Electronic Supplementary Material (ESI) for Chemical Communications.

Enantioselective Adsorption of Ibuprofen and Lysine in Metal-Organic Frameworks

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Simulation details: Grand Canonical Monte Carlo simulations are performed for a minimum of 10^6 steps. The following moves were probed: translation, rotation, insertion, deletion, reinsertion and identity change. Lennard-Jones parameters and charges are given in Table S1 (MIL-47), S2 (MIL-53), S3 (HMOF-1) and S4 and S5 (ibuprofen and lysine) and the corresponding atom identification are given in Figures S1-S3. Lorentz-Berthelot mixing rules are used to compute interactions between unlike species. Cutoff for van der Waals interactions are 12 Å (10 Å in HMOF-1) and Coulombic interactions were handled with Ewald sums. Simulation cells are 4x2x2 cell in MIL-47, 2x2x4 in MIL-53 and 1x1x1 in HMOF-1.

Table S1. Lennard-Jones parameters and charges defined for MIL-47.

MIL-47			
Atom	**ε/k_B [K]**	**σ [Å]**	**Charge (e-)**
V	8.05	2.8	1.68
Oa	48.19	3.03	-0.6
Ob	48.19	3.03	-0.52
Ca	47.86	3.47	-0.15
Cb	47.86	3.47	0.0
Cc	47.86	3.47	0.56
H	7.65	2.85	0.12

Figure S1. Atom labels in MIL-47 structure defined in the force field.

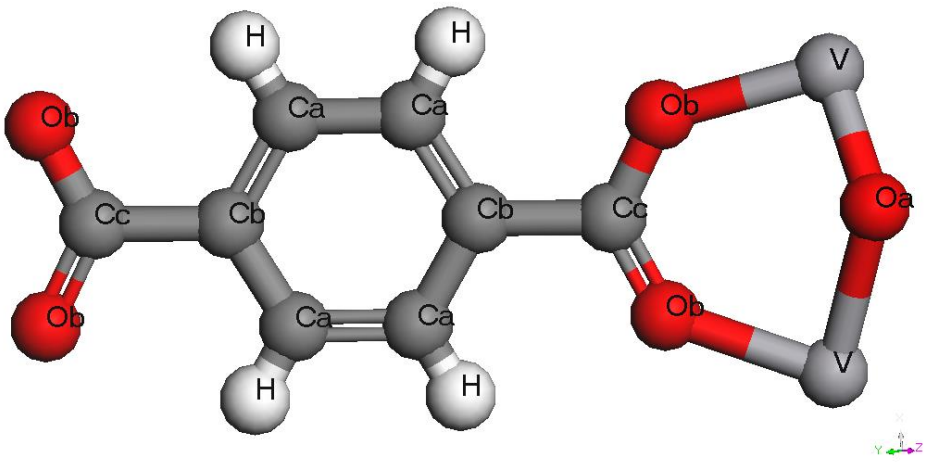

Table S2. Lennard-Jones parameters and charges defined for MIL-53.

MIL-53			
Atom	**ε /k_B [K]**	**σ [Å]**	**Charge (e-)**
Cr	7.54	2.69	1.96
Oa	48.19	3.03	-0.92
Ob	48.19	3.03	-0.7
Ca	47.86	3.47	-0.08
Cb	47.86	3.47	-0.04
Cc	47.86	3.47	0.65
Ha	7.65	2.85	0.13
Hb	7.65	2.85	0.34

Figure S2. Atom labels in MIL-53 structure defined in the force field.

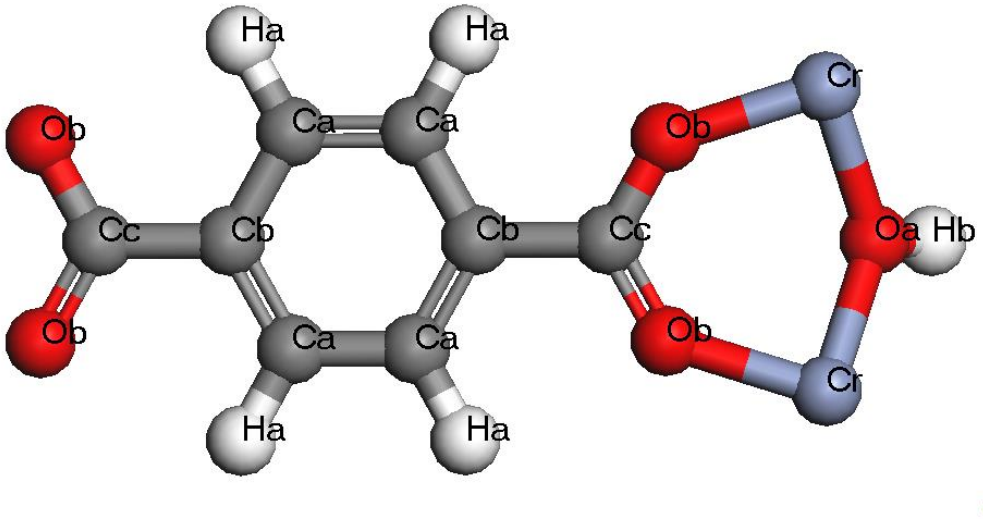

Table S3. Lennard-Jones parameters and **average charges** defined for HMOF-1

HMOF-1			
Atom	**ε /k_B [K]**	**σ [Å]**	**Charge (e-) av.**
Cd	114.74	2.848	0.94
Cl	114.233	3.947	-0.106
N_1	34.723	3.66	-0.434
N_2	34.723	3.66	0.9
O	30.194	3.5	-0.542
C_1	52.839	3.851	0.184
C_2	52.839	3.851	-0.214
C_3	52.839	3.851	0.0
H_1	22.142	2.886	0.157
H_2	22.142	2.886	0.404

Figure S3. Atom labels of chiral link (left) and metal clusters (right) in HMOF-1 structure defined in the force field.

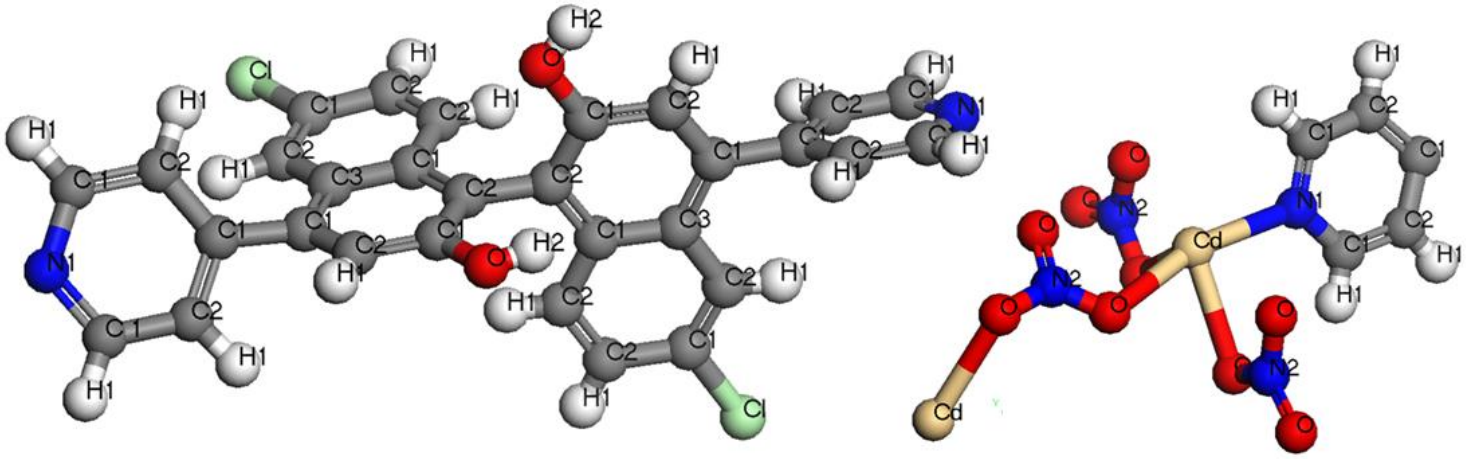

Table S4. Lennard-Jones parameters for the pseudoatoms of ibuprofen.

Ibuprofen			
Atom	**ε /k_B [K]**	**σ [Å]**	**Charge (e-)**
C1_ring (C)	74.501	3.617	-0.222
C2_ring (CH)	74.501	3.617	-0.042
C_CH1 (chiral)	19.632	3.875	-0.342
C_CH2_ib	19.632	3.875	-0.471
C_CH3_ib	19.632	3.875	-0.673
C_COOH	90.609	3.617	0.755
O_COOH	114.772	2.859	-0.618
H_CH	19.129	2.449	0.24
H_OH	zero	zero	0.543

Table S5. Lennard-Jones parameters for the pseudoatoms of lysine.

Lysine			
Atom	**ε /k_B [K]**	**σ [Å]**	**Charge (e-)**
C_chiral	19.632	3.875	-0.1
C_CH2	19.632	3.875	-0.1
N_NH2	84.062	3.501	-0.5
C_COOH	90.609	3.617	0.41
O_COOH	114.772	2.859	-0.38
H_CH	19.129	2.449	0.1
H_OH	zero	zero	0.35
H_NH2	zero	zero	0.15

Equation S1. Expression used for the calculation of the partial fugacities of each component (f_i) in a liquid mixture[1]. In this expression p_i^{sat} is the saturated vapor pressure of pure component *i*, φ_i^{sat} is the fugacity coefficient of pure component *i* in the gas phase at the saturated vapor pressure, γ_i is the activity coefficient in the liquid mixture and calculated from the experimental vapor-liquid equilibrium data and x_i is the mole fraction of component i in the mixture. V_i^{mol} is the molar volume of pure component *i* in the liquid phase and *p*, *R* and *T* are the pressure, the temperature and the gas constant, respectively.

$$f_i = \varphi_i^{sat} p_i^{sat} \gamma_i x_i exp\left[\frac{V_i^{mol}(p - p_i^{sat})}{RT}\right]$$

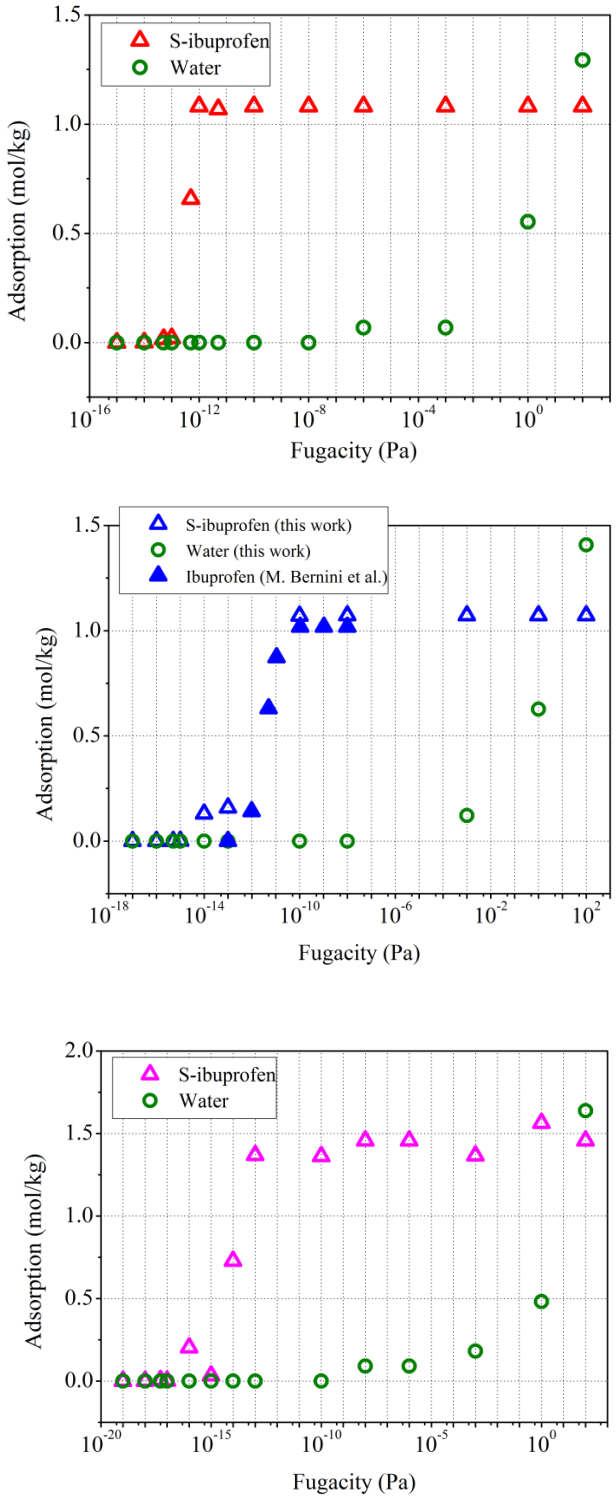

Figure S4. Adsorption isotherms for the mixtures ibuprofen-water in a molar fraction 0.01-0.99, at 300K in the three structures studied: MIL-47, MIL-53 and HMOF-1 (top to bottom). The adsorption data of S-ibuprofen as pure compound in MIL-53 at 310K (Bernini et al)[2] is plotted in blue solid symbols.

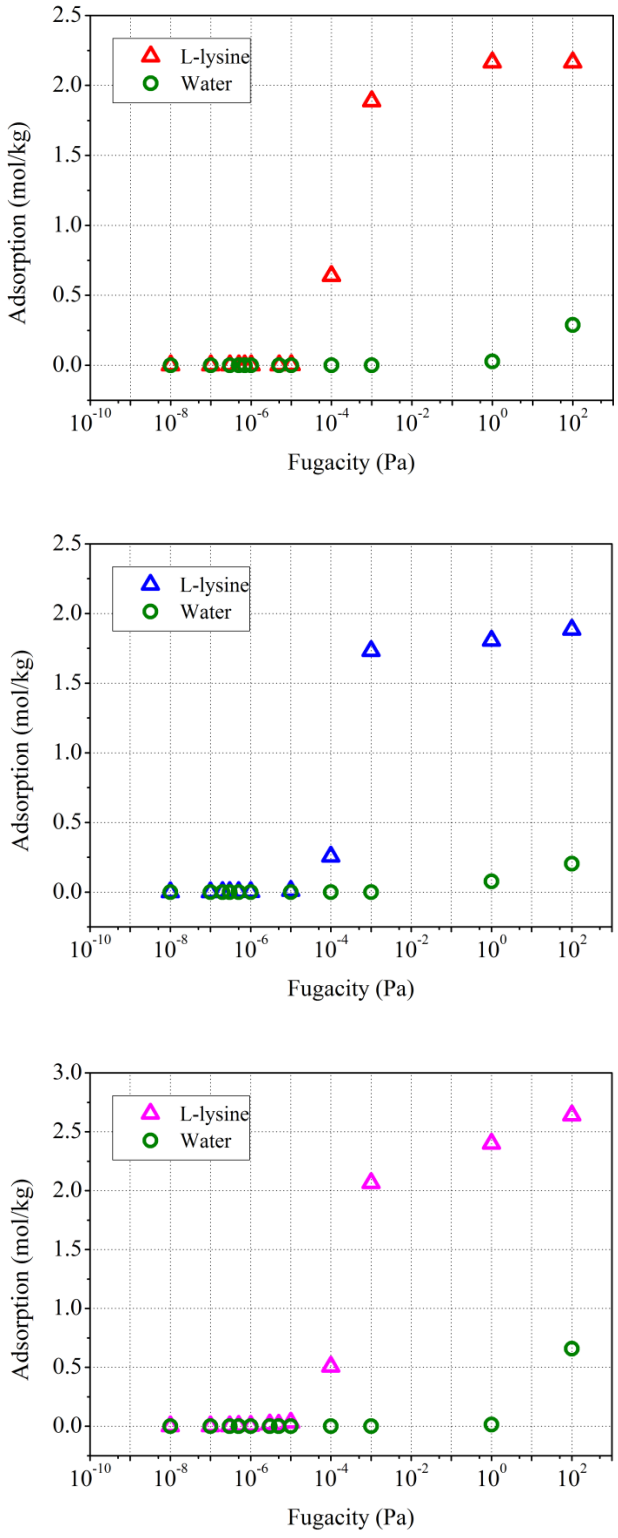

Figure S5. Adsorption isotherms for the mixtures lysine-water in a molar fraction 0.01-0.99, at 300K in the three structures studied: MIL-47, MIL-53 and HMOF-1 (top to bottom).

Simulation details: The molecular association in the system was computed using a geometric criterion of hydrogen bonding, which was applied to every pair of molecules in a considerable number of generated configurations. Specifically, two molecules were considered H-bonded if the following conditions were fulfilled: (1) the intermolecular distance between the oxygen atoms of the carboxyl group is less than 3.6 Å, (2) the distance between the oxygen of the acceptor molecule and the hydrogen of the donor is less than 2.4 Å, and (3) the angle between the O-O direction and the molecular O-H direction of the donor, where H is the hydrogen which forms the bond, is less than 30º. Although molecules were considered flexible, a fixed O-H intramolecular distance corresponding to the equilibrium value was assumed for the calculations involved in the angular condition.

Table S6. a) Fraction of associated molecules for R and S-ibuprofen (f_{ass}^{R} and f_{ass}^{S}, respectively), and fraction of bonds of each type (f_{RR}, f_{SS}, f_{RS}) as a function of the S-ibuprofen concentration in the reservoir (x_S^{res}) or adsorbed (x_S^{ads}) in the three structures. b) Fraction of associated molecules for D and L-lysine (f_{ass}^{D} and f_{ass}^{L}, respectively) and fraction of bonds of each type (f_{DD}, f_{LL}, f_{DL}) as a function of the L-lysine concentration in the reservoir (x_L^{res}) or adsorbed (x_L^{ads}) in the three structures.

a)

HMOF-1							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.35	0.53	0.59	0.65	0.71	1
f_{ass}^{R}	0.21	0.46	0.26	0.34	0.65	0.34	
f_{ass}^{S}		0.33	0.07	0.31	0.18	0.45	0.39
f_{RR}	1.00	0.71	0.51	0.25	0.31	0.00	
f_{SS}		0.28	0.00	0.35	0.01	0.51	1.00
f_{RS}		0.00	0.49	0.40	0.69	0.49	
MIL-47							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.31	0.44	0.50	0.56	0.69	1
f_{ass}^{R}	0.39	0.43	0.73	0.40	0.55	0.35	
f_{ass}^{S}		0.64	0.66	0.40	0.55	0.49	0.73
f_{RR}	1.00	0.20	0.18	0.02	0.00	0.04	
f_{SS}		0.00	0.00	0.03	0.13	0.56	1.00
f_{RS}		0.80	0.82	0.95	0.87	0.39	
MIL-53							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.38	0.50	0.50	0.50	0.63	1
f_{ass}^{R}	0.48	0.79	0.16	0.43	0.48	0.61	
f_{ass}^{S}		0.84	0.35	0.41	0.47	0.49	0.47
f_{RR}	1.00	0.38	0.05	0.03	0.25	0.23	
f_{SS}		0.15	0.44	0.00	0.24	0.38	1.00
f_{RS}		0.47	0.52	0.97	0.50	0.40	

b)

HMOF-1							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.38	0.50	0.53	0.56	0.63	1
f_{as}^{D}	0.53	0.33	0.39	0.32	0.15	0.22	
f_{ass}^{L}		0.33	0.22	0.21	0.22	0.35	0.35
f_{DD}	1.00	0.31	0.29	0.34	0.25	0.06	
f_{LL}		0.09	0.02	0.08	0.50	0.55	1.00
f_{DL}		0.60	0.69	0.58	0.25	0.39	
MIL-47							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.24	0.39	0.48	0.61	0.79	1
f_{as}^{D}	0.28	0.33	0.25	0.26	0.17	0.24	
f_{ass}^{L}		0.09	0.39	0.42	0.36	0.28	0.29
f_{DD}	1.00	0.87	0.24	0.14	0.08	0.00	
f_{LL}		0.00	0.25	0.33	0.60	0.63	1.00
f_{DL}		0.13	0.51	0.53	0.32	0.37	
MIL-53							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.22	0.41	0.50	0.59	0.78	1
f_{as}^{D}	0.28	0.35	0.38	0.52	0.26	0.29	
f_{ass}^{L}		0.38	0.16	0.35	0.25	0.34	0.36
f_{DD}	1.00	0.58	0.60	0.40	0.15	0.00	
f_{LL}		0.05	0.03	0.13	0.34	0.64	1.00
f_{DL}		0.36	0.38	0.47	0.51	0.36	

Table S7. a) Average intermolecular minimum distances d_{min} between oxygen atoms of the carboxyl group for ibuprofen as a function of the S-ibuprofen concentration in the reservoir (x_S^{res}) or adsorbed (x_S^{ads}) in the three structures. b) Average intermolecular minimum distances d_{min} between oxygen atoms of the carboxyl group for lysine as a function of the L-lysine concentration in the reservoir (x_L^{res}) or adsorbed (x_L^{ads}) in the three structures. The subscripts 1 and 2 denote the oxygen atom double bonded to the carbon atom and the oxygen atom of the hydroxyl group, respectively; the type of enantiomer is indicated through a superscript.

a)

HMOF-1							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.35	0.53	0.59	0.65	0.71	1
d_{min}**[Å]**							
O_1^R-O_2^R	2.34	2.49	3.12	3.20	2.59	3.31	
O_2^R-O_2^R	2.57	3.88	3.51	3.23	4.05	5.55	
O_1^S-O_2^S		2.61	5.93	2.55	2.94	2.40	2.43
O_2^S-O_2^S		4.88	5.87	4.30	2.96	3.75	3.52
O_1^R-O_2^S		2.38	2.39	2.44	2.41	2.58	
O_2^R-O_1^S		3.32	2.37	4.74	2.53	2.51	
O_2^R-O_2^S		3.35	4.18	3.16	3.59	3.75	
MIL-47							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.31	0.44	0.50	0.56	0.69	1
d_{min}**[Å]**							
O_1^R-O_2^R	2.34	2.45	2.46	2.80	9.17	2.61	
O_2^R-O_2^R	2.64	4.19	4.41	3.57	9.77	4.53	
O_1^S-O_2^S		8.48	6.34	2.43	2.45	2.38	2.42
O_2^S-O_2^S		9.28	6.95	3.32	4.40	3.79	2.51
O_1^R-O_2^S		3.05	2.39	2.39	2.53	2.46	
O_2^R-O_1^S		2.39	2.44	2.33	2.41	2.78	
O_2^R-O_2^S		3.40	3.50	2.73	4.40	2.89	
MIL-53							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.38	0.50	0.50	0.50	0.63	1
d_{min}**[Å]**							
O_1^R-O_2^R	2.42	2.49	2.39	2.47	2.53	2.49	
O_2^R-O_2^R	3.24	3.91	3.64	4.38	3.23	4.52	
O_1^S-O_2^S		2.47	2.47	8.73	2.56	2.54	2.48
O_2^S-O_2^S		4.22	2.89	9.24	3.63	2.69	2.55
O_1^R-O_2^S		2.47	2.51	2.47	2.53	2.36	
O_2^R-O_1^S		2.45	2.75	2.47	2.52	2.49	
O_2^R-O_2^S		3.49	3.67	3.17	3.51	3.50	

b)

HMOF-1							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.38	0.50	0.53	0.56	0.63	1
d_{min}**[Å]**							
O_1^D-O_2^D	2.57	2.56	2.64	2.65	2.60	3.06	
O_2^D-O_2^D	2.74	2.85	3.00	3.24	3.12	3.46	
O_1^L-O_2^L		2.56	2.72	2.75	2.62	2.53	2.53
O_2^L-O_2^L		4.33	3.04	2.98	3.63	3.56	2.84
O_1^D-O_2^L		2.61	2.70	2.59	2.62	2.63	
O_2^D-O_1^L		2.57	2.58	2.56	2.99	2.87	
O_2^D-O_2^L		3.44	3.01	2.76	2.85	3.86	
MIL-47							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.24	0.39	0.48	0.61	0.79	1
d_{min}**[Å]**							
O_1^D-O_2^D	2.56	2.59	2.70	2.74	3.54	8.17	
O_2^D-O_2^D	3.37	3.90	2.91	3.82	4.65	7.86	
O_1^L-O_2^L		3.30	2.65	2.66	2.62	2.60	2.57
O_2^L-O_2^L		5.05	4.13	4.44	3.75	3.31	3.30
O_1^D-O_2^L		2.59	2.63	2.57	2.62	2.59	
O_2^D-O_1^L		2.77	2.94	2.62	3.12	2.89	
O_2^D-O_2^L		3.73	3.80	3.68	3.85	3.70	
MIL-53							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.22	0.41	0.50	0.59	0.78	1
d_{min}**[Å]**							
O_1^D-O_2^D	2.54	2.58	2.63	2.68	2.97	7.13	
O_2^D-O_2^D	3.36	4.14	2.92	2.90	3.26	7.29	
O_1^L-O_2^L		3.19	2.60	2.75	2.63	2.53	2.50
O_2^L-O_2^L		3.21	3.96	4.08	3.33	3.56	4.05
O_1^D-O_2^L		2.68	2.65	2.62	2.61	2.79	
O_2^D-O_1^L		2.69	2.85	2.57	2.59	2.58	
O_2^D-O_2^L		3.40	4.11	3.00	3.51	3.57	

Table S8. a) Average minimum distances d_{min} from the oxygen atoms of the carboxyl group to the host metal centers for ibuprofen as a function of the S-ibuprofen concentration in the reservoir (x_S^{res}) or adsorbed (x_S^{ads}) in the three structures. b) Average minimum distances d_{min} from the oxygen atoms of the carboxyl group to the host metal centers for lysine as a function of the L-lysine concentration in the reservoir (x_L^{res}) or adsorbed (x_L^{ads}) in the three structures. The subscripts 1 and 2 denote the oxygen atom double bonded to the carbon atom and the oxygen atom of the hydroxyl group, respectively; the type of enantiomer is indicated through a superscript.

a)

HMOF-1							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.35	0.53	0.59	0.65	0.71	1
d_{min}**[Å]**							
O_1^R-Cd	5.44	5.88	6.80	5.92	7.44	6.43	
O_2^R-Cd	5.09	4.90	4.87	5.29	6.32	5.56	
O_1^S-Cd		5.37	5.72	5.57	5.62	5.91	5.11
O_2^S-Cd		6.74	5.10	5.24	5.39	5.03	5.10
MIL-47							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.31	0.44	0.50	0.56	0.69	1
d_{min}**[Å]**							
O_1^R-V	3.91	4.26	4.14	4.32	4.03	4.21	
O_2^R-V	4.14	3.78	4.48	4.29	4.53	4.86	
O_1^S-V		3.89	4.22	3.83	4.40	4.59	3.61
O_2^S-V		3.89	4.33	4.20	4.47	3.92	4.44
MIL-53							
x_S^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_S^{ads}	0	0.38	0.50	0.50	0.50	0.63	1
d_{min}**[Å]**							
O_1^R-Cr	4.42	4.39	4.50	4.64	4.66	5.04	
O_2^R-Cr	4.14	4.42	4.24	4.01	4.84	4.79	
O_1^S-Cr		4.86	4.36	4.76	4.20	4.52	4.36
O_2^S-Cr		4.60	4.76	4.59	4.40	4.21	4.19

b)

HMOF-1							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.38	0.50	0.53	0.56	0.63	1
d_{min}**[Å]**							
O_1^D-Cd	5.49	5.58	5.80	5.88	5.61	5.71	
O_2^D-Cd	4.90	5.18	4.86	4.37	5.36	5.06	
O_1^L-Cd		6.34	5.58	5.07	5.62	5.19	5.39
O_2^L-Cd		5.10	5.03	4.89	5.05	4.93	4.93
MIL-47							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.24	0.39	0.48	0.61	0.79	1
d_{min}**[Å]**							
O_1^D-V	3.71	3.90	3.81	3.85	4.09	4.31	
O_2^D-V	3.87	3.54	3.58	3.75	3.81	3.77	
O_1^L-V		3.77	4.11	3.94	3.74	3.90	3.57
O_2^L-V		3.89	4.04	3.47	3.92	3.76	3.66
MIL-53							
x_L^{res}	0	0.2	0.4	0.5	0.6	0.8	1
x_L^{ads}	0	0.22	0.41	0.50	0.59	0.78	1
d_{min}**[Å]**							
O_1^D-Cr	4.52	4.64	4.62	4.68	4.50	4.97	
O_2^D-Cr	4.12	4.19	4.44	4.30	4.31	4.53	
O_1^L-Cr		4.69	4.19	4.40	4.53	4.33	4.47
O_2^L-Cr		4.47	4.53	4.11	4.39	4.49	4.28

As seen in Table S7, O1-O2 distances are consistently shorter than corresponding O2-O2 distances. This proves the claim made in the main text that the double bonded oxygen in the carboxyl group is more likely to form H-Bonds than the single bonded oxygen.

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