Supporting Information for

Computational design of metal-organic frameworks for aniline recovery from aqueous solution

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1. Structural information of MOFs

Table S1 Structural features of the screened MOF series

MOF ID	Materials	Unit cell (Å)[a]	Cell angle (°)[a]	S_{acc}[b] (m^2 g^{-1})	V_{free}[b] (cm^3 g^{-1})	d_{window}[c] (Å)	d_{pore}[c] (Å)
1	CUK-1[1]	a = 18.10; b = 12.77; c = 10.97	α = γ = 90; β = 103	758	0.36	-	11.1
2	MIL-140C[2]	a = 31.89; b = 15.61; c = 7.93	α = γ = 90; β = 85	907	0.47	-	6.0
3	MIL-53*ht*(Al)[3]	a = 6.61; b = 16.67; c = 12.81	α = β = γ = 90	1408	0.60	-	8.5
4	MIL-68(Al)[4]	a = 41.02; b = 35.92; c = 6.68	α = β = γ = 90	1456	0.77	-	16.0
5	MIL-47(V)[5]	a = 6.82; b = 16.14; c = 13.94	α = β = γ = 90	1501	0.63	-	8.5
6	UIO-66(Zr)[6]	a = b = c = 20.74	α = β = γ = 90	799	0.50	6.0	8.0/11.0
7	Zr_6-AzoBDC[7]	a = b = c = 29.86	α = β = γ = 90	3525	1.37	9.0	13.0/16.8
8	Zr_6-Cl_2AzoBDC[7]	a = b = c = 29.93	α = β = γ = 90	2796	1.13	9.0	13.0/16.8
9	Zn(bpb)[8]	a = b = 13.27; c = 7.25	α = β = γ = 90	2275	0.99	-	13.2
10	Ni(bpb)[8]	a = 6.76; b = 22.73; c = 13.46	α = β = γ = 90	1778	0.75	-	11.7[c]
11	Al-PMOF[9]	a = 31.98; b = 6.58; c = 16.86	α = β = γ = 90	1548	0.75	-	6.0/11.0
12	ZIF-71[10]	a = b = c = 28.55	α = β = γ = 90	1042	0.58	6.0	16.8
13	Co(1,3-BDP)[11]	a = b = 22.85; c = 12.46	α = β = γ = 90	1270	0.55	-	8.0
14	Cu-TDPAT[12]	a = b = 26.86; c = 37.75	α = β = γ = 90	2143	0.93	3.5/11.4	9.1/12.0/17.2
15	$Ni_8(OH)_4(pbp)_6$[13]	a = b = c = 31.36	α = β = γ = 90	4435	1.86	9.0	23.0
16	IRMOF-1[14]	a = b = c = 25.83	α = β = γ = 90	3600	1.36	-	11.2/18.5
17	IRMOF-2[14]	a = b = c = 25.77	α = β = γ = 90	2851	0.99	-	7.5/16.4
18	IRMOF-7[14]	a = b = c = 25.83	α = β = γ = 90	3228	1.06	-	5.5/13.6
19	IRMOF-8[14]	a = b = c = 30.09	α = β = γ = 90	4319	1.87	-	12.6/21.4
20	IRMOF-10[14]	a = b = c = 34.28	α = β = γ = 90	4926	2.66	-	15.4/24.5
21	IRMOF-12[14]	a = b = c = 34.28	α = β = γ = 90	5240	2.23	-	13.0/24.5
22	IRMOF-14[14]	a = b = c = 34.38	α = β = γ = 90	4807	2.30	14.7	13.8/24.5
23	IRMOF-15[14]	a = b = c = 21.46	α = β = γ = 90	5986	2.01	8.1	8.1/12.8
24	IRMOF-16[14]	a = b = c = 21.49	α = β = γ = 90	5968	4.46	23.3	19.1/28.8
25	MOF-HTB'[15]	a = b = c = 52.99	α = β = γ = 90	5474	4.09	14.0/21.6	17.0/34.8
26	$Mn(HCO_2)_2$[16]	a = 11.72; b = 10.25; c = 15.16	α = γ = 90; β = 92	181	0.31	-	6.0

27	mesoMOF-1[17]	a = b = c = 49.62	α = β = γ = 90	5436	3.56	10.0/22.5	14.8/38.5
28	DUT-5[18]	a = 22.69; b = 6.60; c = 19.24	α = β = γ = 90	2383	1.07	-	11.1
29	MOF-525[19]	a = b = c = 19.39	α = β = γ = 90	2748	1.03	6.5	20.0
30	$Zn(bdc)(ted)_{0.5}$[20]	a = b = 10.93; c = 9.61	α = β = γ = 90	2141	0.82	-	7.3
31	CYCU-3[21]	a = 34.07; b = 60.07; c = 6.31	α = β = γ = 90	2804	1.74	-	14.4/28.3
32	Cu-BTC[22]	a = b = c = 26.34	α = β = γ = 90	2006	0.82	3.5	5.0/9.0
33	Niperp-F_4[d]	a = b = c = 37.41	α = β = γ = 90	3326	1.69	9.2	30.0
34	Niperp-$(OH)_4$[d]	a = b = c = 37.41	α = β = γ = 90	3296	1.70	9.2	30.0
35	Niperp-$(NH_2)_4$[d]	a = b = c = 37.41	α = β = γ = 90	3264	1.70	9.2	30.0
36	Niperp-Br_4[d]	a = b = c = 37.41	α = β = γ = 90	2273	1.18	9.2	30.0

[a] Obtained from the crystallographic data in the literature.[1-22]

[b] Calculated with the Materials Studio package.[23]

[c] Obtained from the literature or measured in this work if the data are unavailable for some structures.

[d] Novel MOFs designed in this work.

The accessible surface area (S_{acc}) and the total free volume (V_{free}) of each MOF material were estimated using the "Atoms Volume & Surfaces" calculation within the Materials Studio package.[23] The accessible surface area (S_{acc}) was calculated by a probe molecule with diameter equal to the kinetic diameter of N_2 (3.68 Å). In most cases, the BET surface area of a MOF is derived from experimental N_2 adsorption at 77 K, which is further used to compare the adsorption performance of different materials. Thus, as indicated by others,[24a,b] this makes a nitrogen-sized (3.68 Å) probe particle for the accessible surface area calculations consistent with the findings.

The free volume (V_{free}) reported in Table S1 for each MOF is its total free volume that is not occupied by framework atoms. This quantity was calculated according to the numerical Monte Carlo method of Frost et al.[24c] in which a probe size of 0.0 Å was used. Thus, the free volume determined by such a method is purely based on the geometric feature of a material. It should be noted that V_{free} is different from the pore volume (V_g) of an adsorbent that can be computationally obtained using the helium-based thermodynamic

method proposed by Myers and Monson.[24d] Indeed, the above calculation methods with inconsistent sizes of probe particles have also been successfully used by others and us to explore the structure-property relationships of MOFs for the adsorption of different gases.[24c,e,f]

2. Crystalline structure of the MIL-68(Al)

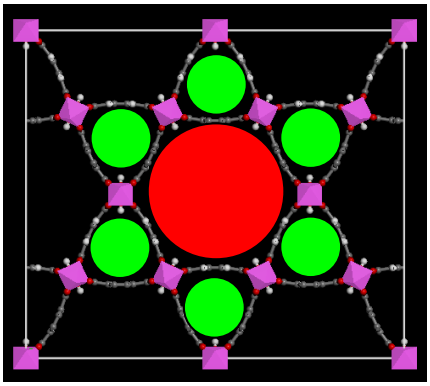

Fig. S1 View of the crystalline structure of MIL-68(Al) along the *c*-axis direction: green and red circles denote the triangular and hexagonal channel-like pores (Al, pink polyhedra; O, red; C, gray; H, white). The two types of channels have a diameter of ~6.0 and 16.0 Å, respectively. In our simulations, the triangular channels were artificially blocked due to their inaccessibility indicated both experimentally and computationally.[4]

3. Force fields

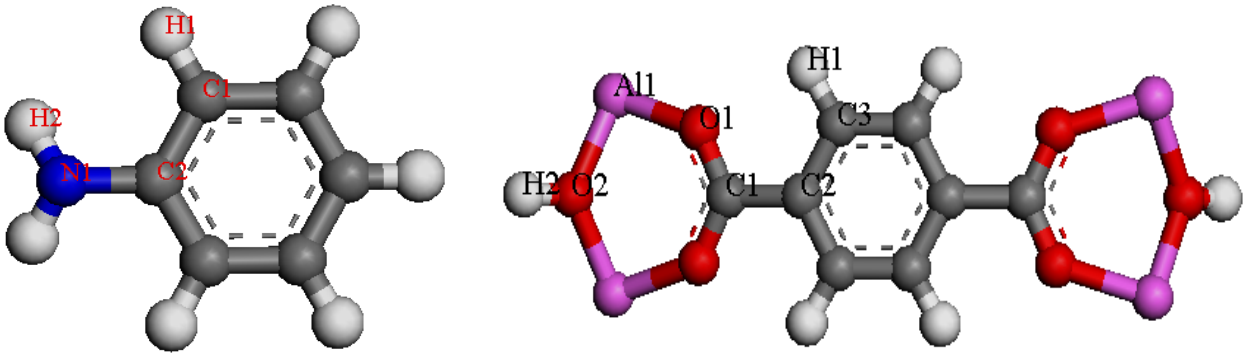

Fig. S2 Labels of the atomic types for aniline molecule (left) and MIL-68(Al) (right).

Table S2 LJ potential parameters and partial charges for the adsorbates

Atomic types	ε/k_B (K)	σ (Å)	q (e)
H_2O_O	76.47	3.151	-0.834
H_2O_H	0.000	0.000	0.417
C_6NH_7_C1	35.25	3.550	-0.115
C_6NH_7_C2	35.25	3.550	0.100
C_6NH_7_H1	15.11	2.420	0.115
C_6NH_7_N1	85.60	3.250	-0.900
C_6NH_7_H2	0.000	0.000	0.400

Table S3 LJ potential parameters and partial charges for MIL-68(Al)

Atomic types	OPLS-AA		UFF		DREIDING		q (e)
	ε/k_B (K)	σ (Å)	ε/k_B (K)	σ (Å)	ε/k_B (K)	σ (Å)	
Al1[a]	0.000	0.000	0.000	0.000	0.000	0.000	1.775
O1	105.7	2.960	30.20	3.118	48.16	3.033	-0.609
O2	30.20	3.118	30.20	3.118	48.16	3.033	-1.006
C1	52.84	3.750	52.84	3.431	47.86	3.479	0.667
C2	35.25	3.550	52.84	3.431	47.86	3.479	0.036
C3	35.25	3.550	52.84	3.431	47.86	3.479	-0.149
H1	15.11	2.420	22.14	2.571	7.649	2.846	0.106
H2[a]	0.000	0.000	0.000	0.000	0.000	0.000	0.433

[a] The LJ potentials of Al and H atoms in the hydroxyl groups are not considered, as explained in the literature.[4]

Table S4 The OPLS-AA potential parameters for MOFs studied in this work

Atoms	$H_{Benzene}$	H_{OH}[a]	H_{NH}[a]	$C_{carboxyl}$	$C_{Benzene}$	C_{alkyl}	N
ε/k_B (K)	15.11	0.000	0.000	52.84	35.25	33.18	85.60
σ (Å)	2.420	0.000	0.000	3.750	3.550	3.500	3.250
Atoms	**$O_{OH,linker}$**	**$O_{carboxyl}$**	**$O_{inorganic}$[b]**	**F**	**Cl**	**Br**	**V[a]**
ε/k_B (K)	85.60	105.7	30.20	30.67	150.8	236.3	0.000
σ (Å)	3.070	2.960	3.118	2.940	3.400	3.470	0.000
Atoms	**Co[b]**	**Ni[b]**	**Cu[b]**	**Zn[b]**	**Zr[b]**	**Mn[b]**	
ε/k_B (K)	7.045	7.548	2.518	62.40	34.72	6.542	
σ (Å)	2.560	2.525	3.114	2.460	2.780	2.638	

[a] The LJ potential parameters of V atom and H atoms in the hydroxyl and amino groups are not considered.[4,25]

[b] Taken from the UFF[26] as they are missed in the OPLS-AA force field.

4. Characterizations of MIL-68(Al)

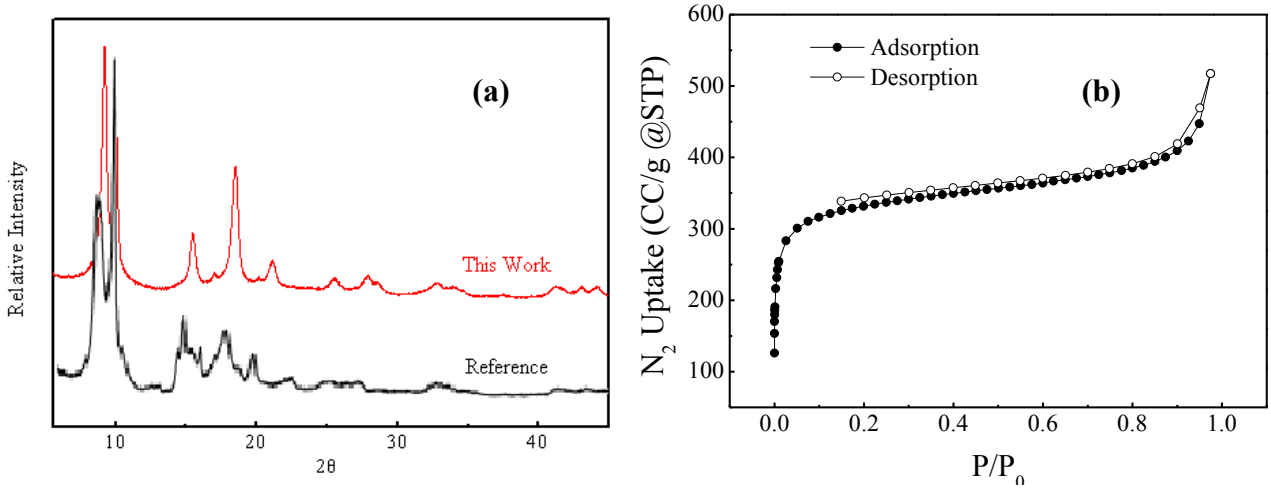

Fig. S3 (a) the powder XRD pattern of MIL-68(Al) compared with that in reference.[4] (b) Adsorption and desorption isotherms of nitrogen in MIL-68(Al) at 77 K.

5. Comparison of the experimental and simulated adsorption isotherms of aniline in MIL-68(Al)

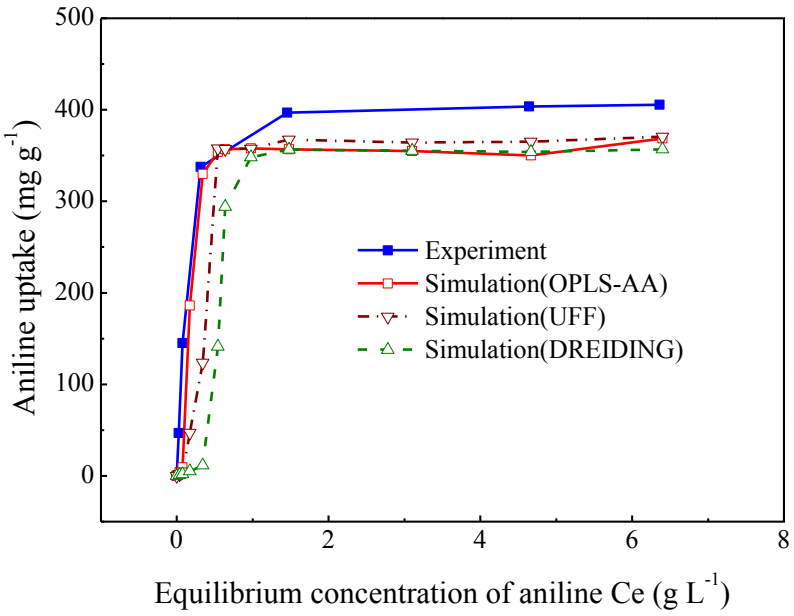

Fig. S4 Comparison of the experimental and simulated adsorption isotherms of aniline at 298 K in MIL-68(Al) using different force fields, as a function of the equilibrium concentration of aniline in the aqueous solution.

6. Relationships between the aniline uptake and S_{acc} as well as Q_{st}^0

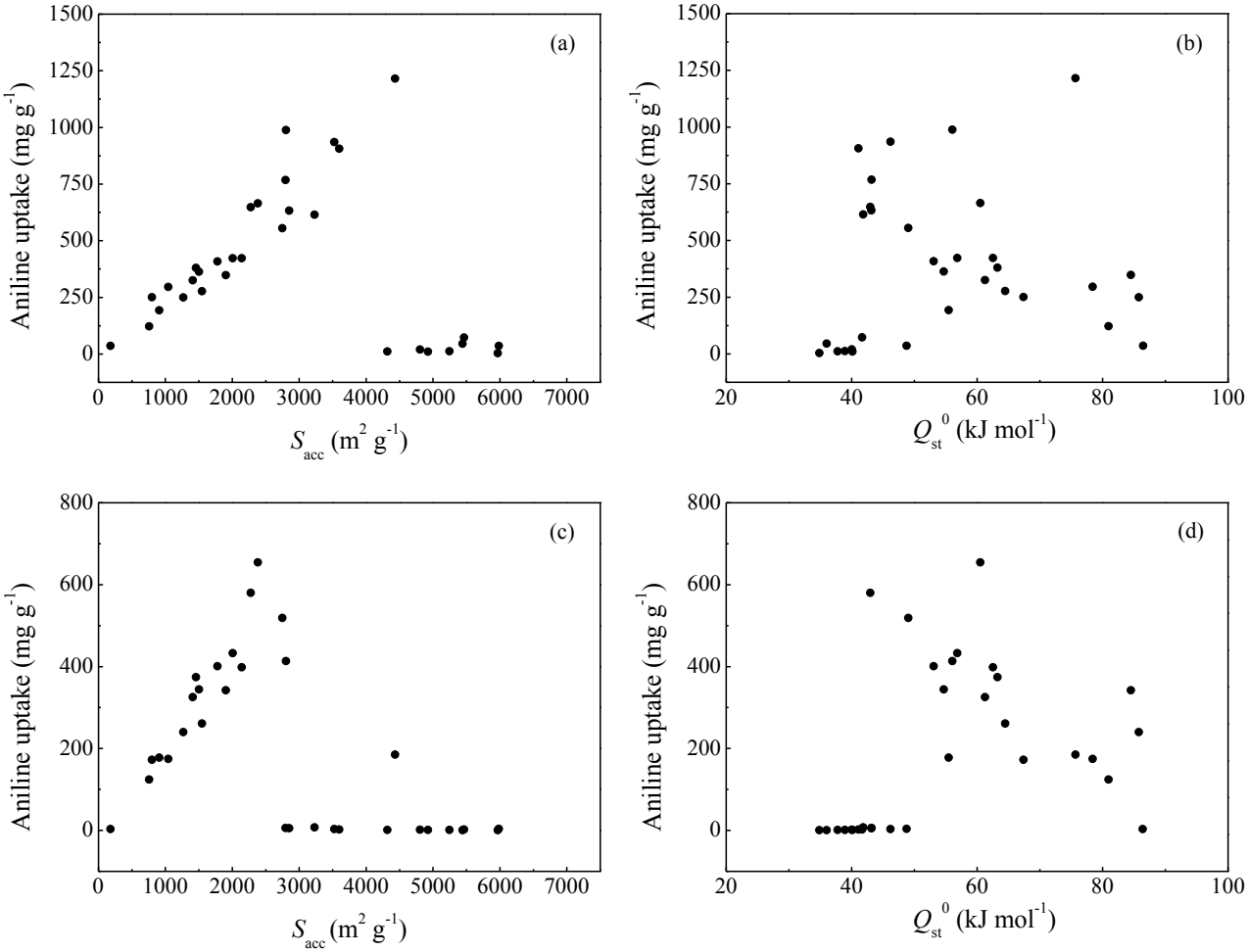

Fig. S5 The correlations between the aniline uptake and S_{acc} as well as Q_{st}^0 at 10.0 g L^{-1} (a, b) and 1.0 g L^{-1} (c, d).

7. Adsorption properties of some selected MOFs

Table S5 Properties of CUK-1, $Mn(HCO_2)_2$, Ni(bpb) and Al-PMOF for aniline recovery

Materials	Q_{st}^0(aniline) (kJ mol^{-1})	Q_{st}^0(water) (kJ mol^{-1})	V_{free} (cm^3 g^{-1})	Q_{st}^0(aniline)/V_{free}	Aniline uptake[a] (mg g^{-1})	Water uptake[a] (mg g^{-1})
CUK-1	80.9	27.8	0.36	225	124.19	90.61
$Mn(HCO_2)_2$	86.5	28.5	0.31	279	2.97	141.47
Ni(bpb)	53.1	13.5	0.75	71	400.81	47.55
Al-PMOF	64.5	47.9	0.75	86	260.87	245.13

[a] The uptake of aniline and water were taken from the simulation at the aniline concentration of 1.0 g L^{-1}.

8. Summary of the aniline uptakes in different conventional materials reported in the literature.

Table S6 Aniline uptakes in some conventional adsorbents from aqueous solutions

Materials	Aniline uptake ($mg\ g^{-1}$)	Ref.	Materials	Aniline uptake ($mg\ g^{-1}$)	Ref.
Activated carbons	420	27	Resin	325	36
	263	28		272	37
	260	29	Dual-cation organobentonite	174	38
	204	30	Modified lignin	127	39
	177	31	Cu-beta zeolite	120	40
	175	32	PAM/SiO_2	52	41
	125	33	Fe_3O_4/graphene	202	42
Carbon fibers	271	34	Multi-walled carbon nanotubes	100	43
MCM-41	14	35		46	44

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