Electronic Supplementary Information for the Manuscript

Elucidating the CO_2 adsorption mechanism in the triangular channels of the bis(pyrazolate) MOF $Fe_2(BPEB)_3$ by *in-situ* synchrotron X-ray diffraction and molecular dynamics simulations

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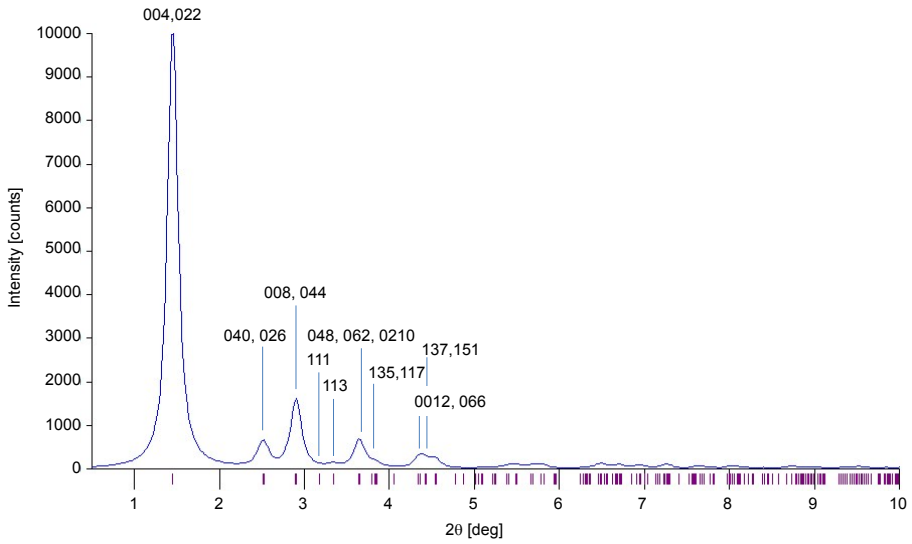

Fig. S1. Portion of the powder X-ray diffraction pattern calculated (λ = 0.400 Å) for **Fe_2(BPEB)$_3$** with the structural model proposed in reference 30 of the main text: a number of *hkl* Bragg reflections with *h* non zero are highlighted.

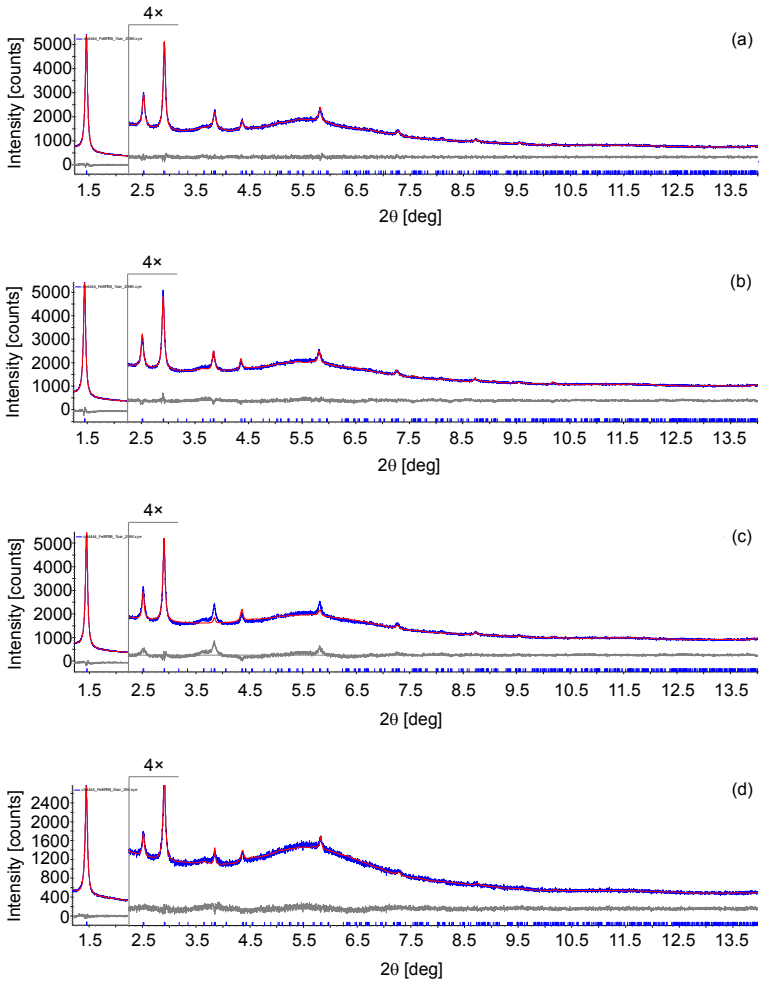

Figure S2. Representative examples of the HR-PXRD data treatment for **$Fe_2(BPEB)_3$**: (a) Whole profile fitting of the data at 298 K and 1 bar of CO_2 with the Le Bail approach (R_{wp} = 0.031, R_p = 0.024); (b) Rietveld refinement of the data at 298 K and 1 bar of CO_2 with a structural model containing the three CO_2 molecules (R_{wp} = 0.039, R_p = 0.031, R_{Bragg} = 0.86, for 43 parameters); (c) Rietveld refinement of the data at 298 K and 1 bar of CO_2 with the structural model adopted in (b) but without the CO_2 molecules (R_{wp} = 0.056, R_p = 0.040, R_{Bragg} = 1.45, for 22 parameters); (d) Rietveld refinement of the data at 298 K and 0 bar of CO_2 with a structural model not containing guest molecules in the channels (R_{wp} = 0.038, R_p = 0.030, R_{Bragg} = 0.59, for 26 parameters). Experimental, calculated and difference curves are depicted in blue, red, and grey, respectively. The positions of the Bragg peaks are shown by blue markers at the bottom. Horizontal axis, 2θ [deg]; vertical axis, intensity [counts].

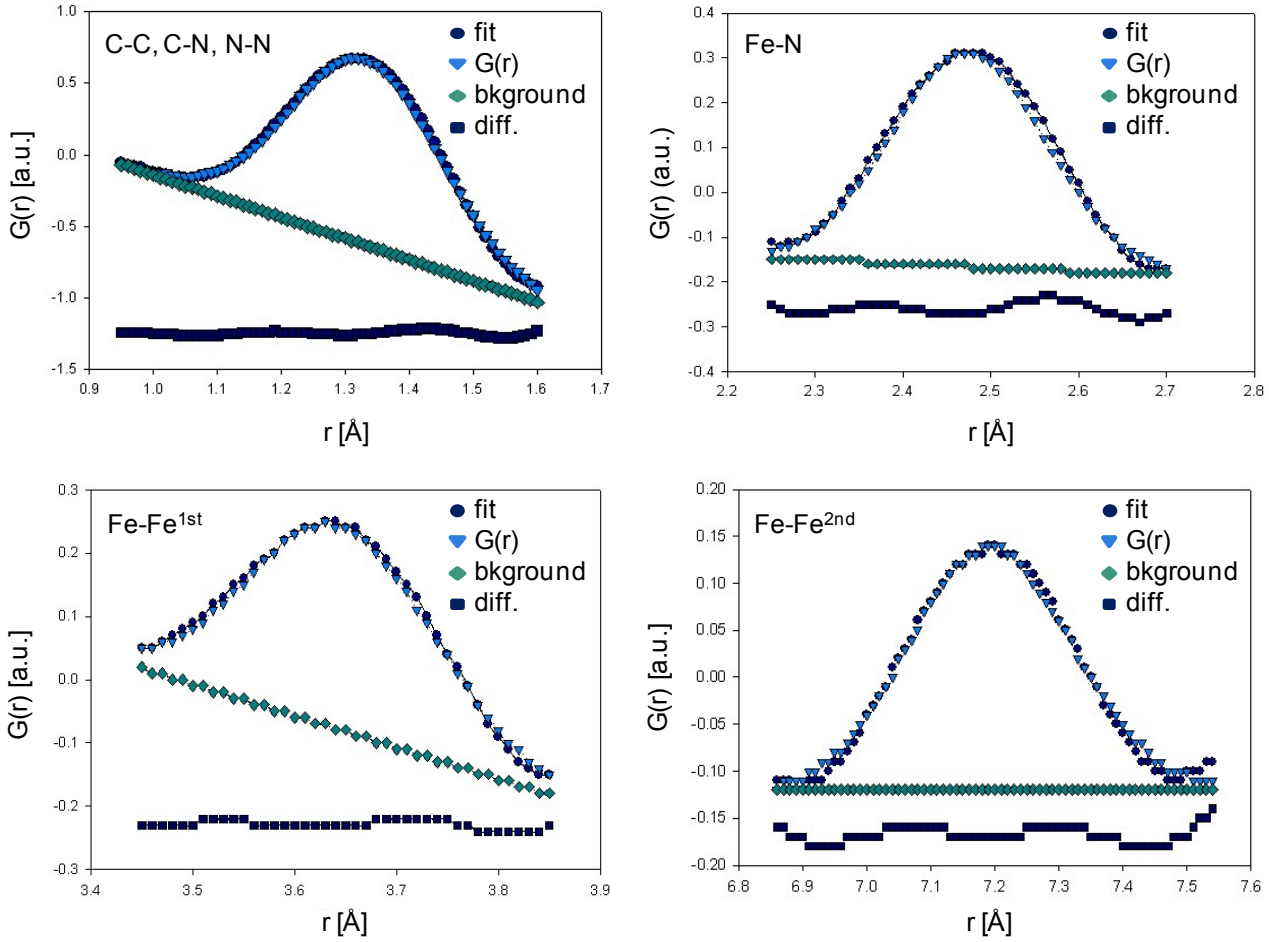

Figure S3. Gaussian fit of the main PDF peaks commented in the text. Fitting of the peaks extracted from the HE-PXRD data acquired at 298 K and 5 bar of CO_2 is shown as a representative example.

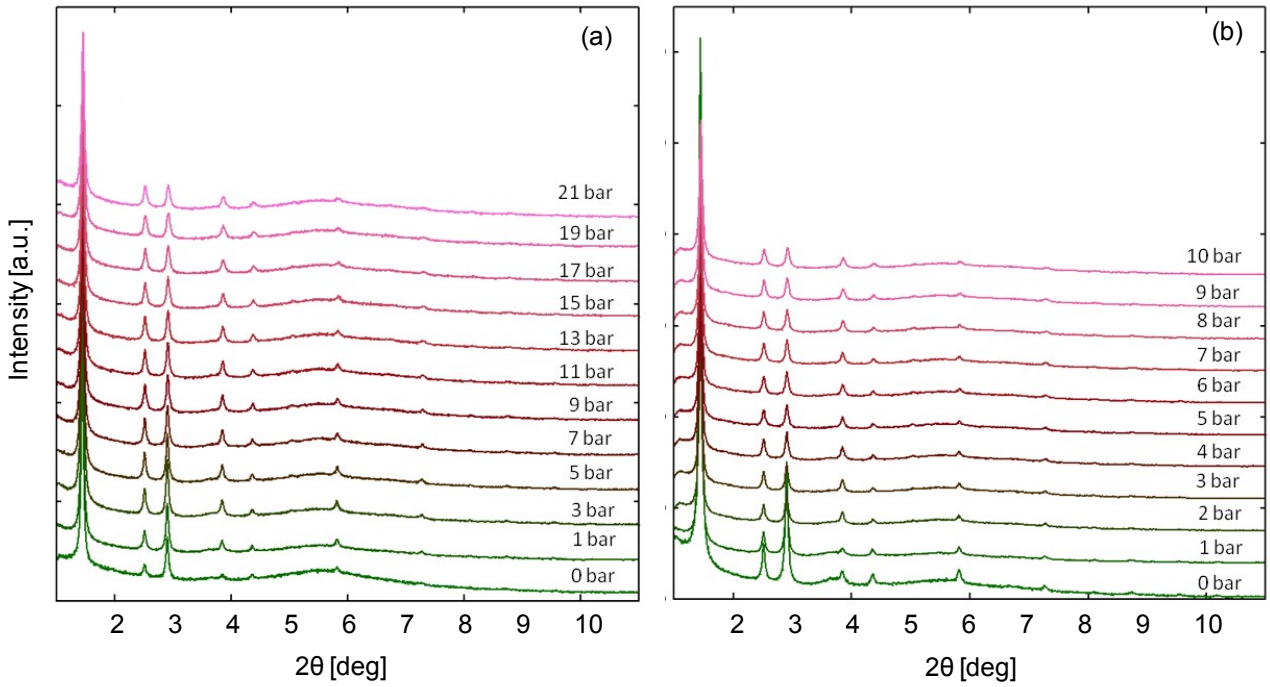

Figure S4. Comparison of the low-to-medium angle portion of the HR-PXRD patterns of **$Fe_2(BPEB)_3$** acquired at (a) 298 K and (b) 273 K, at 0 bar of CO_2 and all the CO_2 loadings essayed at each temperature.

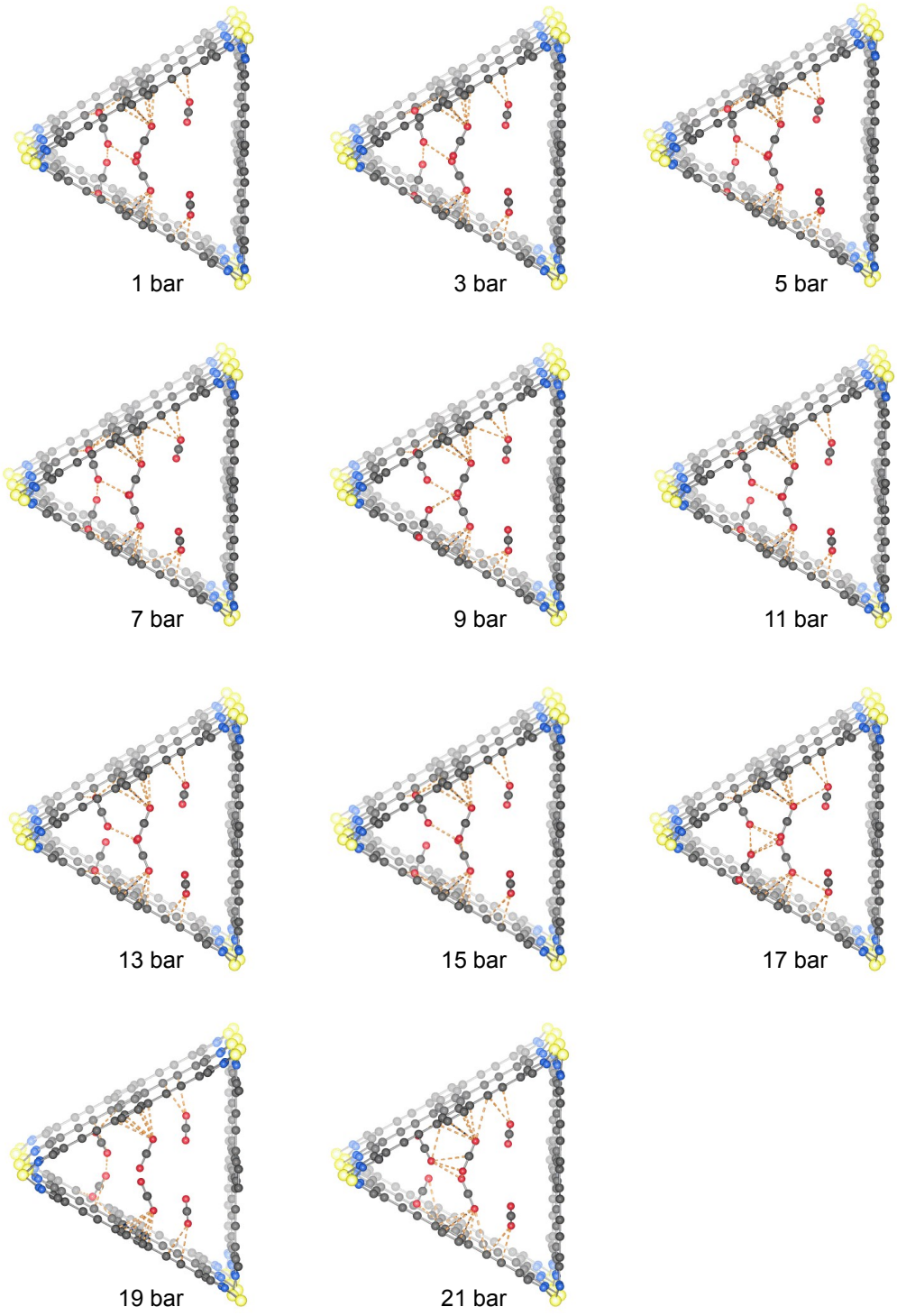

Figure S5. Location of the three independent CO_2 molecules [CO_2-1, CO_2-2, and CO_2-3 in the text] in **Fe_2(BPEB)$_3$** at 298 K and CO_2 loadings in the range 1-21 bar. Depicted with fragmented lines the C···O host-guest and O···O guest-guest interactions. For the sake of clarity, only interactions shorter than 3.6 Å have been depicted.

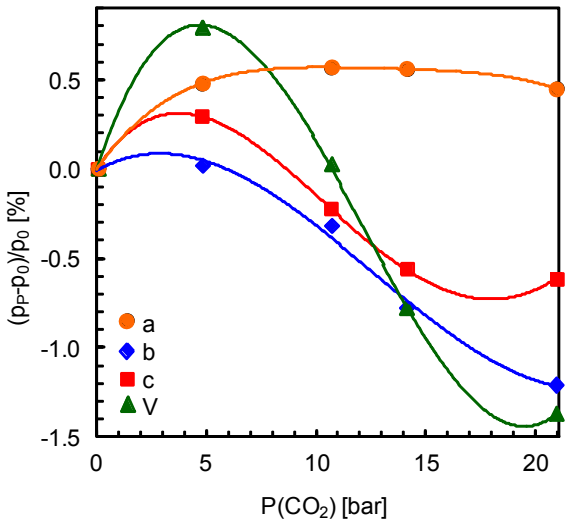

Figure S6. Percentage variation of the unit cell parameters p_p of **$Fe_2(BPEB)_3$** as a function of the pressure of CO_2 at 298 K, obtained by combining the results of the structureless Le Bail refinements and of the PDF analysis (see main text). The values of the parameters at each pressure have been normalized with respect to the values p_0 shown prior to CO_2 dosing. *a*-axis, orange circles; *b*-axis, blue diamonds; *c*-axis, red squares; *V*, green triangles. The lines have been added to guide the eye.

273 K						
Le Bail Refinements						
p [bar]	R_{wp}	R_p				
0.0	0.034	0.026				
1.0	0.030	0.023				
2.0	0.034	0.023				
3.1	0.028	0.022				
3.9	0.030	0.022				
5.0	0.029	0.022				
5.7	0.027	0.021				
6.6	0.026	0.020				
7.3	0.025	0.020				
8.2	0.025	0.020				
8.7	0.025	0.020				
298 K						
Le Bail Refinements			Rietveld Refinements			
p [bar]	R_{wp}	R_p	R_{wp}	R_p	R_{Bragg}	# ref. parameters
0	0.033	0.025	0.038	0.030	0.588	26
1	0.031	0.024	0.039	0.031	0.861	43
3	0.030	0.023	0.038	0.030	0.795	45
5	0.029	0.023	0.037	0.028	0.591	43
7	0.029	0.023	0.037	0.028	0.596	45
9	0.029	0.022	0.036	0.028	0.682	40
11	0.029	0.022	0.036	0.028	0.784	40
13	0.028	0.022	0.036	0.028	0.800	43
15	0.028	0.022	0.036	0.028	0.609	43
17	0.028	0.022	0.036	0.028	0.632	43
19	0.028	0.022	0.036	0.028	0.641	43
21	0.028	0.022	0.035	0.027	0.704	43

Table S1. R_{wp} and R_p figures of merit for all the Le Bail refinements carried out on the HR-PXRD data of **$Fe_2(BPEB)_3$** at 273 and 298 K. R_{wp}, R_p and R_{Bragg} figures of merit and number of refined parameters for all the Rietveld refinements carried out on the HR-PXRD data of **$Fe_2(BPEB)_3$** at 298 K.

		C			O1			O2		
p [bar]		*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
1	CO_2-1	0.0182	-0.1651	0.2572	0.0236	-0.1928	0.2666	0.0601	-0.1375	0.2477
	CO_2-2	0.0511	0.1838	0.2902	0.0676	0.2156	0.2953	0.0345	0.1519	0.2852
	CO_2-3	-0.9163	-0.5477	0.4346	-0.0264	-0.5723	0.4352	-0.8061	-0.5232	0.4341
3	CO_2-1	0.0150	-0.1632	0.2579	0.0263	-0.1919	0.2663	0.0564	-0.1346	0.2494
	CO_2-2	0.0388	0.1814	0.2882	0.0800	0.2124	0.2932	-0.0024	0.1505	0.2831
	CO_2-3	-0.8842	-0.5420	0.4359	0.0003	-0.5655	0.4370	-0.7687	-0.5186	0.4347
5	CO_2-1	0.0170	-0.1610	0.2590	0.0069	-0.1914	0.2663	0.0409	-0.1306	0.2517
	CO_2-2	0.0202	0.1814	0.2887	0.0870	0.2104	0.2939	-0.0466	0.1524	0.2835
	CO_2-3	0.8521	-0.5372	0.4382	0.0238	-0.5586	0.4400	-0.7281	-0.5157	0.4363
7	CO_2-1	0.0245	-0.1595	0.2607	0.0078	-0.1904	0.2675	0.0412	-0.1285	0.2539
	CO_2-2	0.0033	0.1783	0.2864	0.0775	0.2066	0.2916	-0.0710	0.1500	0.2813
	CO_2-3	-0.8587	-0.5370	0.4375	0.0178	-0.5586	0.4395	-0.7352	-0.5155	0.4354
9	CO_2-1	0.0102	-0.1620	0.2631	0.0226	-0.1917	0.2709	0.0430	-0.1323	0.2553
	CO_2-2	-0.0313	0.1759	0.2850	0.0558	0.2020	0.2910	-0.1185	0.1498	0.2789
	CO_2-3	-0.8430	-0.5378	0.4355	0.0419	-0.5614	0.4363	-0.7279	-0.5142	0.4347
11	CO_2-1	0.0370	-0.1597	0.2627	0.0155	-0.1904	0.2698	0.0586	-0.1291	0.2557
	CO_2-2	-0.0168	0.1758	0.2844	0.0560	0.2038	0.2904	-0.0896	0.1479	0.2785
	CO_2-3	-0.8839	-0.5402	0.4370	0.0067	-0.5621	0.4383	-0.7610	-0.5184	0.4357
13	CO_2-1	0.0202	-0.1608	0.2644	0.0023	-0.1915	0.2714	0.0426	-0.1302	0.2573
	CO_2-2	-0.0559	0.1737	0.2835	0.0179	0.2011	0.2901	-0.1297	0.1463	0.2768
	CO_2-3	-0.8800	-0.5394	0.4370	-0.0028	-0.5613	0.4383	-0.7573	-0.5176	0.4356
15	CO_2-1	0.0282	-0.1614	0.2645	0.0054	-0.1919	0.2716	0.0510	-0.1308	0.2573
	CO_2-2	-0.0553	0.1798	0.2849	0.0233	0.2062	0.2921	-0.1339	0.1533	0.2778
	CO_2-3	-0.9656	-0.5422	0.4331	-0.0875	-0.5643	0.4342	-0.8437	-0.5201	0.4321
17	CO_2-1	0.0126	-0.1642	0.2674	0.0158	-0.1943	0.2748	0.0410	-0.1340	0.2600
	CO_2-2	-0.0874	0.1754	0.2825	0.0086	0.1992	0.2898	-0.1835	0.1517	0.2751
	CO_2-3	-0.8830	-0.5430	0.4334	-0.0040	-0.5653	0.4353	-0.7621	-0.5207	0.4334
19	CO_2-1	0.0107	-0.1650	0.2678	0.0193	-0.1950	0.2753	0.0407	-0.1351	0.2603
	CO_2-2	-0.1013	0.1752	0.2828	-0.0014	0.1982	0.2902	-0.2012	0.1521	0.2755
	CO_2-3	-0.9286	-0.5441	0.4332	-0.0490	-0.5666	0.4340	-0.8083	-0.5217	0.4325
21	CO_2-1	0.0085	-0.1663	0.2689	0.0393	-0.1963	0.2763	0.0224	-0.1363	0.2615
	CO_2-2	-0.1258	0.1743	0.2821	-0.0279	0.1978	0.2893	-0.2238	0.1508	0.2748
	CO_2-3	-0.9171	-0.5461	0.4332	-0.0374	-0.5686	0.4339	-0.7969	-0.5236	0.4324

Table S2. Fractional coordinates of the atoms of the three independent CO_2 molecules located in the channels of **Fe_2(BPEB)$_3$** at 298 K and different CO_2 loadings. The guest molecules were described as rigid bodies (see Experimental in the main text).