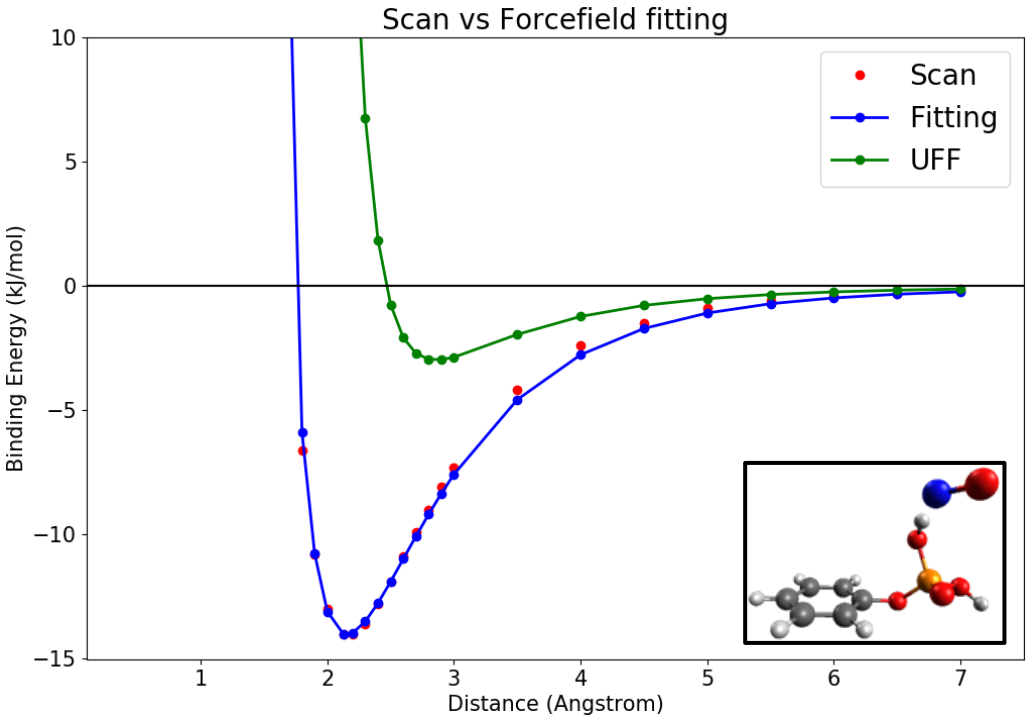
Figure S4: Fitting of the (ε/k_b, σ) parameters of the UFF potential [36] on the QM data obtained from the DFT scan of NO over benzene.



(a)



(b)

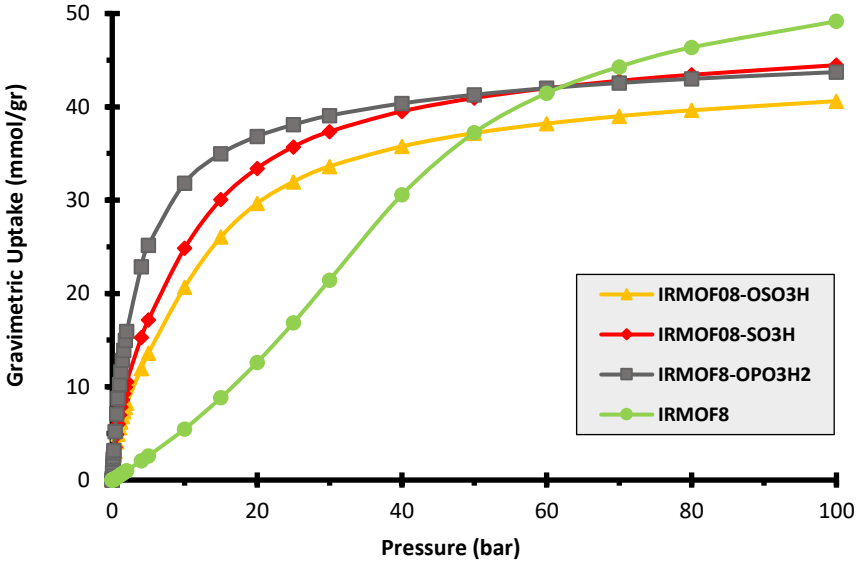


(c)

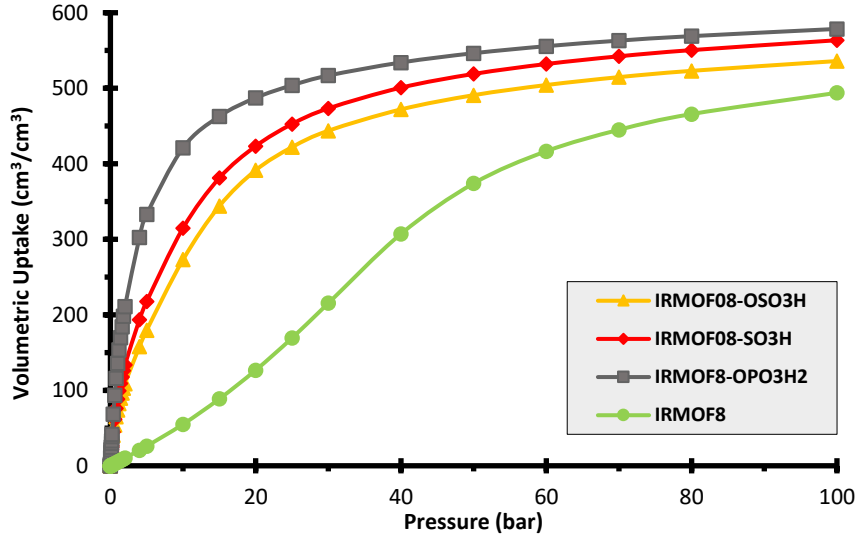
Figure S5: Fitting of the (ε/k_b, σ) parameters of the UFF potential on the QM data obtained from the ab-DFT scan of NO over (a) C_6H_5-OSO_3H (b) C_6H_5-SO_3H (c) C_6H_5- OPO_3H_2

GCMC results

Concerning the cell setup, firstly the organic linkers of the parent and modified IRMOF-8 frameworks were optimized at the DSD-BLYP/def2-TZVPP level of theory. Afterward, we made the appropriate changes to the IRMOF-8's Crystallographic Information File (CIF). Namely, we substituted a hydrogen atom in the naphthalene group with the Functional Group's optimized structure. The coordinates of the organic linker's remaining atoms remained constant. During GCMC simulations the periodic box's dimensions were chosen to be 30.09× 30.09 × 30.09 $Å^3$ in order to guarantee that no finite-size effects affected the results. 5000 initial equilibration steps were conducted that were followed by 5000 production steps that calculated the number of adsorbed gas molecules of nitric oxide. In **Figure S6** the gravimetric (mmol/g) and volumetric (cm^3/cm^3) uptake isotherms can be seen.



(a)



(b)

Figure S6: Gravimetric (a) and Volumetric (b) Nitric Oxide uptake isotherms for IRMOF-8 and IRMOF-8-n (n: $-OSO_3H$, $-SO_3H$, $-OPO_3H_2$)

Table S1: The binding energies of the different local minima calculated at the RI-DSD-BLYP/def2-TZVPP level of theory (without BSSE correction)

FG / Local minimum	$-OSO_3H$	$-SO_3H$	$-OPO_3H_2$
	Binding Energy (kJ/mol)		
1	22	16	16
2	9	10	16
3	8	8	10
4	5	8	10
5	X	8	9
6	X	6	X

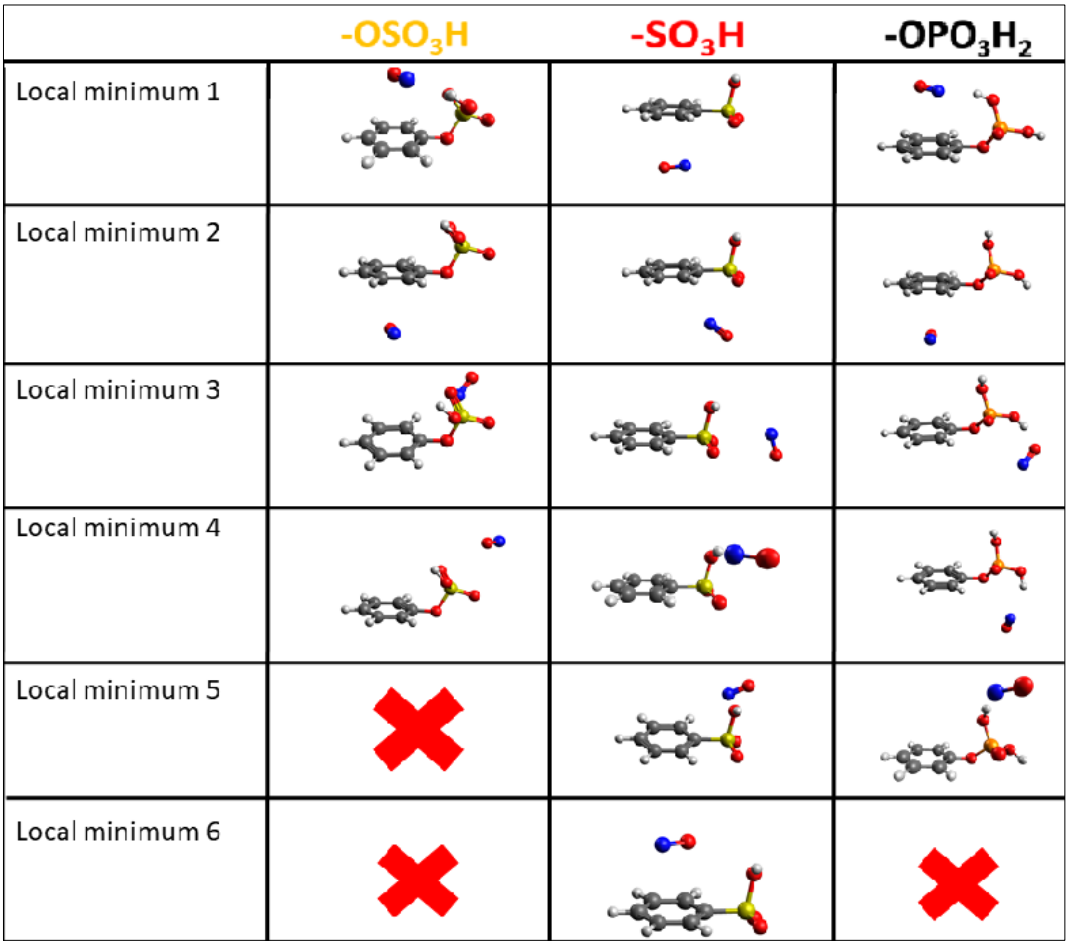


Figure S7: The geometries of the different local minima (RI-DSD-BLYP/def2-TZVPP)

References

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