Supporting Information

Locking of CO_2 in a Bio-inspired Porous-Organic-Polymeric Prison: Impact of Aliphatic Odd-Even Linker Combination

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Computational Details

Section S1: Computational methods for mechanism studies

Geometry optimizations in the gas phase were initially carried out using the global hybrid functional M06-2X[5]with Karlsruhe-family basis set of double-ζ valence def2-SVP[6,7] for all atoms as implemented in *Gaussian 16* rev. A.03.[7] Minima on the potential energy surface (PES) were confirmed as such by harmonic frequency analysis, showing zero imaginary frequency, at the same level of theory.

To refine the energetics, single point (SP) corrections were performed in the gas phase using M06-2X functional and def2-TZVP[5,6] basis set for all atoms. Gibbs energies were evaluated at the room temperature, as was used in the experiments, using a quasi-RRHO treatment of vibrational entropies. Vibrational entropies of frequencies below 100 cm^{-1} were obtained according to a free rotor description, using a smooth damping function to interpolate between the two limiting descriptions.[8] M06-2X/def2-TZVP//M06-2X/def2-SVP Gibbs energies are given and quoted in kcal mol^{-1} throughout. *Unless otherwise stated, these corrected values are used for discussion throughout the main text and in this supporting information.* All molecular structures were visualized using *PyMOL* software.

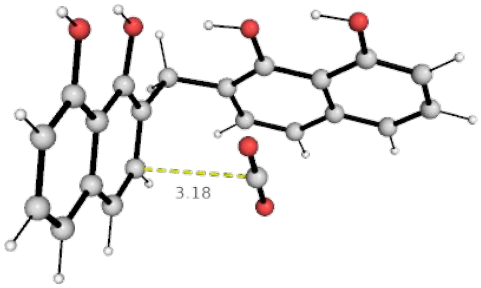
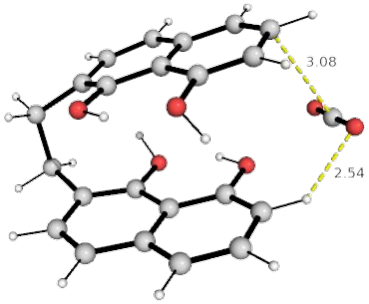
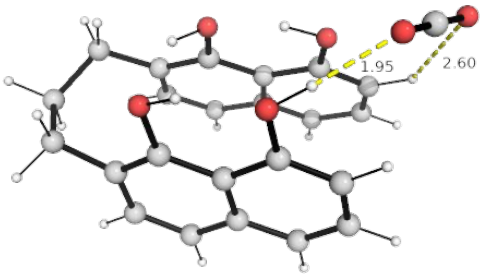
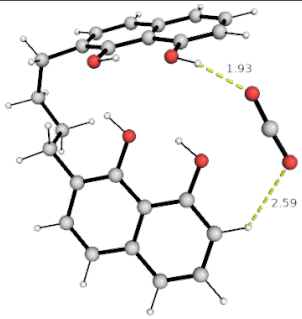
Section S2: Conformational considerations

For the dimer model system, we initially obtained the DFT-optimized structures of ***dimer*-LPOP-n** (n = 1–5) complexes at the M06-2X/def2-SVP level of theory. Subsequently, we utilized these DFT-optimized structures as input to conduct thorough conformational sampling at GFN2-xTB[9–11] level of theory using the CREST program version 2.12 by Grimme and co-workers.[12,13]From the sampling, we extracted the ten lowest-energy conformers for each ***dimer*-LPOP-n** system (optimized at the *xtb* level), resulting in a total of 50 conformers. These *xtb*-optimized conformers were subsequently reoptimized at the DFT (M06-2X/def2-SVP) level of theory. Next, the most stable DFT-optimized conformer of each ***dimer*-LPOP-n** complex was used as input for additional conformational sampling with *crest*, incorporating CO_2 to identify the most stable ***dimer*-LPOP-n_CO_2** structures. From this sampling, we extracted the five lowest-energy conformers for each ***dimer*-LPOP-n_CO_2**system (optimized at the *xtb* level), resulting in a total of 25 conformers. These *xtb*-optimized conformers were subsequently reoptimized at the DFT (M06-2X/def2-SVP) level of theory.

For model cage system, *crest* conformational sampling was performed to identify the most stable conformers. The lowest GFN2-xTB energy structure, *crest_best* conformer for each

LPOP-n_CO_2, was used, resulting in a total of 5 conformers. These *xtb*-optimized conformers were subsequently reoptimized at the DFT (M06-2X/def2-SVP) level of theory.

Section S3: Dimer model system of LPOP-n (n = 1–5) for CO_2 adsorption studies

***dimer*-LPOP-1_CO_2**	***dimer*-LPOP-2_CO_2**
ΔG = 8.7kcal mol^{-1}	ΔG = 9.1 kcal mol^{-1}
	
***dimer*-LPOP-3_CO_2**	***dimer*-LPOP-4_CO_2**
ΔG = 8.9 kcal mol^{-1}	ΔG = 8.4 kcal mol^{-1}
	

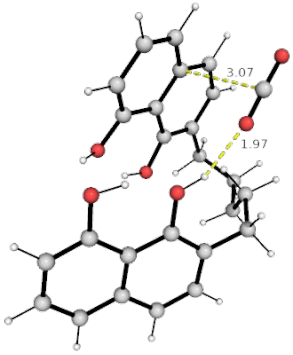
***dimer*-LPOP-5_CO_2**
ΔG = 8.7kcal mol^{-1}


Figure S27: DFT optimized geometries of the studied ***dimer*-LPOP-n_CO_2** complexes. Key bond distances are given in Å. The CO_2 binding free energies (ΔG_{BE}) are given relative to the corresponding ***dimer*-LPOP-n** and CO_2 molecules.

Section S4: Optimized structures and raw energies

Geometries of all optimized structures (in .xyz format with their associated energy in Hartrees) are included in a separate folder named *DFT_optimized_structures*. All these data have been deposited and uploaded to https://zenodo.org/records/14870290 (DOI: 10.5281/zenodo.14870290).

Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and quasi-harmonic Gibbs free energy (at 273.15K) for gas-phase M06-2X/def2-SVP optimized structures are given below. Single point corrections in gas-phase using M06-2X/def2-TZVP functional are also included.

Table S2: Optimized structures and raw energies.

Structure	E/au	ZPE/au	H/au	T.S/au	qh-G/au	SP M062X/def2-TZVP
co2	-188.369743	0.010912	-188.355262	0.028007	-188.383269	-188.596318
***dimer*-LPOP-1_c1**	-1109.555869	0.326207	-1109.212689	0.057005	-1109.266927	-1110.784672
***dimer*-LPOP-1_c2**	-1109.548968	0.325854	-1109.205954	0.056977	-1109.260328	-1110.778951
***dimer*-LPOP-1_c3**	-1109.548968	0.325854	-1109.205955	0.056975	-1109.260327	-1110.77895
***dimer*-LPOP-1_c4**	-1109.548968	0.325856	-1109.205953	0.056975	-1109.260325	-1110.77895
***dimer*-LPOP-1_c5**	-1109.547983	0.325893	-1109.204832	0.057439	-1109.259515	-1110.777585
***dimer*-LPOP-1_c6**	-1109.546087	0.325512	-1109.203156	0.058189	-1109.258359	-1110.77648
***dimer*-LPOP-1_c7**	-1109.545323	0.325457	-1109.202355	0.058513	-1109.257819	-1110.776013
***dimer*-LPOP-1_c8**	-1109.545323	0.325478	-1109.202343	0.058494	-1109.257785	-1110.776017
***dimer*-LPOP-1_c9**	-1109.545114	0.325796	-1109.201962	0.058164	-1109.257061	-1110.77477
***dimer*-LPOP-2_c1**	-1148.820411	0.355099	-1148.447327	0.058665	-1148.503343	-1150.093132
***dimer*-LPOP-2_c2**	-1148.817393	0.354585	-1148.444593	0.059674	-1148.501012	-1150.090706
***dimer*-LPOP-2_c3**	-1148.819485	0.355335	-1148.446218	0.058858	-1148.502048	-1150.091105
***dimer*-LPOP-2_c4**	-1148.819485	0.355335	-1148.446218	0.058858	-1148.502048	-1150.091105
***dimer*-LPOP-2_c5**	-1148.819485	0.355338	-1148.446216	0.05886	-1148.502046	-1150.091106
***dimer*-LPOP-2_c6**	-1148.821016	0.354956	-1148.448614	0.055995	-1148.502675	-1150.089995
***dimer*-LPOP-2_c7**	-1148.813127	0.35427	-1148.440508	0.060113	-1148.497201	-1150.085626
***dimer*-LPOP-2_c8**	-1148.813127	0.35427	-1148.440509	0.060103	-1148.497196	-1150.085624
***dimer*-LPOP-2_c9**	-1148.813127	0.354269	-1148.440509	0.060102	-1148.497197	-1150.085623
***dimer*-LPOP-2_c10**	-1148.813127	0.354271	-1148.440508	0.0601	-1148.497193	-1150.085623
***dimer*-LPOP-3_c1**	-1188.094405	0.384176	-1187.691885	0.057124	-1187.747385	-1189.404365
***dimer*-LPOP-3_c2**	-1188.094406	0.384182	-1187.691883	0.057111	-1187.747376	-1189.404362
***dimer*-LPOP-3_c3**	-1188.090048	0.38343	-1187.687946	0.058368	-1187.744315	-1189.401987
***dimer*-LPOP-3_c4**	-1188.090888	0.383812	-1187.688499	0.058131	-1187.744596	-1189.401455
***dimer*-LPOP-3_c5**	-1188.086395	0.383049	-1187.684361	0.059591	-1187.741643	-1189.398468
***dimer*-LPOP-3_c6**	-1188.086395	0.383047	-1187.684362	0.059551	-1187.741627	-1189.398462

***dimer*-LPOP-3_c7**	-1188.084989	0.383369	-1187.682697	0.058961	-1187.739539	-1189.398118
***dimer*-LPOP-3_c8**	-1188.084989	0.383371	-1187.682696	0.058957	-1187.739535	-1189.398118
***dimer*-LPOP-3_c9**	-1188.088824	0.384143	-1187.686416	0.057348	-1187.741875	-1189.39909
***dimer*-LPOP-3_c10**	-1188.088824	0.384142	-1187.686418	0.057344	-1187.741874	-1189.399087
***dimer*-LPOP-4_c1**	-1227.354777	0.41247	-1226.922699	0.059656	-1226.980679	-1228.710899
***dimer*-LPOP-4_c2**	-1227.352437	0.41224	-1226.920371	0.0608	-1226.978951	-1228.708758
***dimer*-LPOP-4_c3**	-1227.35395	0.412718	-1226.921559	0.060197	-1226.97979	-1228.708188
***dimer*-LPOP-4_c4**	-1227.350896	0.412626	-1226.918405	0.060932	-1226.977056	-1228.707804
***dimer*-LPOP-4_c5**	-1227.350896	0.412632	-1226.918399	0.060933	-1226.97705	-1228.707807
***dimer*-LPOP-4_c6**	-1227.353276	0.413189	-1226.920811	0.059453	-1226.978228	-1228.70753
***dimer*-LPOP-4_c7**	-1227.353276	0.413189	-1226.920811	0.059453	-1226.978227	-1228.707529
***dimer*-LPOP-4_c8**	-1227.353276	0.413193	-1226.920809	0.059444	-1226.97822	-1228.707528
***dimer*-LPOP-4_c9**	-1227.343529	0.411874	-1226.91131	0.063431	-1226.971415	-1228.702745
***dimer*-LPOP-4_c10**	-1227.345303	0.411884	-1226.913161	0.062396	-1226.972832	-1228.701697
***dimer*-LPOP-5_c1**	-1266.618162	0.440932	-1266.156201	0.063655	-1266.217299	-1268.019004
***dimer*-LPOP-5_c2**	-1266.617963	0.441731	-1266.155471	0.062981	-1266.215983	-1268.018031
***dimer*-LPOP-5_c3**	-1266.616593	0.441137	-1266.154628	0.063102	-1266.215184	-1268.017077
***dimer*-LPOP-5_c4**	-1266.615835	0.441309	-1266.153661	0.063692	-1266.214557	-1268.015701
***dimer*-LPOP-5_c5**	-1266.613384	0.441043	-1266.15128	0.063895	-1266.212416	-1268.014062
***dimer*-LPOP-5_c6**	-1266.612256	0.440688	-1266.150262	0.065512	-1266.212277	-1268.012854
***dimer*-LPOP-5_c7**	-1266.612193	0.440665	-1266.150283	0.06505	-1266.212182	-1268.012067
***dimer*-LPOP-5_c8**	-1266.611063	0.4408	-1266.149069	0.064229	-1266.210515	-1268.012391
***dimer*-LPOP-5_c9**	-1266.608724	0.441026	-1266.146418	0.065495	-1266.208486	-1268.011758
***dimer*-LPOP-5_c10**	-1266.603328	0.440877	-1266.141126	0.065388	-1266.203069	-1268.005178
***dimer*-LPOP-1_CO2_c1**	-1297.939358	0.339339	-1297.579564	0.064751	-1297.640642	-1299.390459
***dimer*-LPOP-1_CO2_c2**	-1297.941117	0.339444	-1297.58124	0.064547	-1297.642176	-1299.390324
***dimer*-LPOP-1_CO2_c3**	-1297.934282	0.339328	-1297.574146	0.070352	-1297.637957	-1299.386278
***dimer*-LPOP-1_CO2_c4**	-1297.934282	0.339327	-1297.574147	0.070337	-1297.637953	-1299.386279
***dimer*-LPOP-1_CO2_c5**	-1297.934669	0.339002	-1297.574867	0.067435	-1297.637343	-1299.386668
***dimer*-LPOP-2_CO2_c1**	-1337.208474	0.36834	-1336.819342	0.063323	-1336.88022	-1338.699712
***dimer*-LPOP-2_CO2_c2**	-1337.207886	0.368182	-1336.818813	0.063641	-1336.87987	-1338.699221
***dimer*-LPOP-2_CO2_c3**	-1337.206213	0.368812	-1336.816247	0.065718	-1336.878449	-1338.697531
***dimer*-LPOP-2_CO2_c4**	-1337.203714	0.368665	-1336.813717	0.066575	-1336.8764	-1338.69688
***dimer*-LPOP-2_CO2_c5**	-1337.205567	0.368848	-1336.815651	0.066846	-1336.878095	-1338.69666
***dimer*-LPOP-3_CO2_c1**	-1376.476926	0.39737	-1376.057506	0.067371	-1376.121185	-1378.008874
***dimer*-LPOP-3_CO2_c2**	-1376.473614	0.397363	-1376.05424	0.067183	-1376.11791	-1378.006765
***dimer*-LPOP-3_CO2_c3**	-1376.474025	0.397281	-1376.054681	0.066719	-1376.11819	-1378.006352
***dimer*-LPOP-3_CO2_c4**	-1376.472216	0.397238	-1376.052943	0.067001	-1376.116362	-1378.005763

***dimer*-LPOP-3_CO2_c5**	-1376.471817	0.397383	-1376.052571	0.065344	-1376.115392	-1378.004402
***dimer*-LPOP-4_CO2_c1**	-1415.738282	0.426359	-1415.288706	0.07144	-1415.355499	-1417.31609
***dimer*-LPOP-4_CO2_c2**	-1415.737419	0.425617	-1415.288659	0.068309	-1415.354038	-1417.316053
***dimer*-LPOP-4_CO2_c3**	-1415.738455	0.426197	-1415.289199	0.068899	-1415.35468	-1417.31461
***dimer*-LPOP-4_CO2_c4**	-1415.73667	0.425912	-1415.287504	0.068994	-1415.353312	-1417.312914
***dimer*-LPOP-4_CO2_c5**	-1415.736662	0.425952	-1415.287475	0.068965	-1415.353249	-1417.312882
***dimer*-LPOP-5_CO2_c1**	-1455.003652	0.454713	-1454.524556	0.072656	-1454.592945	-1456.624979
***dimer*-LPOP-5_CO2_c2**	-1455.001963	0.454259	-1454.523326	0.072139	-1454.591482	-1456.623664
***dimer*-LPOP-5_CO2_c3**	-1454.998815	0.454329	-1454.51997	0.072726	-1454.5885	-1456.622446
***dimer*-LPOP-5_CO2_c4**	-1454.998815	0.454337	-1454.51996	0.072701	-1454.58848	-1456.622447
***dimer*-LPOP-5_CO2_c5**	-1454.995907	0.454349	-1454.51689	0.073291	-1454.58574	-1456.619126
LPOP-1	-2295.317342	0.669675	-2294.6153	0.088385	-2294.69845	-2297.840544
LPOP-1_CO2	-2483.704198	0.682896	-2482.98519	0.097896	-2483.07591	-2486.446909
LPOP-2	-2452.362495	0.785445	-2451.5403	0.097321	-2451.63112	-2455.056655
LPOP-2_CO2	-2640.749011	0.798605	-2639.91013	0.105076	-2640.00783	-2643.664258
LPOP-3	-2609.423275	0.899961	-2608.48263	0.103514	-2608.58002	-2612.287327
LPOP-3_CO2	-2797.808918	0.913138	-2796.85159	0.111337	-2796.95583	-2800.893938
LPOP-4	-2766.445437	1.013371	-2765.38522	0.120533	-2765.49626	-2769.494297
LPOP-4_CO2	-2954.827162	1.027195	-2953.74986	0.128962	-2953.86768	-2958.097167
LPOP-5	-2923.498388	1.128017	-2922.31944	0.131747	-2922.43909	-2926.720523
LPOP-5_CO2	-3111.887791	1.141211	-3110.69206	0.138846	-3110.81845	-3115.330806

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