Impact of linker functionalization on the adsorption of nitrogen-containing compounds in HKUST-1

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1. fmj, tbo, tpo topology

(a) fmj topology

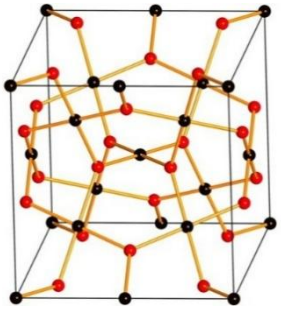

Figure S1. fmj topology

RCSR reference: http://rcsr.net/nets/fmj

- names: 3S net
- key words: bipartite

embed type: 1b
space group: Immm (orthorhombic)
vertices: 5
edges: 4

(b) tbo topology

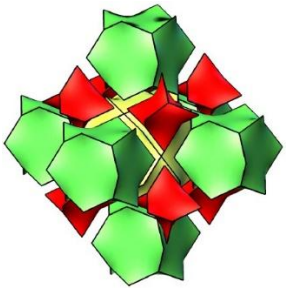

Figure S2. tbo topology

RCSR reference: http://rcsr.net/nets/tbo

- names: twisted boracite, 3S net, HKUST-1
- key words: bipartite, good
- references: Acta Cryst. A62, 350-355 (2006)

embed type: 1b
space group: Fm-3m (cubic)
vertices: 2
edges: 1

(c) pto topology

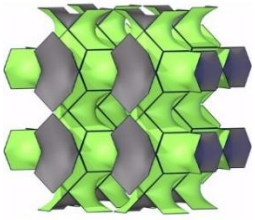

Figure S3. pto topology

RCSR reference: http://rcsr.net/nets/pto

- names: Pt_3O_4, 3S net
- key words: bipartite, good
- references: Acta Cryst. A62, 350-355 (2006)

embed type: 1a
space group: Pm-3n (cubic)
vertices: 2
edges: 1

2. Adsorption Structures

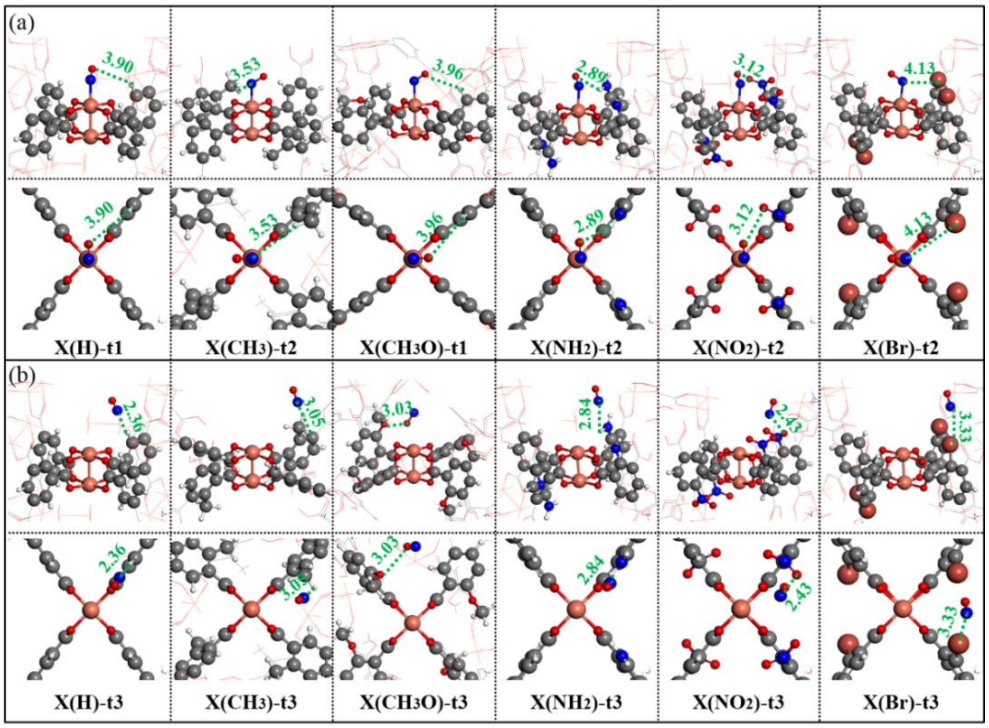

Figure S4. Top (upper row) and side (down row) views of the most favorable NO adsorption configuration on (a) open metal site, and (b) functional group site of pristine and X-functionalized HKUST-1. The shortest distance between the adsorbates and functional group are provided, in Å. Largest: Br; second-largest spheres: Cu. White, red, blue, and grey spheres with increasing size: H, O, N, and C, the same below.

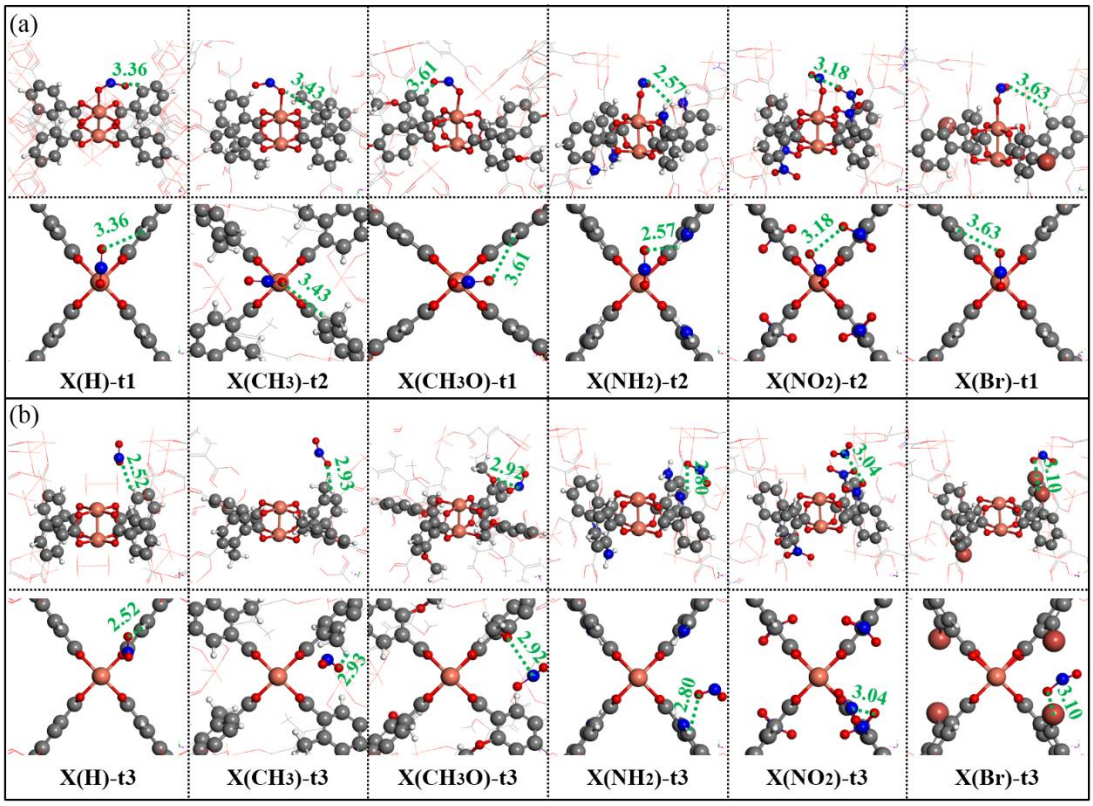

Figure S5. Top (upper row) and side (down row) views of the most favorable NO_2 adsorption configuration on the (a) open metal site, and (b) functional group site of the pristine and X-functionalized HKUST-1.

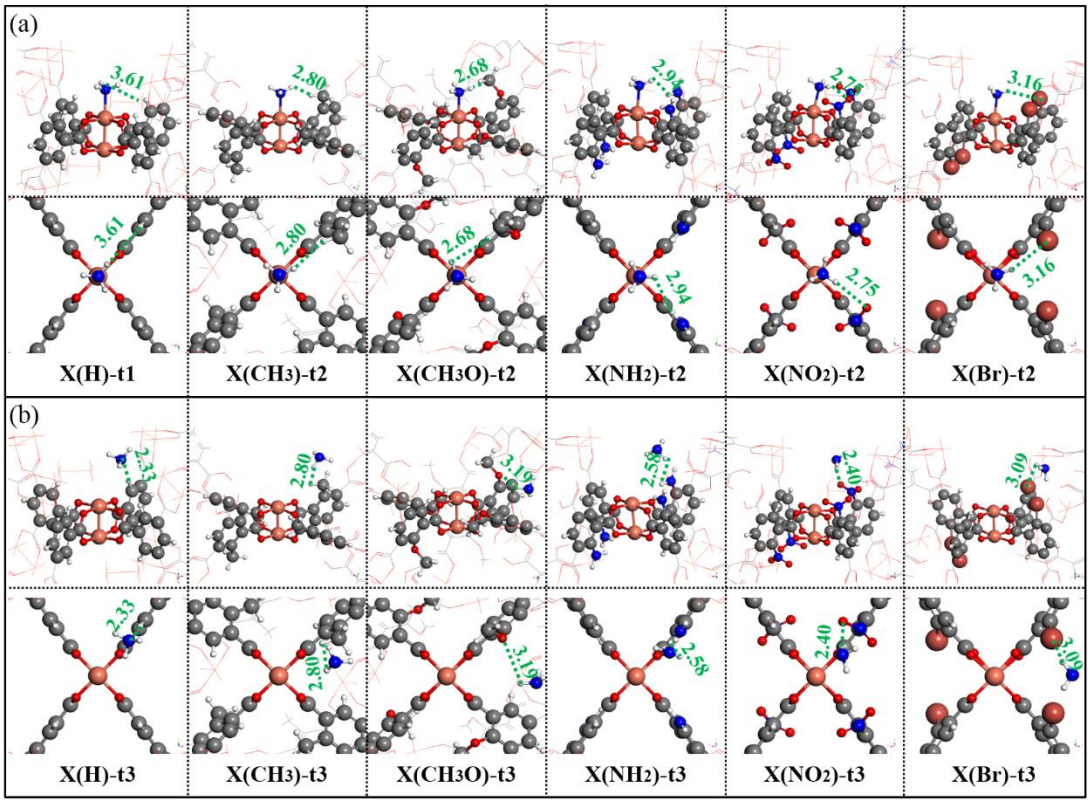

Figure S6. Top (upper row) and side (down row) views of the most favorable NH_3

adsorption configuration on (a) open metal site, and (b) functional group site of pristine and X-functionalized HKUST-1.

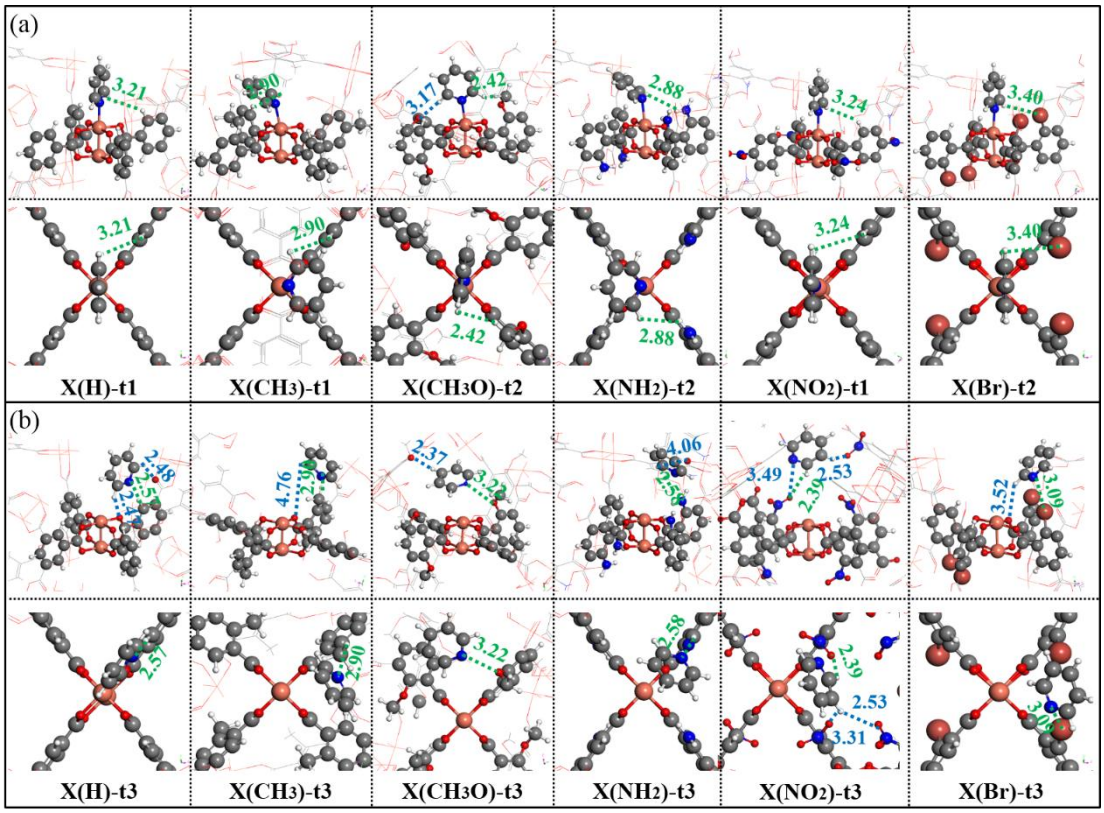

Figure S7. Top (upper row) and side (down row) views of the most favorable pyridine C_5H_5N adsorption configuration on the (a) open metal site, and (b) functional group site of pristine and X-functionalized HKUST-1.

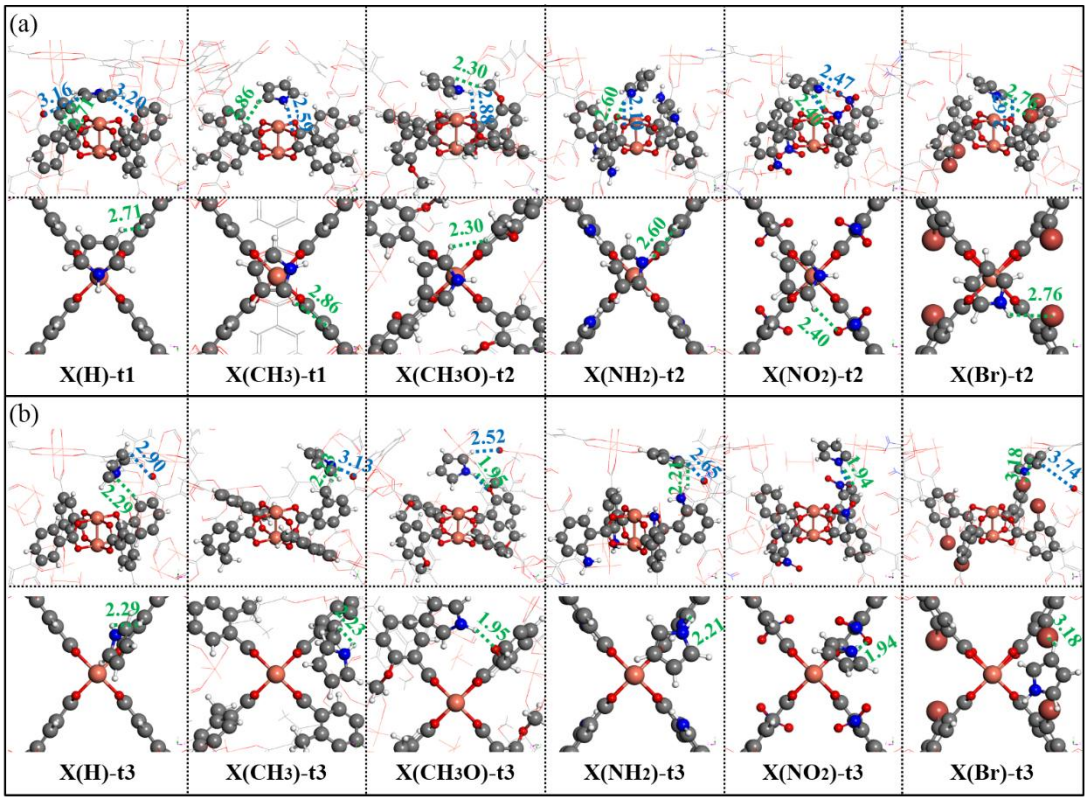

Figure S8. Top (upper row) and side (down row) views of the most favorable pyrrole C_4H_5N adsorption configuration on the (a) open metal site, and (b) functional group site of the pristine and X-functionalized HKUST-1.

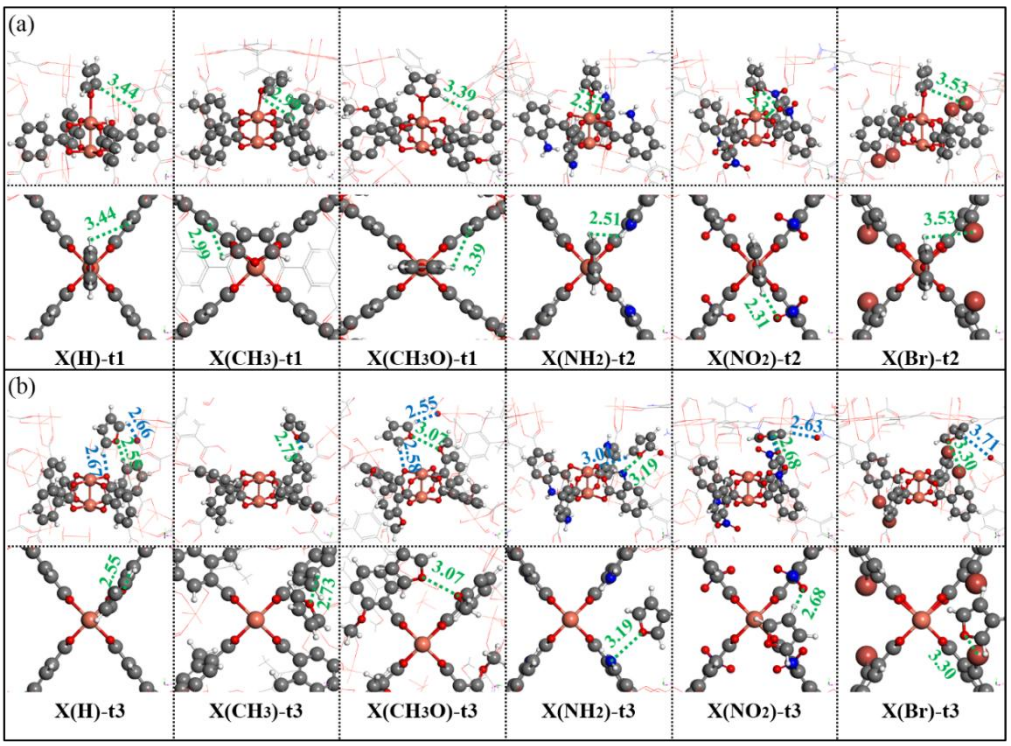

Figure S9. Top (upper row) and side (down row) views of most favorable C_4H_4O adsorption configuration on the (a) open metal site, and (b) functional group site of

pristine and X-functionalized HKUST-1.

3. Adsorption energy of CO_2, CH_4, and H_2O

Table S1. Adsorption energies (E_{ads}, in kJ mol^{-1}) of the most stable adsorption configuration of each species on the pristine (X = H) and X-functionalized (X = CH_3- or CH_3O) HKUST-1.

X	CO_2	CH_4	H_2O
H	-51.2	-53.7	-61.1
CH_3	-75.1(t3)	-68.7(t2)	-63.2(t1)
CH_3O	-59.6(t3)	-73.4(t2)	-117.1(t1)

4. Electron density difference map for CH_3-functionalized HKUST-1 system.

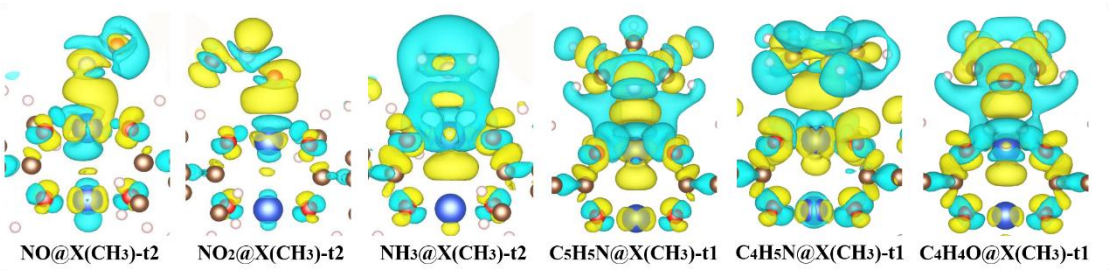

Figure S10. Electron density difference map for six adsorbates on open metal center (t1 or t2, only the more stable one is shown here) of CH_3-functionalized HKUST-1. Accumulation region in yellow; depletion regions in blue.

5. Electron localization function for furan C_4H_4O

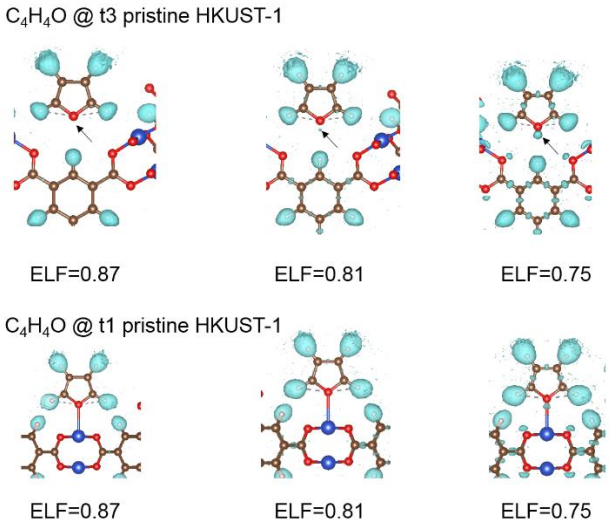

Figure S11. Electron localization function for furan C_4H_4O adsorption on t3 and t1 sites of pristine HKUST-1 at different iso-value.