Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Understanding Structural Flexibility of the Paddle-Wheel Zn-SBU motif in MOFs: Influence of Pillar Ligands

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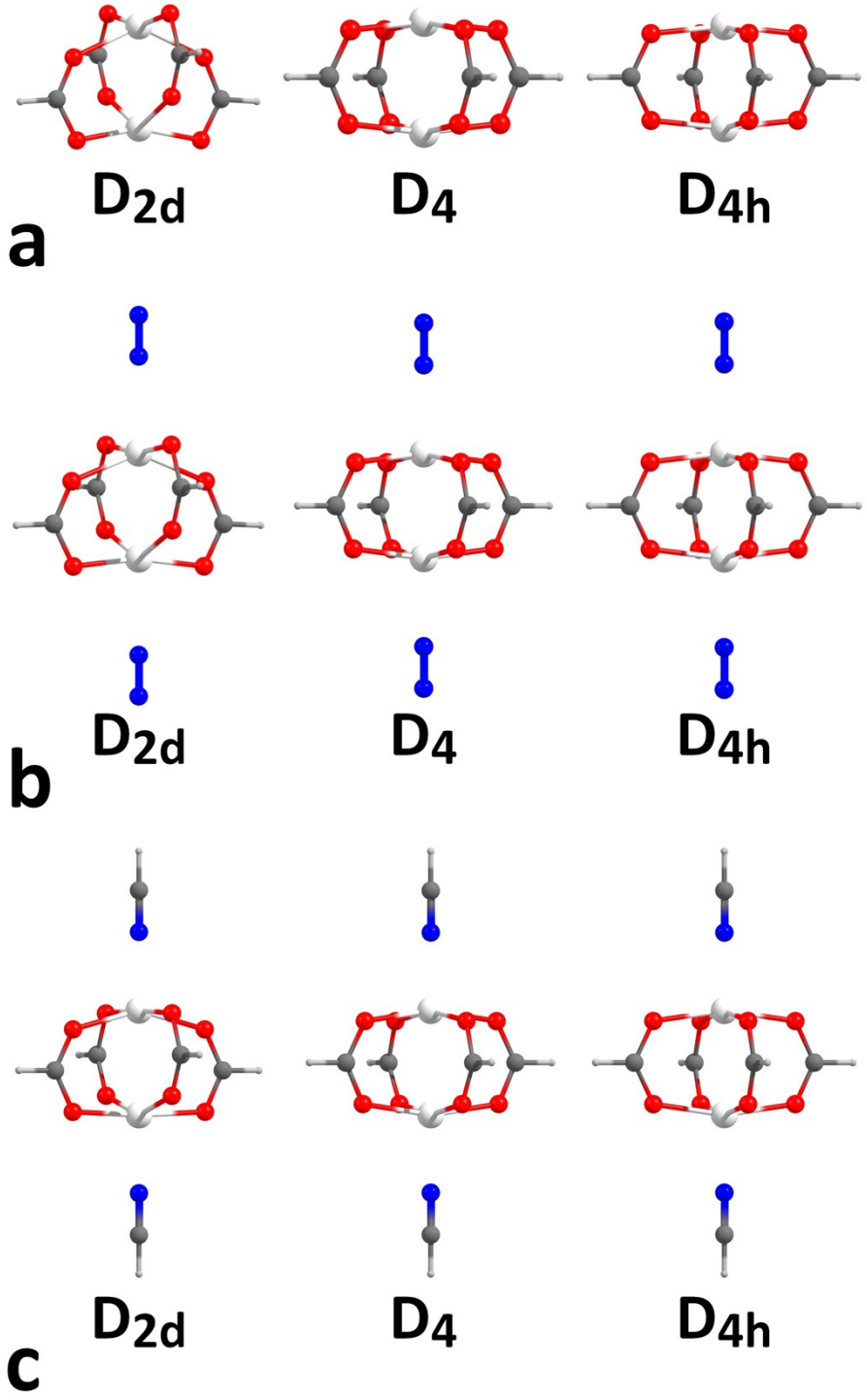

Figure S1. D_{2d}, D_4 and D_{4h} symmetries of Zn-SBU without pillar ligands (a), with N_2 (b) and NCH (c) molecules as pillar ligands.

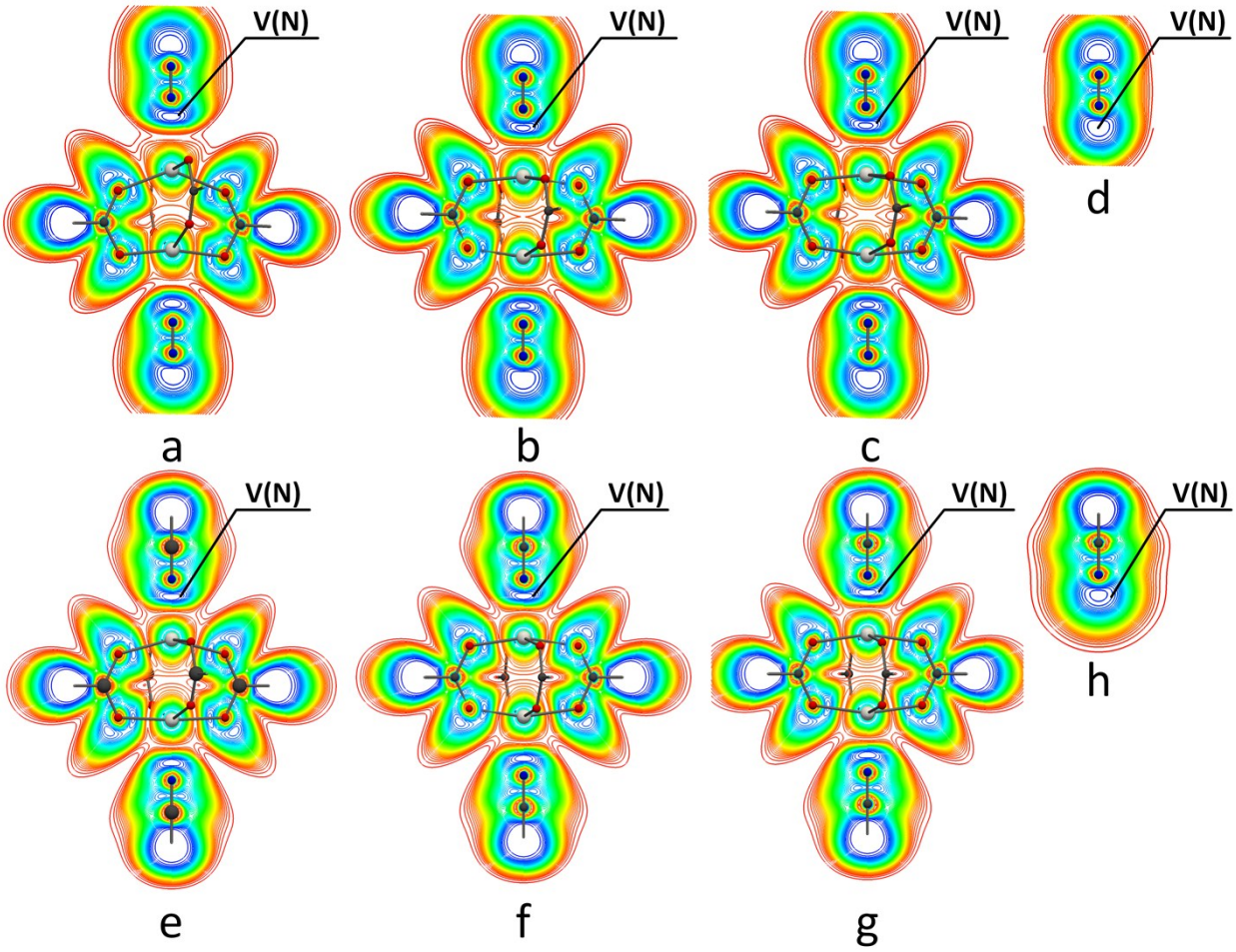

Figure S2. ELF maps calculated for the D_{2d} (a), D_4 (b) and D_{4h} (c) forms of the Zn-SBU+2N_2 system, NCH (d) molecule, the D_{2d} (e), D_4 (f) and D_{4h} (g) forms of the Zn-SBU+2NCH system and N_2 (h) molecule.

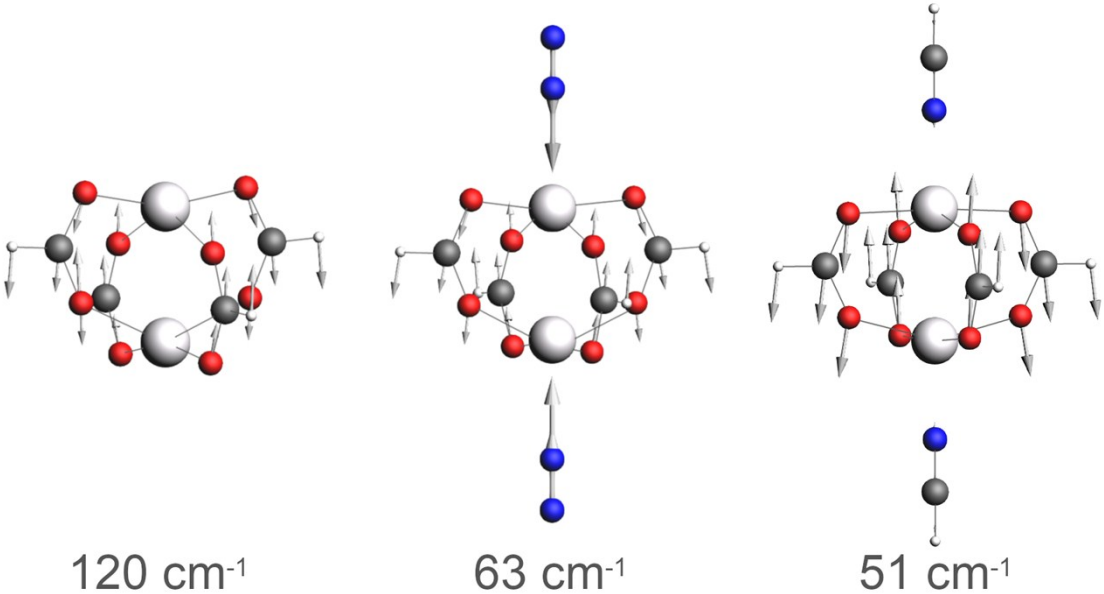

Figure S3. Vibrational modes, which can promote transition between two D2d forms of Zn-SBU, Zn-SBU+2N2 and Zn-SBU+2NCH.

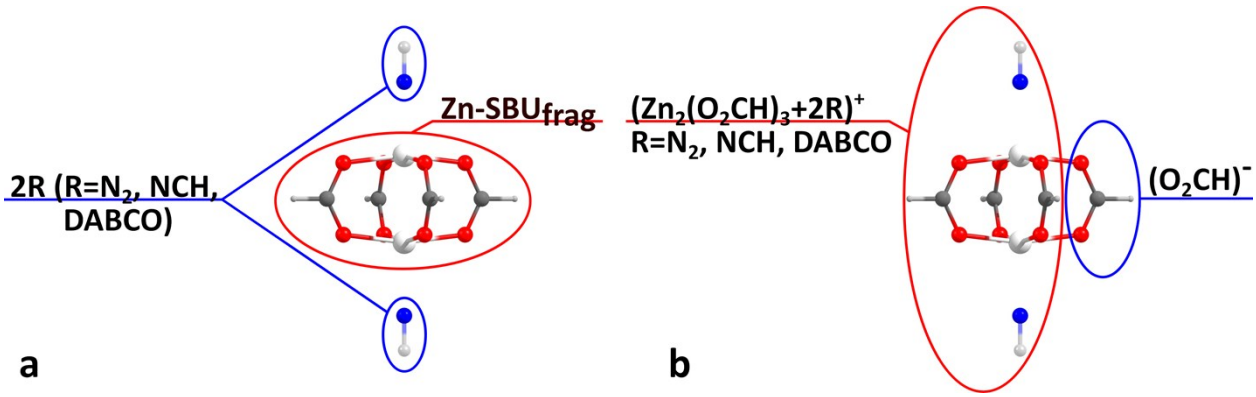

Figure S4. Zn-SBU_{frag} and 2R fragments (a) and $Zn_2(O_2CH)_3$+2R)$^+$ and (O2CH)$^-$ fragments (b) (R=N_2, NCH, DABCO) used for the energy decomposition analysis.

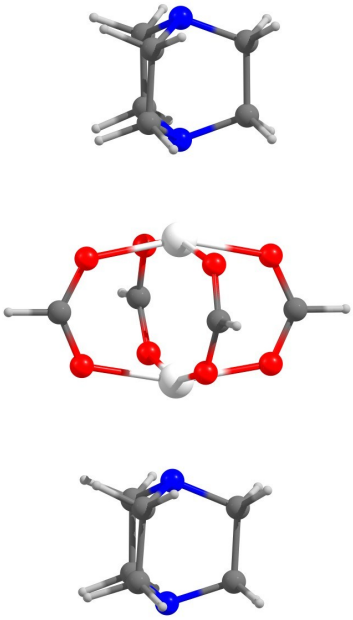

Figure S5. Local minimum with C_1 symmetry of Zn-SBU with DABCO as pillar ligands.

Table S1. Energy decomposition calculated for Zn-SBU+2N_2, Zn-SBU+2NCH and Zn-SBU+2DABCO systems at the S12h/TZP level of theory. E_{elstat}, E_{Pauli}, E_{orb}, E_{disp}, E_{int} are the energies of electrostatic interaction, Pauli repulsion, orbital interactions, dispersion energy, and interaction energy, respectively, calculated relative to Zn-SBU_{frag} and 2R (R=N_2, NCH, DABCO) fragments. All values are given in kcal/mol.

	Zn-SBU+2N_2			Zn-SBU+2NCH			Zn-SBU+2DABCO
	D_{2d}	D_4	D_{4h}	D_{2d}	D_4	D_{4h}	C_1
E_{elstat}	-14.28	-24.63	-24.61	-65.89	-68.91	-68.79	-142.48
E_{Pauli}	16.48	28.08	28.07	65.38	67.00	66.94	123.17
E_{orb}	-9.84	-18.47	-18.44	-32.40	-34.12	-34.04	-50.99
E_{disp}	-2.80	-3.13	-3.14	-3.18	-3.25	-3.25	-14.91
E_{int}	-10.44	-18.15	-18.12	-36.09	-39.28	-39.14	-85.21

Table S2. Comparison of bonding energies of Zn-SBU_{frag} and 2R (R=N_2, NCH, DABCO) fragments calculated at different theoretical levels. All values are in kcal/mol.

	Zn-SBU+2N2			Zn-SBU+2NCH			Zn-SBU+2DABCO
	D_{2d}	D_4	D_{4h}	D_{2d}	D_4	D_{4h}	C_1
S12h/TZP	-10.44	-18.15	-18.12	-36.09	-39.28	-39.14	-85.21
CCSD(T)/Def2TZVP//S12h/TZP	-10.93	-18.71	-18.67	-38.82	-41.81	-41.67	n/a
sSAPT0/aug-cc-pvdz//S12h/TZP	-10.88	-17.37	-17.35	-39.52	-41.96	-41.84	-79.65

Table S3. Contribution of electrostatic, exchange, induction and dispersion (E_{elstat}, E_{exch}, E_{ind}, E_{disp}, respectively) components in interaction energy (E_{int}) of Zn-SBUfrag and 2R (R=N_2, NCH, DABCO) fragments calculated by SAPT0 and sSAPT0 method on dimmer and monomer basis with aug-cc-pvdz basis set. All values are in kcal/mol.

	Zn-SBU+2N_2			Zn-SBU+2NCH			Zn-SBU+2DABCO
	D_{2d}	D_4	D_{4h}	D_{2d}	D_4	D_{4h}	C_1
Dimer Basis SAPT0							
E_{elstat}	-11.94	-20.76	-20.76	-61.09	-64.45	-64.32	-135.66
E_{exch}	15.05	25.52	25.53	57.75	60.09	60.08	117.35
E_{ind}	-5.40	-11.41	-11.39	-21.85	-23.16	-23.11	-36.65
E_{disp}	-7.89	-10.27	-10.29	-15.62	-15.88	-15.90	-32.68
E_{int}	-10.18	-16.92	-16.91	-40.80	-43.39	-43.26	-87.64
Monomer Basis SAPT0							
E_{elstat}	-11.82	-21.12	-21.11	-63.91	-67.61	-67.47	-137.19
E_{exch}	14.49	26.17	26.17	61.07	63.95	63.92	120.25
E_{ind}	-6.31	-13.26	-13.24	-24.65	-26.23	-26.18	-42.26
E_{disp}	-7.34	-9.47	-9.48	-13.98	-14.19	-14.22	-30.07
E_{int}	-10.98	-17.68	-17.66	-41.47	-44.07	-43.95	-89.27
Dimer Basis sSAPT0							
E_{elstat}	-11.94	-20.76	-20.76	-61.09	-64.45	-64.32	-135.66
E_{exch}	15.05	25.52	25.53	57.75	60.09	60.08	117.35
E_{ind}	-5.05	-10.14	-10.12	-14.97	-15.73	-15.69	-14.22
E_{disp}	-7.87	-10.23	-10.25	-15.45	-15.70	-15.73	-32.22
E_{int}	-9.81	-15.61	-15.60	-33.75	-35.79	-35.66	-64.75
Monomer Basis sSAPT0							
E_{elstat}	-11.82	-21.12	-21.11	-63.91	-67.61	-67.47	-137.19
E_{exch}	14.49	26.17	26.18	61.07	63.95	63.92	120.25
E_{ind}	-6.22	-12.97	-12.95	-22.79	-24.20	-24.15	-32.92
E_{disp}	-7.33	-9.45	-9.47	-13.89	-14.11	-14.13	-29.79
E_{int}	-10.88	-17.37	-17.35	-39.52	-41.96	-41.84	-79.65

Table S4. Energy decomposition calculated for Zn-SBU+2N_2, Zn-SBU+2NCH and Zn-SBU+2DABCO systems at the S12h/TZP level of theory. E_{elstat}, E_{Pauli}, E_{orb}, E_{disp}, E_{int} are the energies of electrostatic interaction, Pauli repulsion, orbital interactions, dispersion energy, and interaction energy, respectively, calculated relative to $(O_2CH)^-$ and $(Zn_2(O_2CH)_3+2R)^+$ (R=*, N_2, NCH, DABCO) fragments. All values are given in kcal/mol.

	Zn-SBU			Zn-SBU+2N_2			Zn-SBU+2NCH			Zn-SBU+DABCO
	D_{2d}	D_4	D_{4h}	D_{2d}	D_4	D_{4h}	D_{2d}	D_4	D_{4h}	C_1
E_{Pauli}	129.78	138.99	138.91	129.65	131.38	131.4	121.44	121.26	121.38	116.42
E_{elstat}	-249.24	-245.74	-245.69	-237.52	-230.49	-230.55	-206.29	-205	-205.14	-197.34
E_{orb}	-74.5	-74.53	-74.6	-72.28	-70.71	-70.79	-64.51	-64.44	-64.54	-63.33
E_{disp}	-3.18	-3.36	-3.35	-3.72	-3.9	-3.89	-3.95	-3.98	-3.97	-5.49
E_{int}	-197.14	-184.64	-184.73	-183.87	-173.72	-173.83	-153.31	-152.16	-152.27	-149.74
steric	-119.46	-106.75	-106.78	-107.87	-99.11	-99.15	-84.85	-83.74	-83.76	-80.92