Electronic Supplementary Information (ESI)

Unveiling the Impact of Enhanced Hydrophobicity in ZIF-71 on Butanol Purification: Insights from Experimental and Molecular Simulations

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The cell parameters were refined using the Le Bail pattern fitting method. Initial refinement parameters were based on those from ZIF-71.[1] Peak profiles were calculated within ten times the full width at half maximum (FWHM) and pseudo-Voigt peak shape functions. A third-order polynomial fitting modelled the background.

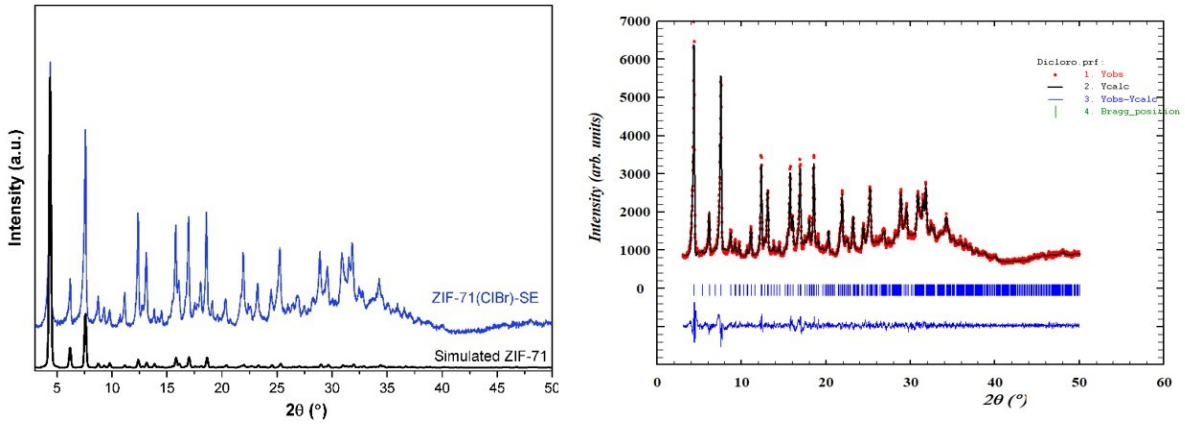

Fig. S1 XRD patterns of ZIF-71(ClBr)-SE and comparation to simulated ZIF-71 (left), profile refinement plots from 2θ = 3 to 50° for ZIF-71(ClBr)-SE (right). Experimental, calculated and difference profiles, and allowed Bragg peaks are shown.

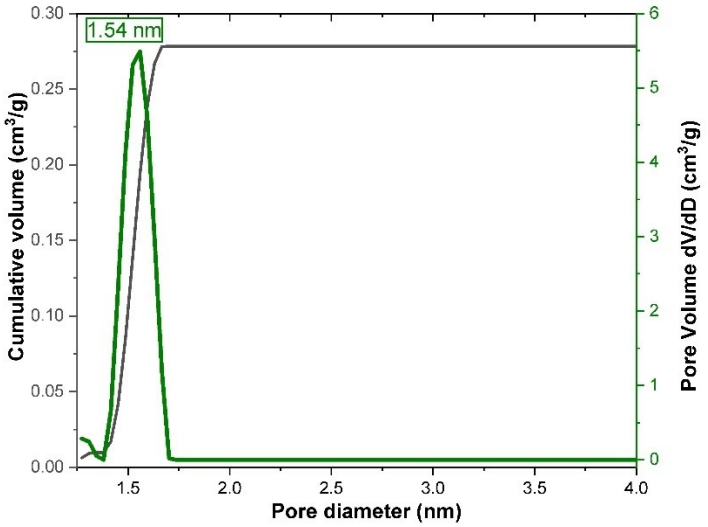

Fig. S2 DFT pore distribution of ZIF-71(ClBr)-SE.

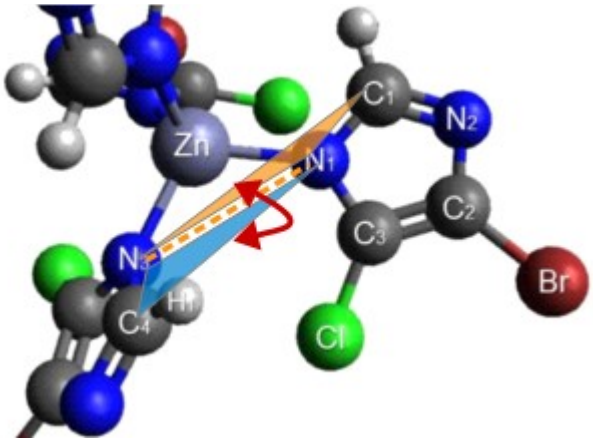

Fig. S3 The dihedral angle among C1-N1-N3-C4 atoms can be described as the angle between two planes, the first plane defined by C1-N1-N3 group of atoms and the second one by N1-N3-C4.

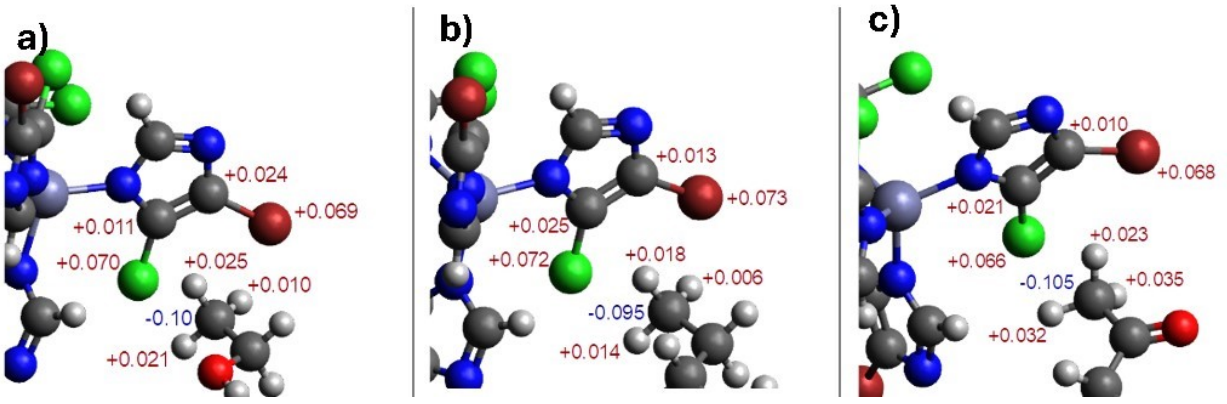

Fig. S4 Partial charges of the system a) ZIF-71(ClBr)-SE – ethanol, b) ZIF-71(ClBr)-SE – butanol and, c) ZIF-71(ClBr)-SE – acetone.

Table S1. Total energy and geometrical parameters for optimized structures of ZIF-71 and ZIF-71(ClBr)-SE.

MOF	Energy (eV)	Optimized Geometries									
		Distances (Å)						Angles (°)			
		$Zn\text{-}N_1$	$C_2\text{-}Br$	$C_3\text{-}Cl$	$C_2\text{-}C_3$	$C_3\text{-}N_1$	$C_2\text{-}N_2$	$N_3\text{-}Zn\text{-}N_3$	$C_1\text{-}N_1(Zn)\text{-}C_3$	$N_1\text{-}C_3\text{-}Cl$	Dihedral
ZIF-71	-9450.6	2.03	NA	1.71	1.43	1.36	1.35	110.0	104.4	124.3	114.0
ZIF-71(ClBr)-SE	-9220.1	2.02	1.86	1.71	1.43	1.36	1.35	109.4	103.4	124.0	117.0

Table S2. Energies of interaction and geometrical parameters for optimized structures of alcohol-ZIF systems.

MOF	Alcohol	Orientation toward MOF	Interaction Energy Kcal/mol	Optimized Geometries								
				Intermolecular distances (Å)								Angle (°)
				$^{Alcohol}C\text{-}C_3(Cl)$	$^{Alcohol}C\text{-}C_2(Cl\ or\ Br)$	$^{Alcohol}C\text{-}Cl\ C_3(Cl)$	$(^{Alcohol}C)H\text{-}Cl\ C_3(Cl)$	$(^{Alcohol}C)H\text{-}Cl\ C_2(Cl\ o\ Br)$	$O\text{-}C_2$	$(OH)H\text{-}N_2$	$H_1\text{-}C_{alcohol}$	Change in dihedral
ZIF -71	**BuOH**	Alkyl	-4.4	3.66	3.89	3.52	3.13	2.93	-	-	3.24	-18.9
		Hydroxy	-15.1	3.85	3.68	-	3.30	3.00	3.12	2.56	2.10	-43.7
ZIF -71 (ClBr)-SE		Alkyl	-5.4	3.62	3.85	3.56	3.07	3.05	-	-	3.51	-11.5
		Hydroxy	-13.3	3.78	3.74	-	3.17	3.20	3.21	2.70	2.08	-46.0
ZIF -71	**EtOH**	Alkyl	-4.0	3.66	3.90	3.51	3.10	2.95	-	-	3.26	-17.5
		Hydroxy	-13.8	3.83	3.66	-	3.29	2.98	3.12	2.54	2.11	-43.6
ZIF -71 (ClBr)-SE		Alkyl	-4.3	3.64	3.86	3.58	3.14	3.04	-	-	3.52	-11.8
		Hydroxy	-13.2	3.77	3.72	-	3.17	3.17	3.31	2.68	2.09	-46.1

Table S3. Intramolecular geometrical parameters of ZIFs for optimized structures of alcohol-ZIF systems.

MOF	Solute	Orientation toward MOF	Interaction Energy Kcal/mol	Change in dihedral angle
ZIF -71	**Butanol**	Alkyl	-4.4	-18.9
		Hydroxy	-15.1	-43.7
ZIF -71 (ClBr)-SE		Alkyl	-5.4	-11.5
		Hydroxy	-13.3	-46.0
ZIF -71	**Ethanol**	Alkyl	-4.0	-17.5
		Hydroxy	-13.8	-43.6
ZIF -71 (ClBr)-SE		Alkyl	-4.3	-11.8
		Hydroxy	-13.2	-46.1

Table S4. Hirshfeld Atomic charges of the system ZIF-71 and ZIF-71(ClBr)-SE with butanol, ethanol and acetone.

		Butanol					
		Alkyl			Hydroxy		
		Species	ZIF-71(ClBr)-SE	ZIF-71	Species	ZIF-71(ClBr)-SE	ZIF-71
	Atom #		Charge			Charge	
MOF	1	Zn	0.403	0.404	Zn	0.4	0.400
	2	C	0.017	0.017	C	0.023	0.023
	3	C	0.005	0.022	C	0.01	0.026
	4	C	0.033	0.035	C	0.04	0.040
	5	C	0.037	0.038	C	0.036	0.037
	6	C	0.008	0.024	C	0.008	0.024
	7	C	0.019	0.020	C	0.021	0.021
	8	C	0.037	0.039	C	0.041	0.040
	9	C	0.007	0.023	C	0.007	0.022
	10	C	0.018	0.018	C	0.018	0.018
	11	**C2**	0.013	0.027	**C2**	0.004	0.022
	12	**C3**	0.025	0.023	**C3**	0.014	0.015
	13	C	0.036	0.037	C	0.034	0.036
	14	H	0.045	0.046	H	0.022	0.021
	15	H	0.049	0.049	H	0.045	0.045
	16	H	0.045	0.045	H	0.046	0.046
	17	H	0.026	0.026	H	0.033	0.035
	18	N	-0.132	-0.132	N	-0.128	-0.128
	19	N	-0.179	-0.179	N	-0.172	-0.170
	20	N	-0.177	-0.177	N	-0.177	-0.177
	21	N2	-0.133	-0.133	N	-0.131	-0.131
	22	N	-0.178	-0.177	N	-0.177	-0.178
	23	N	-0.132	-0.132	N	-0.131	-0.131
	24	**N1**	-0.176	-0.176	**N1**	-0.18	-0.179
	25	**N2**	-0.13	-0.132	**N2**	-0.13	-0.129
	*26	Br	0.052	0.035	Br	0.057	0.038
	27	Cl	0.046	0.050	Cl	0.049	0.050
	*28	Br	0.057	0.038	Br	0.057	0.038
	29	Cl	0.049	0.050	Cl	0.045	0.050
	*30	Br	0.055	0.037	Br	0.055	0.037
	31	Cl	0.058	0.061	Cl	0.055	0.061
	*32	**Br**	0.073	0.047	**Br**	0.055	0.047
	33	**Cl**	0.072	0.075	**Cl**	0.056	0.075
Butanol	34	C	-0.044	-0.038	**O**	-0.151	-0.144
	35	**H**	0.018	0.020	**C**	-0.049	-0.048
	36	**$C_{(methyl)}$**	-0.095	-0.094	**$H_{(OH)}$**	0.106	0.106
	37	**H**	0.006	0.003	**$C_{(C-O)}$**	0.012	0.014
	38	**H**	0.014	0.020	**H**	-0.003	0.002
	39	H	0.019	0.025	**H**	0.019	0.020
	40	C	-0.053	-0.053	H	0.022	0.021
	41	H	0.024	0.024	H	0.026	0.028
	42	H	0.02	0.025	C	-0.037	-0.043
	43	H	0.027	0.020	H	0.024	0.019
	44	C	0.015	0.013	C	-0.085	-0.087
	45	O	-0.177	-0.185	H	0.023	0.021
	46	H	0.02	0.015	H	0.031	0.029
	47	H	0.029	0.029	H	0.027	0.027
	48	H	0.127	0.125	H	0.028	0.025
		MOF Charge	0.048	0.048		0.007	0.008
		Butanol Charge	-0.048	-0.048		-0.007	-0.008

* In this case for ZIF-71 correspond to a Cl atom.

		Etanol					
		Alkyl			Hydroxy		
		Species	ZIF-71(ClBr)-SE	ZIF-71	Species	ZIF-71(ClBr)-SE	ZIF-71
	Atom #		Charge			Charge	
MOF	1	**N1**	-0.13	-0.131	**N1**	-0.13	-0.129
	2	**C3**	0.024	0.025	**C3**	0.014	0.015
	3	**C2**	0.011	0.029	**C2**	0.004	0.022
	4	**N2**	-0.177	-0.174	**N2**	-0.18	-0.179
	5	C	0.036	0.039	C	0.034	0.036
	*6	**Br**	0.069	0.054	**Br**	0.055	0.04
	7	**Cl**	0.07	0.076	**Cl**	0.056	0.061
	8	Zn	0.404	0.404	Zn	0.401	0.4
	9	N	-0.131	-0.132	N	-0.131	-0.131
	10	C	0.04	0.04	C	0.041	0.04
	11	N	-0.176	-0.176	N	-0.177	-0.178
	12	C	0.008	0.024	C	0.007	0.022
	13	C	0.019	0.019	C	0.018	0.018
	*14	Br	0.057	0.038	Br	0.054	0.034
	15	Cl	0.059	0.061	Cl	0.055	0.055
	16	N	-0.132	-0.132	N	-0.128	-0.128
	17	C	0.017	0.016	C	0.023	0.023
	18	C	0.006	0.02	C	0.011	0.026
	19	N	-0.177	-0.179	N	-0.171	-0.169
	20	C	0.036	0.033	C	0.041	0.041
	21	Cl	0.046	0.046	Cl	0.048	0.048
	*22	Br	0.051	0.03	Br	0.059	0.038
	23	N	-0.133	-0.133	N	-0.131	-0.131
	24	C	0.036	0.037	C	0.035	0.036
	25	N	-0.178	-0.178	N	-0.178	-0.178
	26	C	0.007	0.023	C	0.008	0.024
	27	C	0.018	0.019	C	0.021	0.021
	*28	Br	0.054	0.035	Br	0.056	0.035
	29	Cl	0.047	0.048	Cl	0.044	0.046
	30	H	0.048	0.045	H	0.045	0.045
	31	H	0.046	0.049	H	0.046	0.046
	32	H	0.049	0.046	H	0.033	0.035
	33	H	0.026	0.027	H	0.023	0.022
Etanol	34	$\mathbf{C_{(methyl)}}$	-0.1	-0.101	**O**	-0.152	-0.151
	35	C	0.015	0.014	C	-0.092	-0.093
	36	O	-0.184	-0.181	$\mathbf{H_{(OH)}}$	0.105	0.104
	37	**H**	0.025	0.025	$\mathbf{C_{(C-O)}}$	0.015	0.015
	38	**H**	0.01	0.009	**H**	-0.001	0.022
	39	**H**	0.021	0.023	**H**	0.021	0
	40	H	0.018	0.018	H	0.035	0.035
	41	H	0.018	0.017	H	0.032	0.032
	42	H	0.128	0.129	H	0.028	0.027
		MOF Charge	0.049	0.047		0.008	0.008
		Ethanol Charge	-0.049	-0.047		-0.008	-0.008

* In this case for ZIF-71 correspond to a Cl atom.

		Acetone									
		Alkyl			Alkyl			Carbonyl			
		Species	ZIF-71(ClBr)-SE	ZIF-71	Species	ZIF-71(ClBr)-SE	ZIF-71	Species	ZIF-71(ClBr)-SE	ZIF-71
	Atom #		Charge			Charge			Charge	
MOF	1	C	0.017	0.017	C	0.021	0.021	C	0.019	0.019
	2	N	-0.132	-0.133	N	-0.132	-0.131	N	-0.132	-0.128
	3	C	0.005	0.031	C	0.037	0.042	C	0.034	0.043
	4	N	-0.18	-0.177	N	-0.177	-0.175	N	-0.18	-0.178
	5	C	0.03	0.025	C	0.009	0.026	C	0.006	0.022
	6	Zn	0.403	0.403	Zn	0.404	0.404	Zn	0.407	0.406
	7	N	-0.132	-0.132	N	-0.131	-0.132	N	-0.129	-0.128
	8	C	0.018	0.018	C	0.018	0.017	C	0.022	0.013
	9	C	0.007	0.02	C	0.006	0.021	C	0.009	0.019
	10	C	0.036	0.035	N	-0.179	-0.176	N	-0.179	-0.175
	11	N	-0.178	-0.18	C	0.032	0.034	C	0.039	0.038
	12	Cl	0.047	0.049	Cl	0.05	0.071	Cl	0.049	0.057
	*13	Br	0.053	0.034	Br	0.054	0.05	Br	0.053	0.035
	*14	Br	0.057	0.04	Br	0.059	0.04	Br	0.05	0.033
	15	Cl	0.059	0.053	Cl	0.049	0.062	Cl	0.042	0.058
	16	**N**	**-0.132**	**-0.132**	**N**	-0.132	-0.132	**N**	-0.127	-0.132
	17	**C**	**0.021**	**0.021**	C	0.016	0.02	C	0.014	0.02
	18	**C**	**0.01**	**0.026**	C	0.006	0.024	C	0.004	0.022
	19	**N**	**-0.177**	**-0.177**	**N**	-0.177	-0.177	**N**	-0.174	-0.18
	20	**C**	**0.034**	**0.039**	C	0.034	0.038	C	0.037	0.035
	*21	**Br**	**0.068**	**0.068**	**Cl**	0.062	0.049	**Cl**	0.053	0.044
	22	**Cl**	**0.066**	**0.045**	**Br**	0.069	0.038	**Br**	0.055	0.032
	23	N	-0.132	-0.132	N	-0.13	-0.132	N	-0.128	-0.129
	24	C	0.038	0.038	C	0.041	0.019	C	0.042	0.022
	25	N	-0.176	-0.177	C	0.009	0.022	C	0.007	0.025
	26	C	0.009	0.023	N	-0.175	-0.179	N	-0.178	-0.179
	27	C	0.02	0.021	C	0.021	0.033	C	0.019	0.04
	*28	Br	0.059	0.037	Br	0.06	0.051	Br	0.051	0.053
	29	Cl	0.051	0.061	Cl	0.061	0.035	Cl	0.054	0.035
	30	H	0.041	0.042	H	0.042	0.043	H	0.021	0.022
	31	H	0.049	0.049	H	0.047	0.048	H	0.046	0.045
	32	H	0.044	0.045	H	0.046	0.046	H	0.048	0.049
	33	H	0.026	0.026	H	0.026	0.027	H	0.03	0.029
Acetone	34	C	-0.105	-0.105	C	-0.101	-0.104	C	-0.1	-0.1
	35	**$C_{(CO)}$**	0.154	0.155	**$C_{(CO)}$**	0.154	0.156	**$C_{(CO)}$**	0.163	0.162
	36	C	-0.096	-0.095	O	-0.2	-0.199	O	-0.177	-0.098
	37	O	-0.204	-0.202	C	-0.098	-0.097	C	-0.098	-0.179
	38	H	0.023	0.023	H	0.014	0.016	H	0.025	0.027
	39	H	0.035	0.037	H	0.046	0.046	H	0.047	0.047
	40	H	0.032	0.034	H	0.033	0.027	H	0.035	0.034
	41	H	0.044	0.044	H	0.04	0.042	H	0.039	0.04
	42	H	0.041	0.041	H	0.04	0.041	H	0.043	0.042
	43	H	0.045	0.045	H	0.026	0.027	H	0.037	0.037
	MOF Charge		0.030	0.024		0.046	0.046		-0.015	-0.013
	Acetone Charge		-0.030	-0.024		-0.046	-0.046		0.015	0.013

Table S5. Energies of interaction and geometrical parameters for optimized structures of acetone-ZIF systems.

MOF	Acetone Orientation toward MOF	Pattern	Interaction Energy (Kcal/mol)	Optimized Geometries												
				Intermolecular distances (Å)												Angle (°)
				C_{CM}-C_3(Cl)	C_{CM}-Cl C_3	C_{CM}-C_2(X)	C_{FM}-C_2(X)	C_{CM}-X (C_2)	C_{FM}-X (C_2)	(C_{CM})H-X (C_2)	(C_{FM})H-X (C_2)	(C_4)H-H(C_{CM})	O-C_3	H_1-O	C_O-C_2	Change in dihedral
ZIF -71	Methyl	Non-Symm	-13.3	3.59	3.54	3.81	-	3.81	-	3.37	-	2.41	-	-	-	-10.1
	Methyl	Symm	-4.9	3.58	3.62	3.66	4.40	3.78	3.79	3.03	2.82	2.52	-	-	4.07	-15.2
	Carbonyl	Semi-Symm	-14.5	3.84	4.01	3.71	3.67	3.68	4.13	2.87	3.35	-	3.24	2.05	3.35	-37.4
ZIF -71 (ClBr)-SE	Methyl	Non-Symm	-4.3	3.63	3.60	3.80	-	3.99	-	3.01	-	2.73	-	-	-	-16.2
	Methyl	Non-Symm	-2.8	3.59	3.55	3.81	-	4.05	-	3.45	-	2.41	-	-	-	-12.8
	Methyl	Symm	-5.3	3.71	3.80	3.84	4.45	4.12	3.95	3.17	2.96	2.45	-	-	4.19	-17.8
	Carbonyl	Semi-Symm	-14.1	3.87	4.03	3.74	3.69	3.78	4.24	2.97	3.49	-	3.19	2.02	3.36	-42.1
	Oxygen, Methyl	Non-Symm	-10.8	-	-	4.31	-	3.88	-	3.02	-	-	3.12	2.08	4.24	-29.7