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

Supporting Information for

Hydrophobic dipeptide crystals: a promising Ag-free class of ultramicroporous materials showing argon/oxygen adsorption selectivity

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Excess Adsorption Data

Table S1. Excess adsorption data of N_2, O_2 and Ar, in VI, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16510	0.00476	0.16925	0.00826	0.17750	0.01137
0.50695	0.01466	0.46455	0.02286	0.44705	0.02871
0.81425	0.02355	1.23095	0.05925	0.90025	0.05664
1.81380	0.05113	2.27120	0.10578	2.05805	0.12388
3.09950	0.08570	3.33520	0.14963	3.19380	0.18329
4.34980	0.11540	4.40800	0.19088	4.33810	0.23897
5.71800	0.14616	5.46010	0.23143	5.48840	0.29021

Table S2. Excess adsorption data of N_2, O_2 and Ar, in IA, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16245	0.00614	0.16600	0.01003	0.16605	0.01128
0.50025	0.01952	0.46610	0.02895	0.46815	0.03203
0.81410	0.03222	1.23460	0.07516	1.23485	0.08207
1.80980	0.06901	2.26705	0.13299	2.22630	0.14426
3.12210	0.11622	3.36080	0.19194	3.34065	0.20948
4.33470	0.15712	4.40370	0.24282	4.40005	0.26696
5.69235	0.19790	5.46590	0.29066	5.46715	0.31900

Table S3. Excess adsorption data of N_2, O_2 and Ar, in IV, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
1.236575	0.06919	1.197925	0.09949	1.135380	0.10963
2.711740	0.14335	2.643270	0.20472	2.467635	0.22065
4.190250	0.21043	3.252615	0.24481	3.832200	0.31849
		4.174085	0.30144		

Table S4. Excess adsorption data of N_2, O_2 and Ar, in VV, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16145	0.01148	0.16065	0.01302	0.16310	0.01570
0.49685	0.03586	0.46545	0.03840	0.46485	0.04500
0.81245	0.05777	1.23520	0.09792	1.23340	0.11329
1.80800	0.12083	2.26765	0.17165	2.26650	0.19774
3.09710	0.19549	3.33775	0.24008	3.33670	0.27517
4.33860	0.25859	4.39855	0.30255	4.39670	0.34509
5.69340	0.31898	5.46215	0.36145	5.46570	0.40821

Table S5. Excess adsorption data of N_2, O_2 and Ar, in VI, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16890	0.00355	0.16390	0.00582	0.17665	0.00827
0.50090	0.01092	0.46660	0.01697	0.44650	0.02099
0.81445	0.01768	1.23150	0.04394	0.89850	0.04148
1.81030	0.03798	2.27065	0.07929	2.05580	0.09225
3.09765	0.06466	3.33550	0.11312	3.19300	0.13822
4.34370	0.08957	4.40360	0.14567	4.33940	0.18197
5.71600	0.11539	5.47050	0.17667	5.48900	0.22311

Table S6. Excess adsorption data of N_2, O_2 and Ar, in IA, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16165	0.00421	0.16665	0.00746	0.16110	0.00831
0.49715	0.01396	0.46460	0.02108	0.46420	0.02412
0.81305	0.02309	1.23210	0.05426	1.23280	0.06176
1.80660	0.05058	2.26450	0.09757	2.26550	0.11211
3.09200	0.08680	3.33500	0.14099	3.33780	0.15957
4.33740	0.11983	4.40070	0.18234	4.39780	0.20517
5.70440	0.15311	5.46595	0.22109	5.46550	0.24957

Table S7. Excess adsorption data of N_2, O_2 and Ar, in IV, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.424140	0.01725	1.215075	0.07165	1.201995	0.08657
1.718925	0.06768	2.703170	0.15121	2.647605	0.17930
3.187710	0.12031	4.172250	0.22220	4.069070	0.26061
4.853850	0.17511				

Table S8. Excess adsorption data of N_2, O_2 and Ar, in VV, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.1614	0.00856	0.16115	0.01012	0.16885	0.01271
0.49665	0.02680	0.4651	0.02925	0.4648	0.03427
0.81255	0.04335	1.2329	0.07550	1.231	0.08691
1.8071	0.09341	2.2667	0.13394	2.2662	0.15428
3.0914	0.15459	3.3359	0.18966	3.33575	0.21786
4.3383	0.20794	4.3988	0.24234	4.3971	0.27694
5.694	0.26029	5.465	0.29092	5.46545	0.33123

Table S9. Excess adsorption data of N_2, O_2 and Ar, in VI, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16630	0.00261	0.16805	0.00459	0.18690	0.00642
0.50060	0.00836	0.46650	0.01295	0.44760	0.01547
0.82100	0.01360	1.23370	0.03348	0.91385	0.03128
1.80920	0.02971	2.27040	0.06042	2.05205	0.06914
3.10940	0.05042	3.33590	0.08677	3.19230	0.10481
4.34440	0.06953	4.40630	0.11278	4.33290	0.13917
5.71700	0.08981	5.47010	0.13742	5.50225	0.17281

Table S10. Excess adsorption data of N_2, O_2 and Ar, in IA, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.15825	0.00326	0.16180	0.00520	0.16410	0.00609
0.49605	0.01102	0.46520	0.01539	0.46450	0.01768
0.81370	0.01769	1.23185	0.04032	1.23030	0.04581
1.80755	0.03859	2.26570	0.07537	2.26690	0.08306
3.09395	0.06659	3.36050	0.10815	3.33720	0.11944
4.33670	0.09175	4.40550	0.14118	4.39845	0.15514
5.70400	0.11815	5.47560	0.17227	5.46555	0.18869

Table S11. Excess adsorption data of N_2, O_2 and Ar, in IV, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
1.255430	0.03623	1.232690	0.05261	1.216250	0.06667
2.721895	0.07620	2.685640	0.11030	2.590125	0.13595
4.191800	0.11404	4.182265	0.16527	3.987230	0.20072

Table S12. Excess adsorption data of N_2, O_2 and Ar, in VV, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16195	0.00621	0.16320	0.00758	0.16740	0.00966
0.49630	0.02076	0.46430	0.02204	0.46480	0.02646
0.81360	0.03312	1.23310	0.05707	1.23695	0.06733
1.80240	0.07087	2.26660	0.10258	2.26580	0.11930
3.09090	0.11812	3.33460	0.14575	3.33880	0.16919
4.33865	0.16049	4.39810	0.18755	4.39560	0.21625
5.69555	0.20298	5.46360	0.22726	5.46300	0.26023

Absolute adsorption results

Absolute adsorption was calculated like the excess adsorption, except for the substitution of real density for apparent density in the calculation. Apparent density calculated from the experimentally determined real density and the crystallographic porosity [1].

Table S13. Absolute adsorption results of N_2, O_2 and Ar, in VI, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16510	0.00506	0.16925	0.00857	0.17750	0.01169
0.50695	0.01558	0.46455	0.023702	0.44705	0.02952
0.81425	0.02503	1.23095	0.06149	0.90025	0.05829
1.81380	0.05444	2.27120	0.10993	2.05805	0.12764
3.09950	0.09136	3.33520	0.15574	3.19380	0.18913
4.34980	0.12335	4.40800	0.19896	4.33810	0.24692
5.71800	0.15663	5.46010	0.24145	5.48840	0.30028

Table S14. Absolute adsorption results of N_2, O_2 and Ar, in IA, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16245	0.00644	0.16600	0.01033	0.16605	0.01158
0.50025	0.02043	0.46610	0.02980	0.46815	0.03288
0.81410	0.03370	1.23460	0.07741	1.23485	0.08432
1.80980	0.07230	2.26705	0.13712	2.22630	0.14832
3.12210	0.12191	3.36080	0.19808	3.34065	0.21558
4.33470	0.16502	4.40370	0.25086	4.40005	0.27500
5.69235	0.20828	5.46590	0.30066	5.46715	0.32900

Table S15. Absolute adsorption results of N_2, O_2 and Ar, in IV, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
1.236575	0.07218	1.197925	0.10239	1.135380	0.11223
2.711740	0.14991	2.643270	0.21112	2.467635	0.22631
4.190250	0.22058	3.252615	0.25269	3.832200	0.32731
		4.174085	0.31156		

Table S16. Absolute adsorption results of N_2, O_2 and Ar, in VV, at 5 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16140	0.01196	0.16065	0.01349	0.16310	0.01618
0.49685	0.03733	0.46545	0.03978	0.46485	0.04638
0.81245	0.06017	1.23520	0.10157	1.23340	0.11694
1.80800	0.12618	2.26765	0.17837	2.26650	0.20446
3.09710	0.20467	3.33775	0.24999	3.33670	0.28507
4.33860	0.27146	4.39855	0.31563	4.39670	0.35816
5.69340	0.33588	5.46215	0.37771	5.46570	0.42447

Table S17. Absolute adsorption results of N_2, O_2 and Ar, in VI, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16890	0.00384	0.16390	0.00610	0.17665	0.00857
0.50090	0.01178	0.46660	0.01778	0.44650	0.02176
0.81445	0.01909	1.23150	0.04607	0.89850	0.04304
1.81030	0.04111	2.27065	0.08322	2.05580	0.09581
3.09765	0.07003	3.33550	0.11890	3.19300	0.14376
4.34370	0.09710	4.40360	0.15332	4.33940	0.18951
5.71600	0.12531	5.47050	0.18618	5.48900	0.23266

Table S18. Absolute adsorption results of N_2, O_2 and Ar, in IA, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16165	0.00449	0.16665	0.00775	0.16110	0.00859
0.49715	0.01481	0.46460	0.02188	0.46420	0.02492
0.81305	0.02449	1.23210	0.05638	1.23280	0.06389
1.80660	0.05370	2.26450	0.10148	2.26550	0.11602
3.09200	0.09214	3.33500	0.14676	3.33780	0.16535
4.33740	0.12732	4.40070	0.18996	4.39780	0.21279
5.70440	0.16298	5.46595	0.23056	5.46550	0.25905

Table S19. Absolute adsorption results of N_2, O_2 and Ar, in IV, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.424140	0.01823	1.215075	0.07443	1.201995	0.08932
1.718925	0.07162	2.703170	0.15742	2.647605	0.18538
3.187710	0.12761	4.172250	0.23180	4.069070	0.26996
4.853850	0.18625				

Table S20. Absolute adsorption results of N_2, O_2 and Ar, in VV, at 20 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16140	0.00894	0.16115	0.01050	0.16885	0.01310
0.49665	0.02796	0.46510	0.03034	0.46480	0.03536
0.81255	0.04525	1.23290	0.07839	1.23100	0.08980
1.80710	0.09765	2.26670	0.13926	2.26620	0.15960
3.09140	0.16185	3.33590	0.19750	3.33575	0.22570
4.33830	0.21813	4.39880	0.25269	4.39710	0.28729
5.69400	0.27367	5.46500	0.30379	5.46545	0.34411

Table S21. Absolute adsorption results of N_2, O_2 and Ar, in VI, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16630	0.00288	0.16805	0.00486	0.18690	0.00672
0.50060	0.00918	0.46650	0.01372	0.44760	0.01620
0.82100	0.01495	1.23370	0.03551	0.91385	0.03278
1.80920	0.03268	2.27040	0.06416	2.05205	0.07252
3.10940	0.05554	3.33590	0.09227	3.19230	0.11008
4.34440	0.07669	4.40630	0.12006	4.33290	0.14632
5.71700	0.09924	5.47010	0.14646	5.50225	0.18190

Table S22. Absolute adsorption results of N_2, O_2 and Ar, in IA, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.15825	0.00352	0.16180	0.00546	0.16410	0.00636
0.49605	0.01227	0.46520	0.01615	0.46450	0.01844
0.81370	0.01983	1.23185	0.04234	1.23030	0.04782
1.80755	0.04362	2.26570	0.07909	2.26690	0.08679
3.09395	0.07544	3.36050	0.11368	3.33720	0.12493
4.33670	0.10419	4.40550	0.14843	4.39845	0.16238
5.70400	0.13451	5.47560	0.18129	5.46555	0.19770

Table S23. Absolute adsorption results of N_2, O_2 and Ar, in IV, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
1.255430	0.03897	1.232690	0.05530	1.216250	0.06946
2.721895	0.08213	2.685640	0.11617	2.590125	0.14189
4.191800	0.12318	4.182265	0.17441	3.987230	0.20988

Table S24. Absolute adsorption results of N_2, O_2 and Ar, in VV, at 35 ºC.

N_2		O_2		Ar	
P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}	P / bar	n / mol.kg^{-1}
0	0	0	0	0	0
0.16195	0.00665	0.16320	0.00801	0.16740	0.01010
0.49630	0.02209	0.46430	0.02328	0.46480	0.02771
0.81360	0.03529	1.23310	0.06037	1.23695	0.07063
1.80240	0.07569	2.26660	0.10865	2.26580	0.12536
3.09090	0.12638	3.33460	0.15468	3.33880	0.17813
4.33865	0.17209	4.39810	0.19933	4.39560	0.22802
5.69555	0.21821	5.46360	0.24191	5.46300	0.27488

Fitting results

Table S25. Fitting parameters determined for N_2, in VI, IA, IV and VV, at 5 ºC, 20 ºC and 35 ºC.

	n_{max} / mol.kg^{-1}	b / bar^{-1}		
		5 ºC	20 ºC	35 ºC
VI	2.54736	0.012297	0.0094729	0.0073619
IA	3.36315	0.012455	0.0093799	0.0075898
IV	2.99153	0.020315	0.014409	0.010501
VV	2.92024	0.026118	0.020331	0.015339

Table S26. Minimised sum of the squares for N_2, in VI, IA, IV and VV, at 5 ºC, 20 ºC and 35 ºC.

	VI	IA	IV	VV
5 ºC	1.734×10^{-6}	2.389×10^{-6}	7.575×10^{-6}	3.146×10^{-6}
20 ºC	2.334×10^{-6}	4.079×10^{-6}	9.196×10^{-6}	4.795×10^{-6}
35 ºC	4.129×10^{-7}	2.727×10^{-6}	5.995×10^{-6}	1.421×10^{-6}
Total	4.481×10^{-6}	9.195×10^{-6}	2.277×10^{-5}	9.363×10^{-6}

Table S27. Fitting parameters determined for O_2, in VI, IA, IV and VV, at 5 ºC, 20 ºC and 35 ºC.

	n_{max} / mol.kg^{-1}	b / bar^{-1}		
		5 ºC	20 ºC	35 ºC
VI	3.18554	0.016245	0.012081	0.0092383
IA	3.91143	0.016633	0.012179	0.0092791
IV	3.36954	0.026821	0.018863	0.013610
VV	3.61289	0.024010	0.018580	0.014082

Table S28. Minimised sum of the squares for O_2, in VI, IA, IV and VV, at 5 ºC, 20 ºC and 35 ºC.

	VI	IA	IV	VV
5 ºC	1.806×10^{-6}	3.162×10^{-6}	5.385×10^{-6}	1.419×10^{-6}
20 ºC	1.708×10^{-7}	1.375×10^{-6}	6.597×10^{-6}	4.908×10^{-7}
35 ºC	8.774×10^{-8}	4.524×10^{-6}	6.073×10^{-6}	7.004×10^{-7}
Total	2.065×10^{-6}	9.060×10^{-6}	1.805×10^{-5}	2.610×10^{-6}

Table S29. Fitting parameters determined for Ar, in VI, IA, IV and VV, at 5 ºC, 20 ºC and 35 ºC.

	n_{max} / mol.kg^{-1}	b / bar^{-1}		
		5 ºC	20 ºC	35 ºC
VI	3.17554	0.021140	0.015584	0.011701
IA	4.04617	0.017754	0.013366	0.0098906
IV	3.31336	0.031719	0.023587	0.017922
VV	3.52994	0.028729	0.022153	0.016819

Table S30. Minimised sum of the squares for Ar, in VI, IA, IV and VV, at 5 ºC, 20 ºC and 35 ºC.

	VI	IA	IV	VV
5 ºC	4.353×10^{-7}	3.145×10^{-6}	5.820×10^{-6}	1.331×10^{-6}
20 ºC	1.451×10^{-6}	1.413×10^{-6}	6.493×10^{-6}	2.427×10^{-6}
35 ºC	1.363×10^{-6}	3.735×10^{-7}	6.373×10^{-6}	5.604×10^{-7}
Total	3.250×10^{-6}	4.931×10^{-6}	1.869×10^{-5}	4.318×10^{-6}

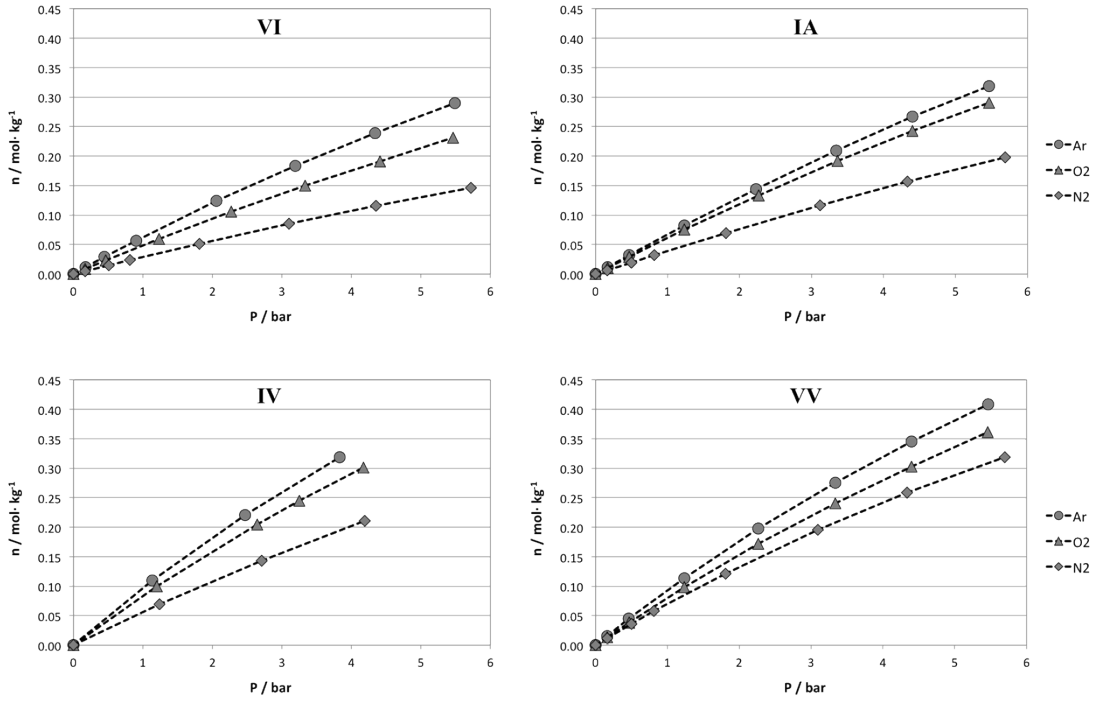

Figure S1. Excess adsorption isotherms of Ar, O_2 and N_2 on VI, IA, IV and VV, at 5 ºC, grouped per material.

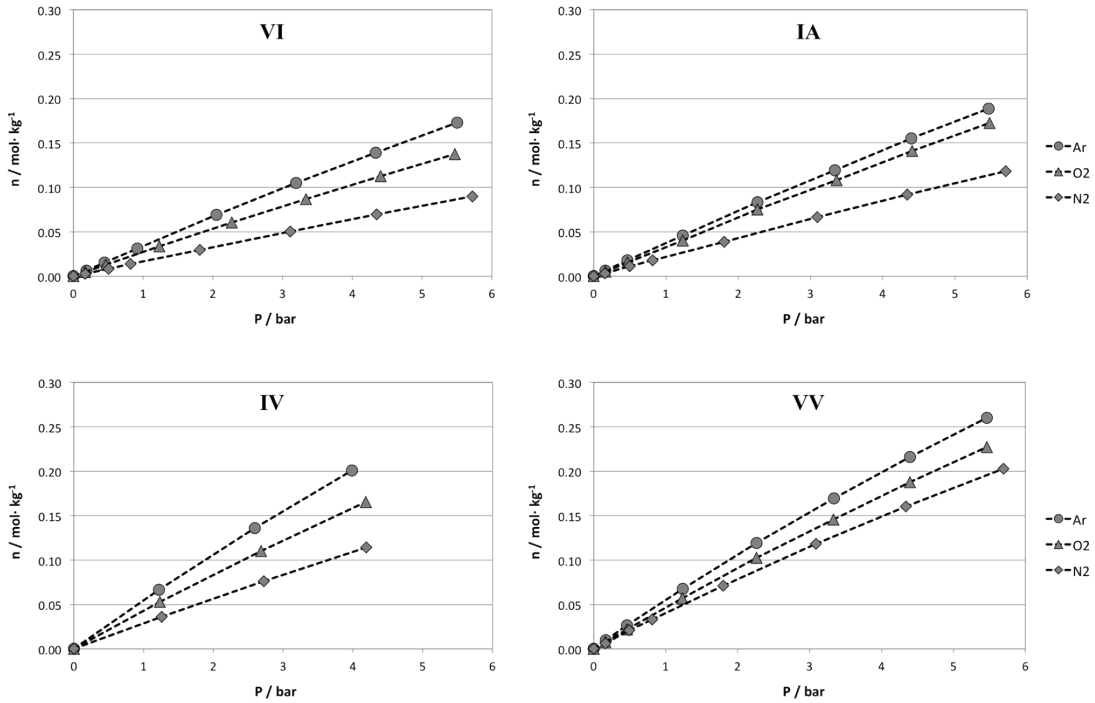

Figure S2. Excess adsorption isotherms of Ar, O_2 and N_2 on VI, IA, IV and VV, at 35 ºC, grouped per material.

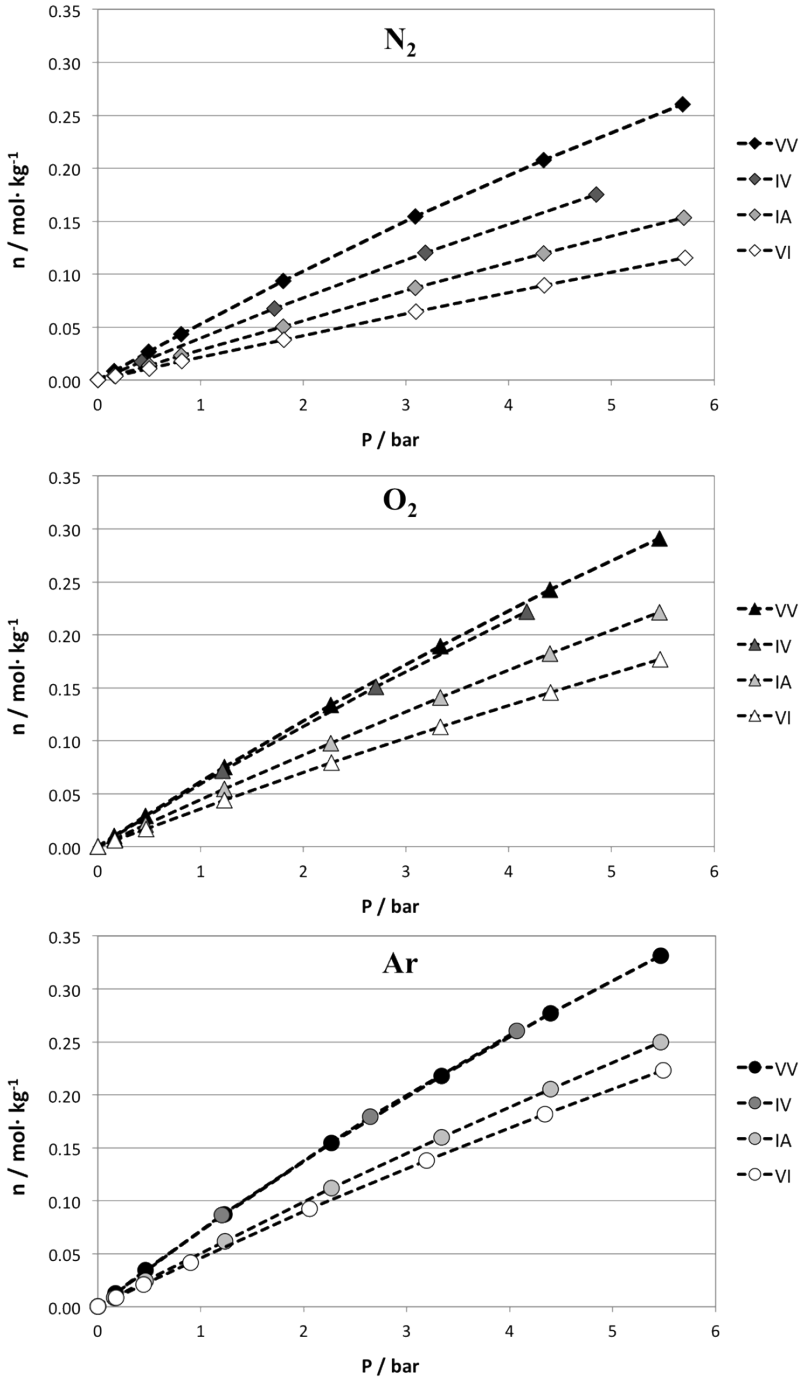

Figure S3. Excess adsorption isotherms of Ar, O_2 and N_2 on VI, IA, IV and VV, at 20 ºC, grouped per gas.

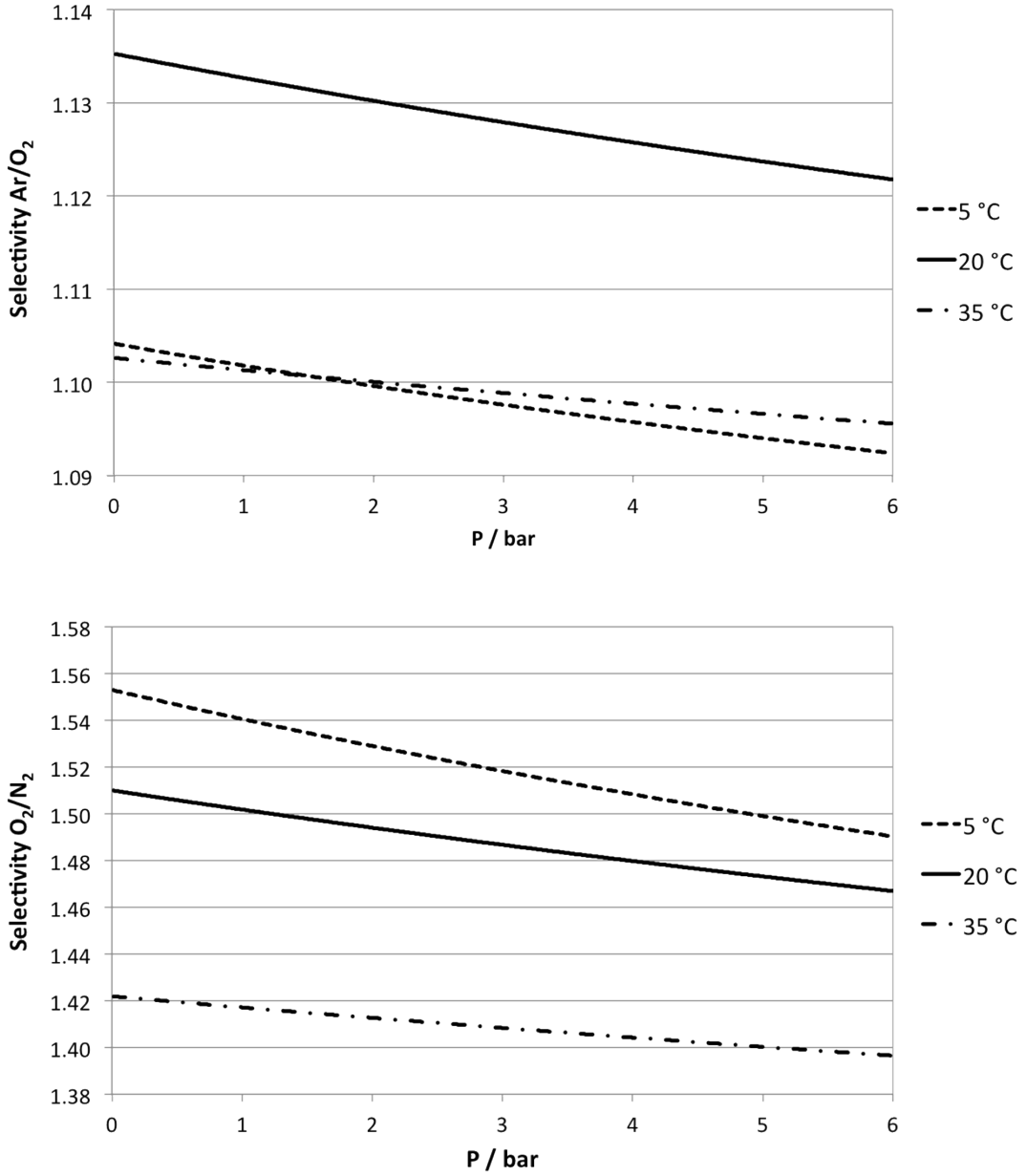

Figure S4. Variation of Ar/O_2 and O_2/N_2 selectivities with pressure, for IA, at 5 ºC, 20 ºC and 35 ºC.

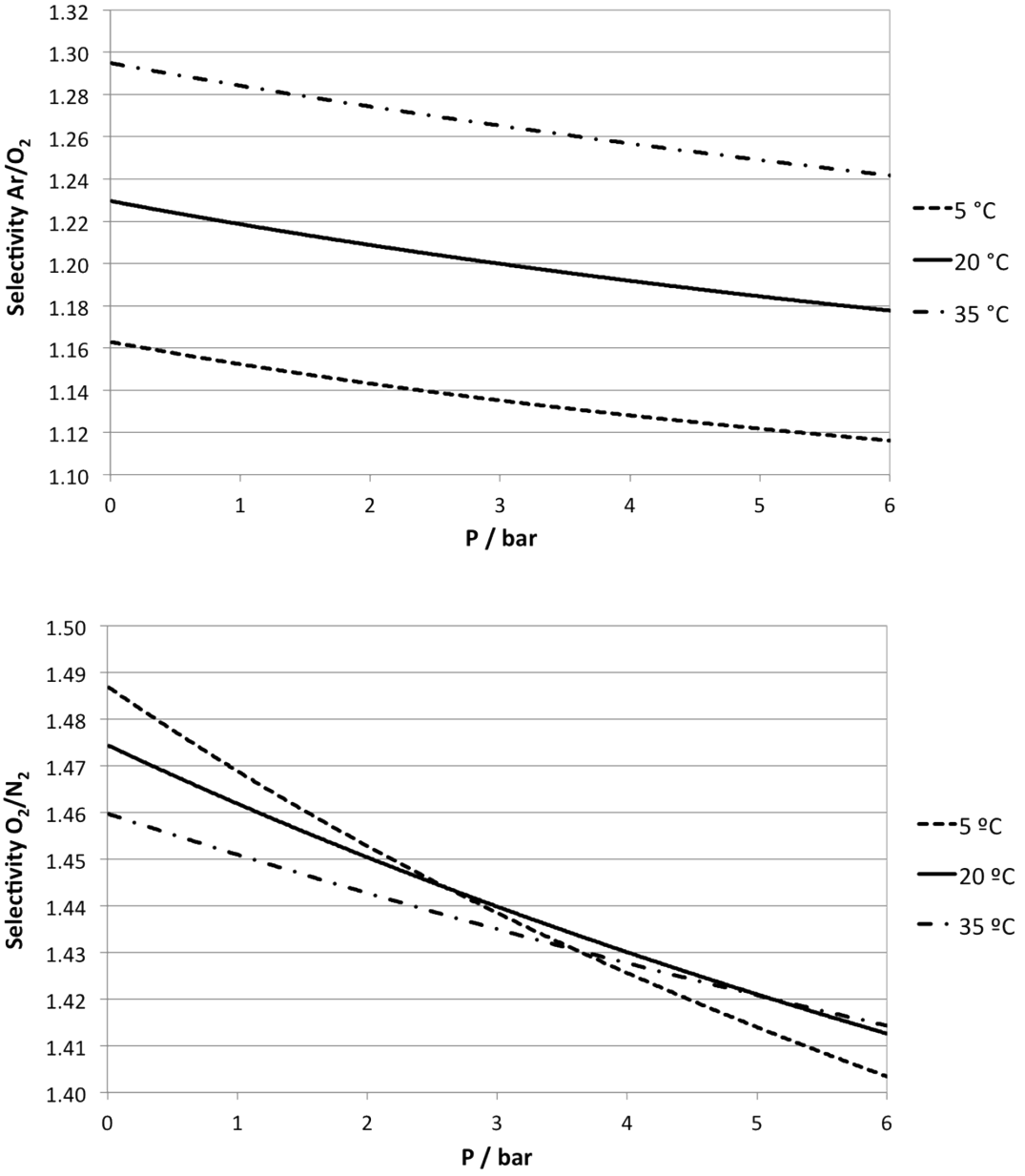

Figure S5. Variation of Ar/O_2 and O_2/N_2 selectivities with pressure, for IV, at 5 ºC, 20 ºC and 35 ºC.

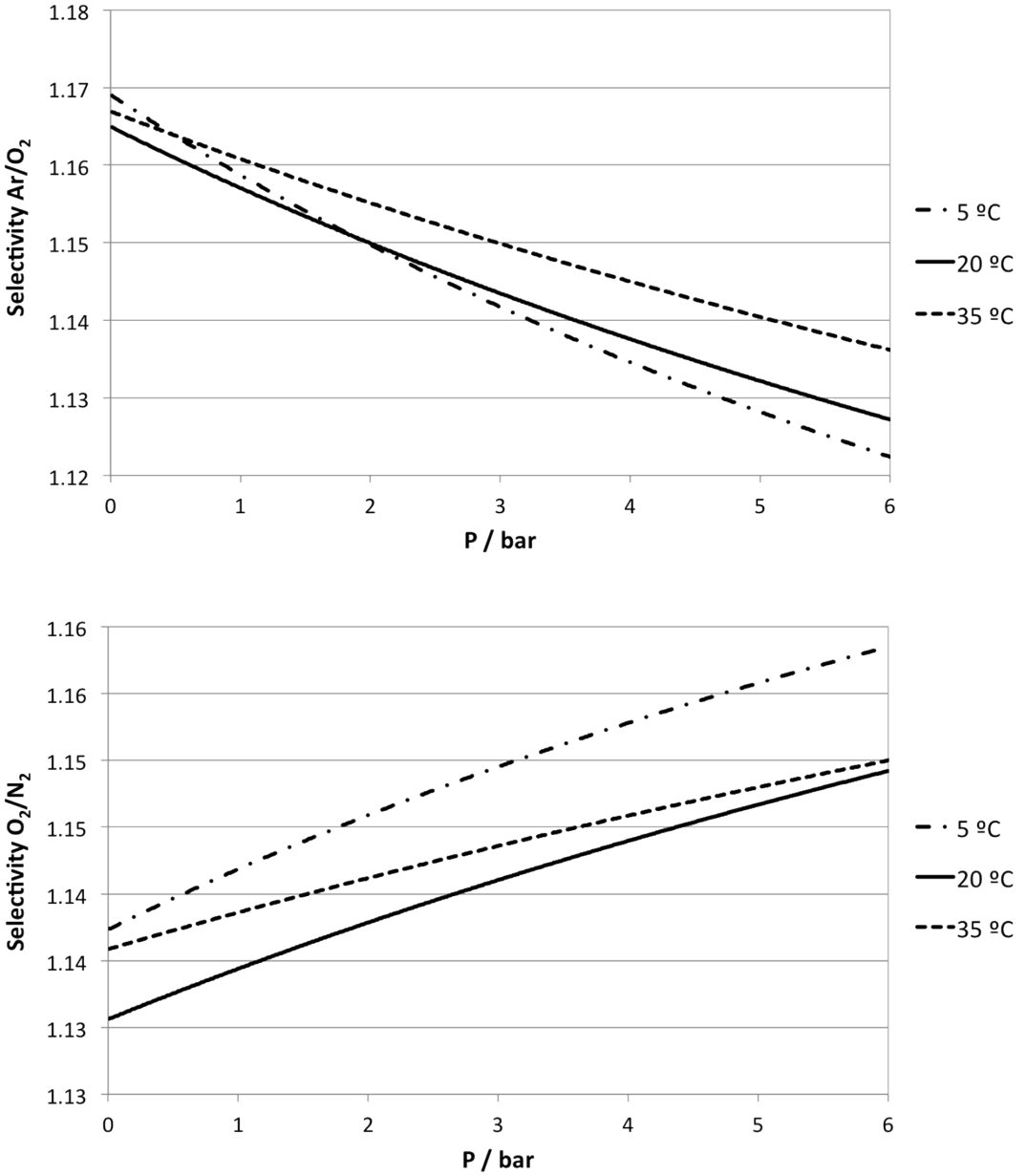

Figure S6. Variation of Ar/O_2 and O_2/N_2 selectivities with pressure, for VV, at 5 ºC, 20 ºC and 35 ºC.

Bibliography

[1] D.V. Soldatov, I.L. Moudrakovski, E.V. Grachev, J.A. Ripmeester, Micropores in Crystalline Dipeptides as Seen from the Crystal Structure, He Pycnometry, and 129Xe NMR Spectroscopy, J. Am. Chem. Soc., 128 (2006) 6737-6744.