Size exclusion effect in binary inclusion compounds of α-cyclodextrin

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Electronic Supplementary Information

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Equation used for calculation of formation Gibbs energy for an inclusion compound formed in two steps (ΔG_c)

$$\Delta G_c = (S_1 \cdot \Delta G_{c1} + S_2 \cdot \Delta G_{c2}) / (S_1 + S_2), \quad \text{(EqS1)}$$

where ΔG_{c1} and ΔG_{c2} are Gibbs energies of inclusion at first and second inclusion steps; S_1 and S_2 — guest uptake in the first and second inclusion steps, respectively.

Curves of simultaneous TG/DSC analysis for aCD hydrates prepared by saturation of anhydrous aCD with water vapors at various activities

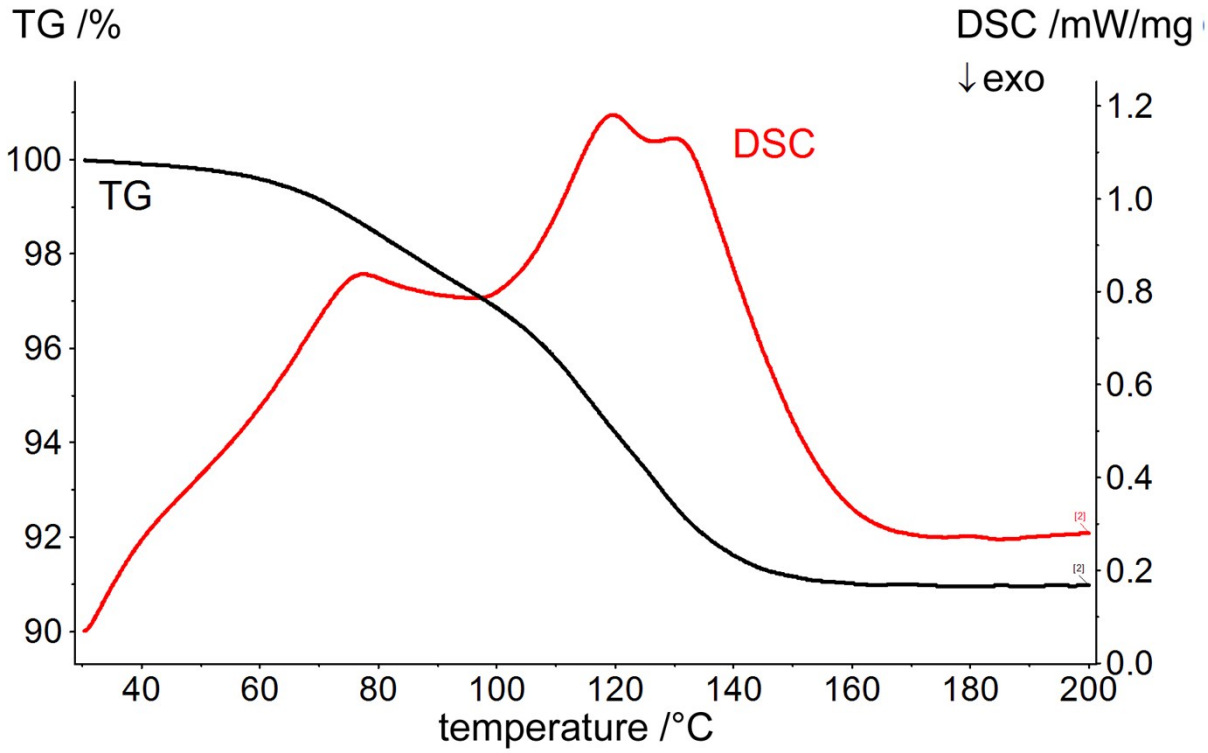

Figure S1. Curves of simultaneous TG/DSC analysis for aCD·5.3H_2O hydrate prepared by saturation of anhydrous aCD with water vapors at activity P/P_0 = 0.33 (from saturated $MgCl_2$ solution), T = 298 K.

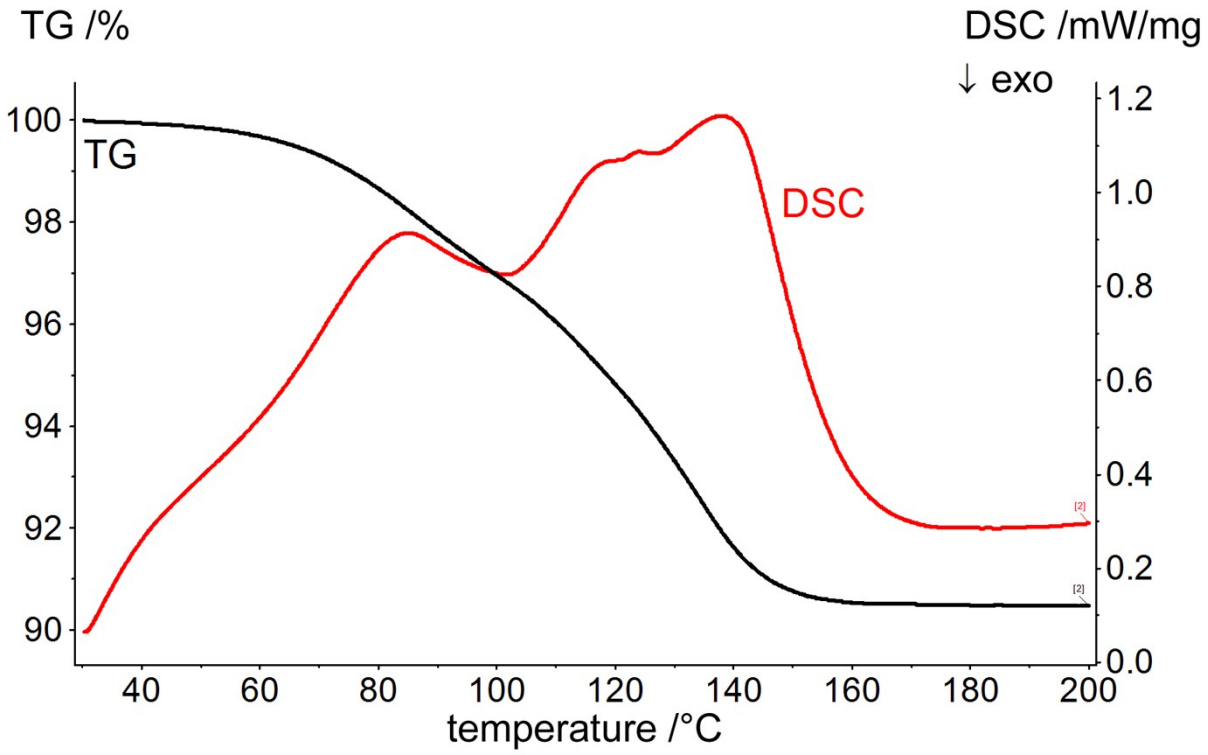

Figure S2. Curves of simultaneous TG/DSC analysis for aCD·5.9H_2O hydrate prepared by saturation of anhydrous aCD with water vapors at activity P/P_0 = 0.11 (from saturated LiCl solution), T = 298 K.

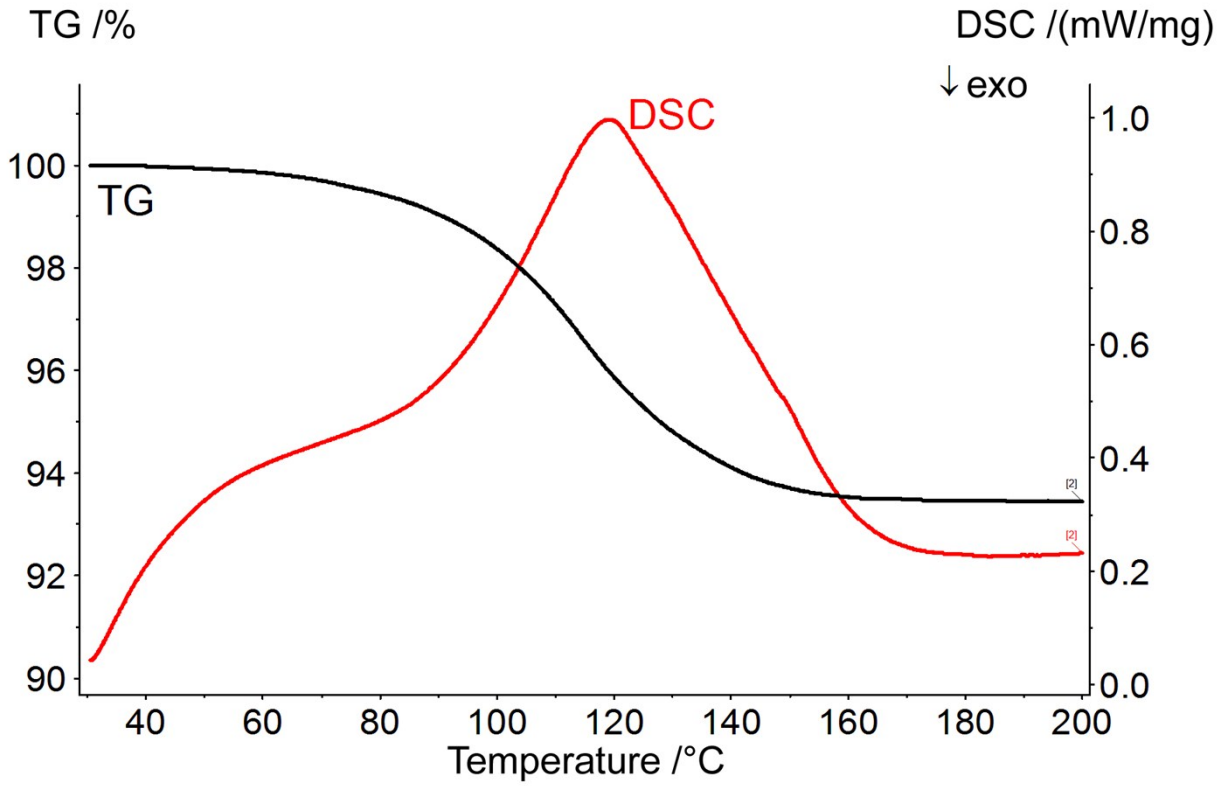

Figure S3. Curves of simultaneous TG/DSC analysis for aCD·3.8H_2O hydrate prepared by saturation of anhydrous aCD with water vapors at activity P/P_0 = 0.082 (from saturated KOH solution), T = 298 K.

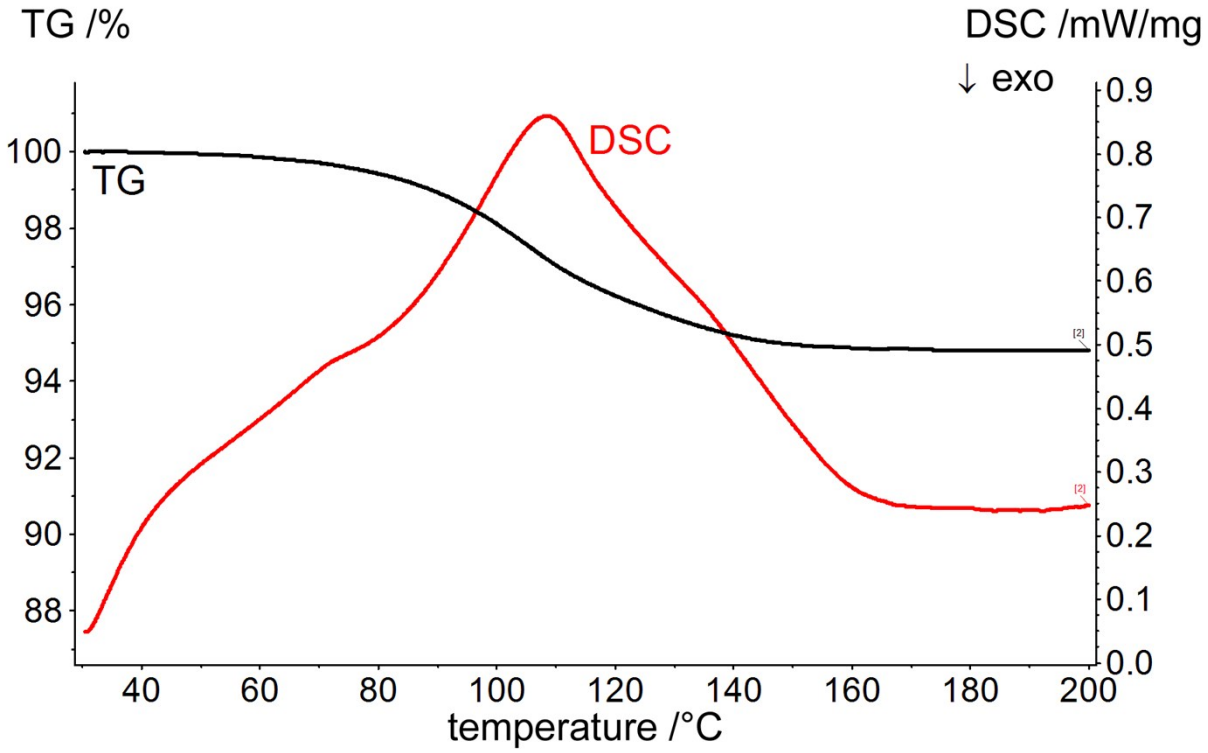

Figure S4. Curves of simultaneous TG/DSC analysis for aCD·2.9H_2O hydrate prepared by saturation of anhydrous aCD with water vapors at activity P/P_0 = 0.078 (from saturated $ZnBr_2$ solution), T = 298 K.

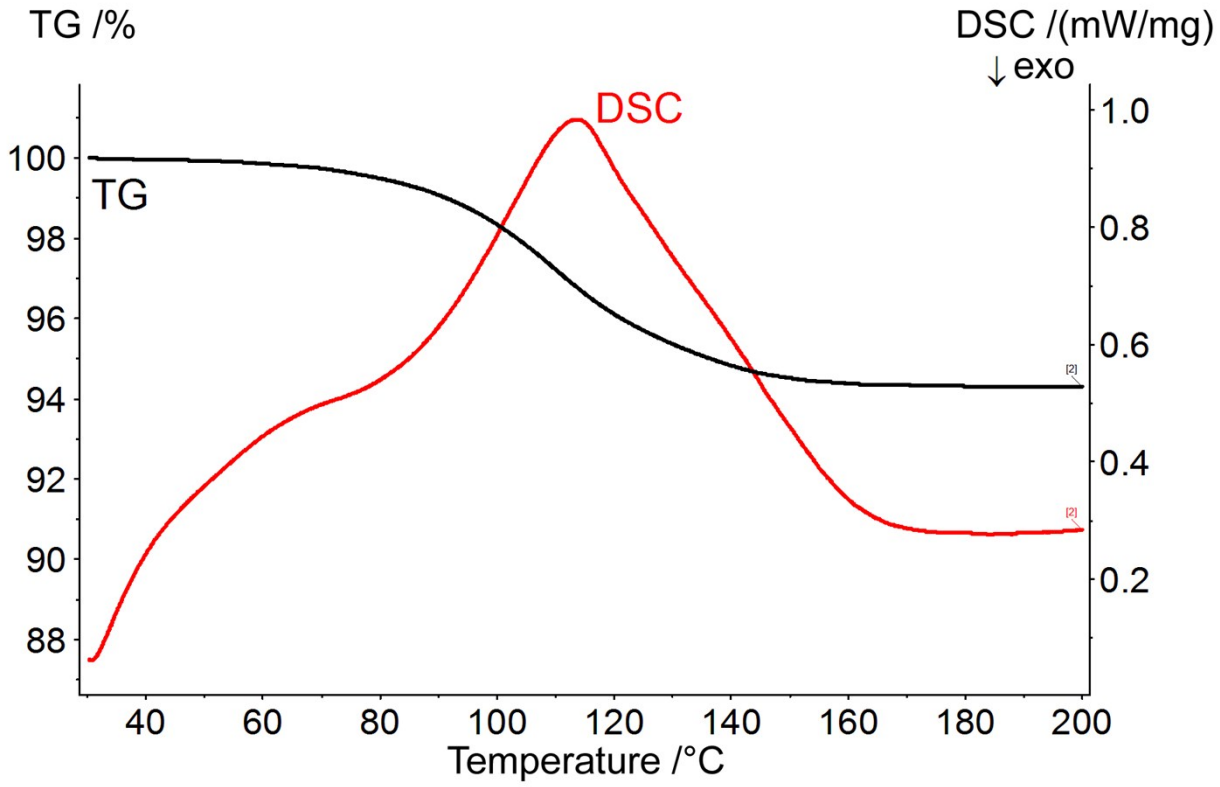

Figure S5. Curves of simultaneous TG/DSC analysis for aCD·3.2H_2O hydrate prepared by saturation of anhydrous aCD with water vapors at activity P/P_0 = 0.064 (from saturated LiBr solution), T = 298 K.

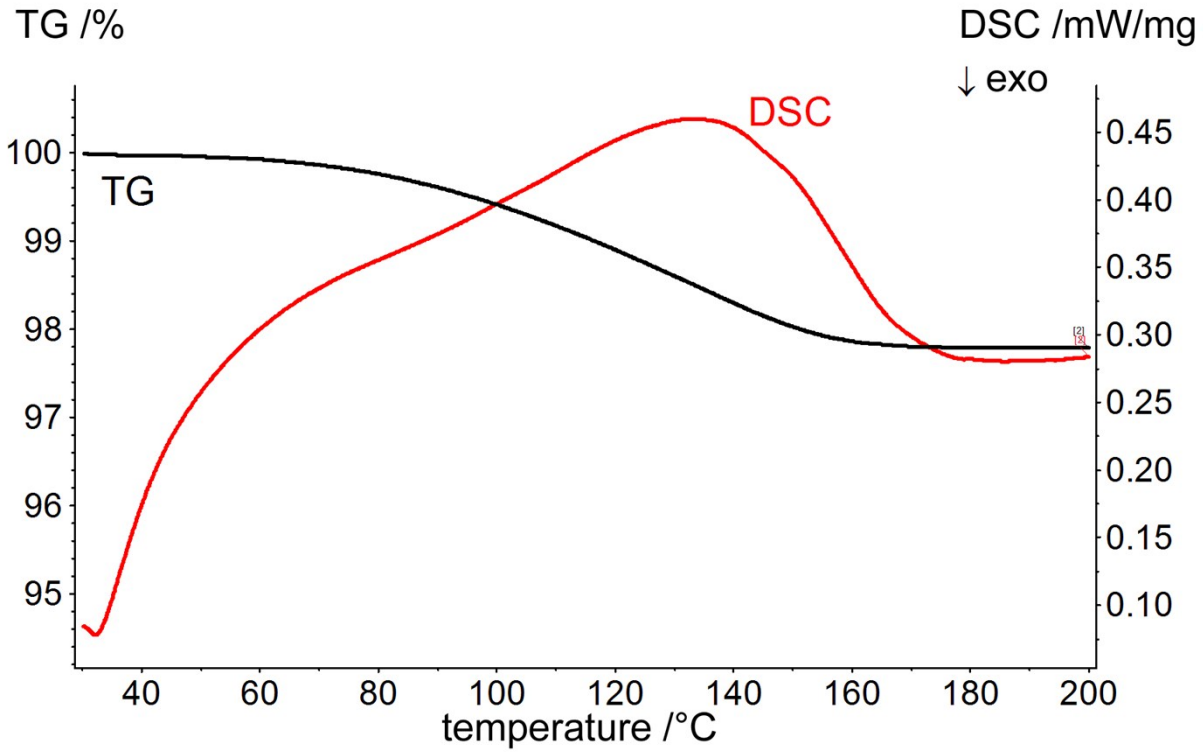

Figure S6. Curves of simultaneous TG/DSC analysis for aCD·1.2H_2O hydrate prepared by saturation of anhydrous aCD with water vapors at activity P/P_0 = 0.034 (from saturated CsF solution), T = 298 K.

Data of TG/DSC/MS analysis for aCD hydrates prepared by saturation of anhydrous aCD with water vapors at various humidities

Table S1. Data of TG/DSC/MS analysis for aCD hydrates prepared by equilibration of dried aCD with water vapors created by saturated salt solutions.

Water activity, P/P_0	Δm/ %	A_h/ mol water per mol aCD	T_{max}/°C	Dehydration enthalpy, kJ per mol H_2O	ΔH_{hydr} [a]/ kJ per mol H_2O
1	9.8	5.9	81;111	50	9
0.328	9.0	5.3	81;115;127	51	11
0.113	9.5	5.9	87;116;134	54	13
0.082	6.5	3.8	114	48	7
0.077	5.2	2.9	106	47	7
0.063	5.9	3.2	110	50	9
0.035	2.2	1.2	132	48	8

[a] The enthalpy of hydrate formation from anhydrous aCD and liquid water, calculated by equation: $\Delta H_{hydr} = \Delta H_{dehydr} - \Delta H_{vap}$. The enthalpy of water vaporization ΔH_{vap} = 40.7 (kJ per mol H_2O) is taken at 373K [1]. The error of ΔH_{dehydr} and ΔH_{hydr} determination is ±3 kJ/mol.

Dependence of dehydration enthalpies on aCD hydration for hydrates prepared by saturation of anhydrous aCD with water vapors at various humidities

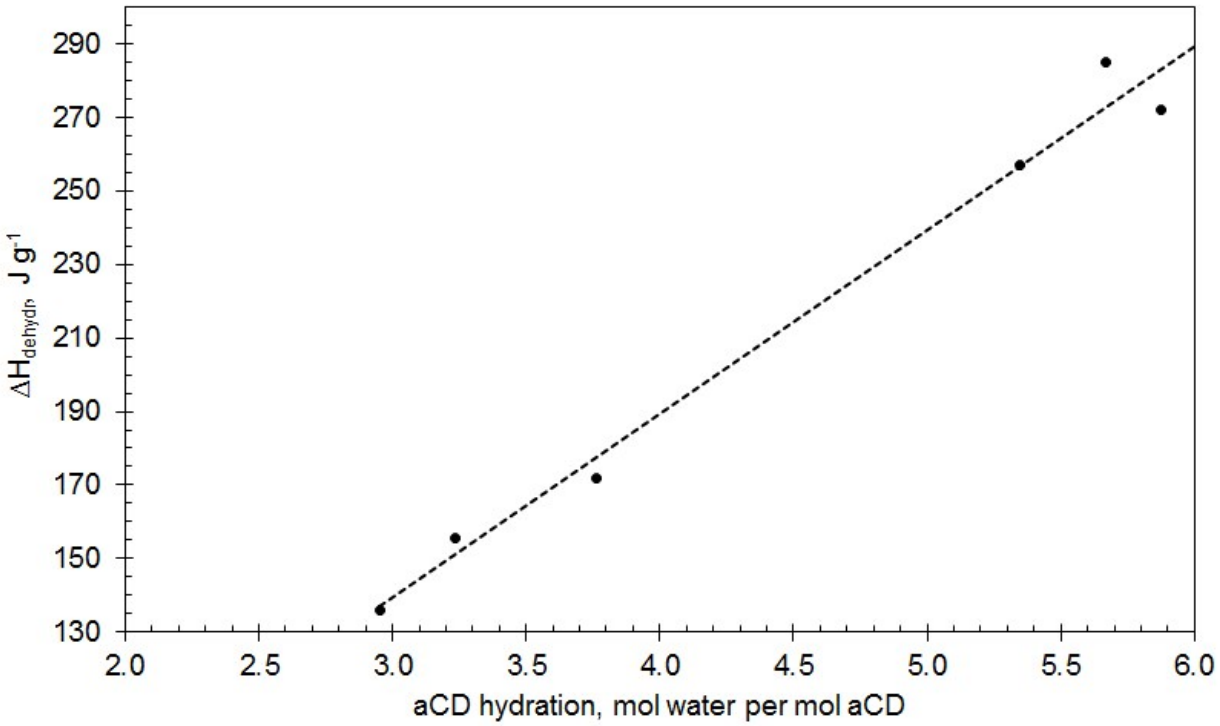

Figure S7. Dehydration enthalpies of aCD hydrates with various hydration. Extrapolation to saturated hexahydrate aCD·6H_2O gives the dehydration enthalpy of 289 J g^{-1} or 52 kJ per mol aCD.

DSC curves for dried aCD, its saturated hydrate and clathrates with organic guests

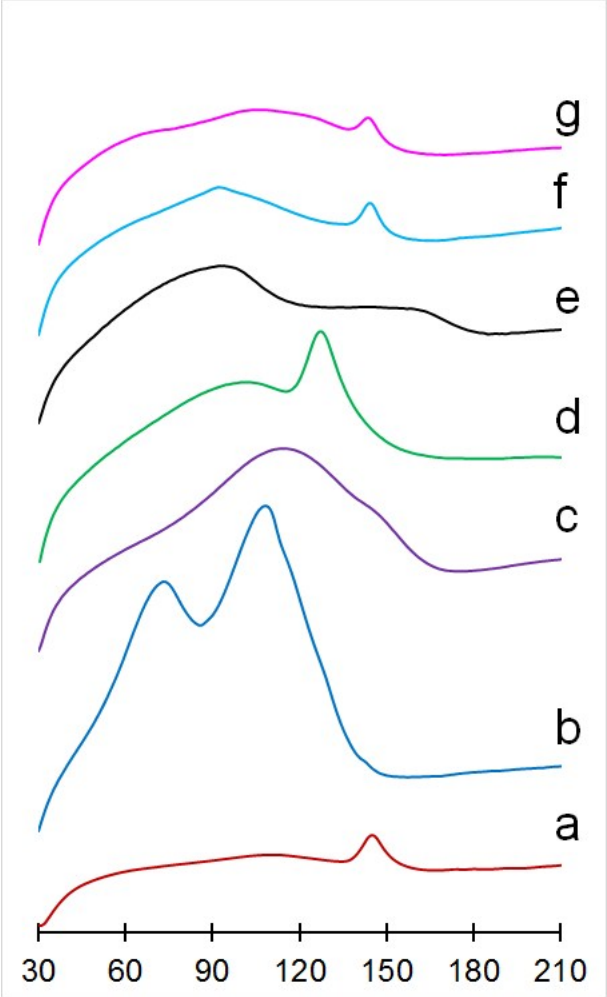

Figure S8. DSC curves for: (a) dried aCD; (b) saturated hydrate aCD·5.9H_2O; (c) aCD·3.3MeOH; (d) aCD·2.2EtOH; (e) aCD·1.9MeCN; (f) aCD·1.0*n*-PrOH; (g) aCD·1.2*i*-PrOH.

Enthalpies of guest release from aCD clathrates with organic guests

Table S2. Enthalpies of guest release from aCD clathrates with organic guests (TG/DSC data).

Guest	Enthalpy of guest release/ $J \cdot g^{-1}$	Enthalpy of guest release/ kJ per mol of guest	Enthalpy of liquid guest vaporization /$kJ \cdot mol^{-1}$ (Ref. [1])
MeOH	135	44±4	37.6
EtOH	112	50±5	42.3
n-PrOH	54.6	59±6	47.0
i-PrOH	56	54±6	45.0

Curves of simultaneous TG/MS analysis for products of equilibration of anhydrous aCD with saturated guest vapors

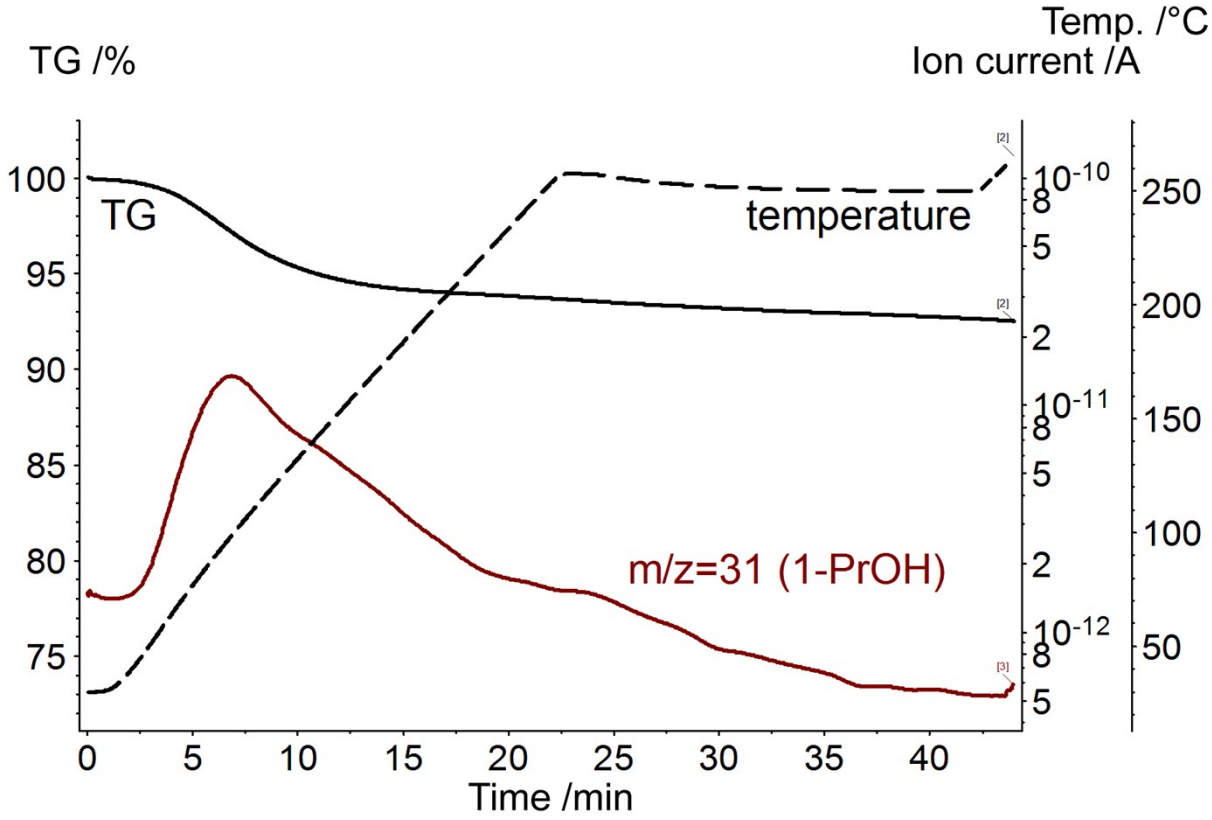

Figure S9. Curves of simultaneous TG/MS analysis for aCD·1.0*n*-PrOH clathrate prepared by equilibration of anhydrous aCD with saturated 1-propanol vapors at 298 K.

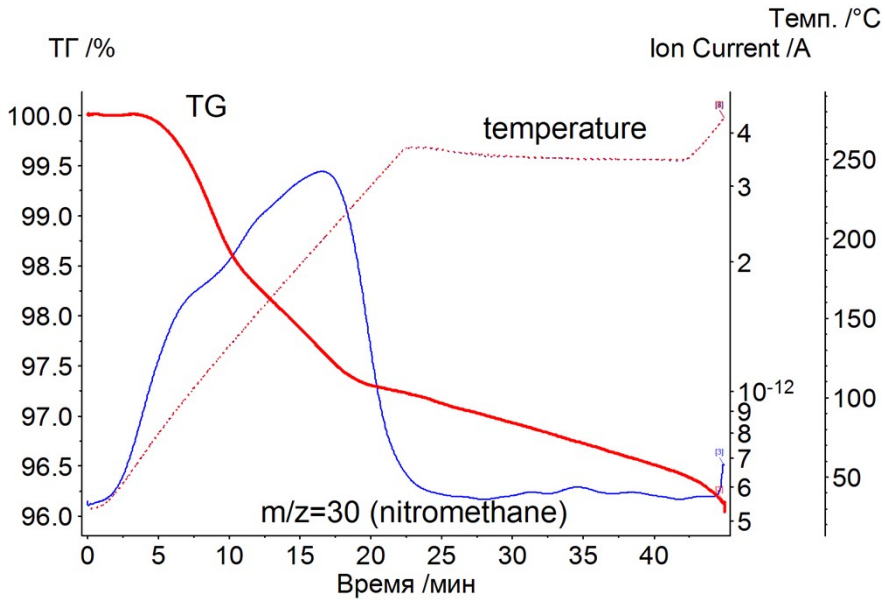

Figure S10. Curves of simultaneous TG/MS analysis for aCD-nitromethane clathrate prepared by equilibration of anhydrous aCD with saturated nitromethane vapors at 298 K.

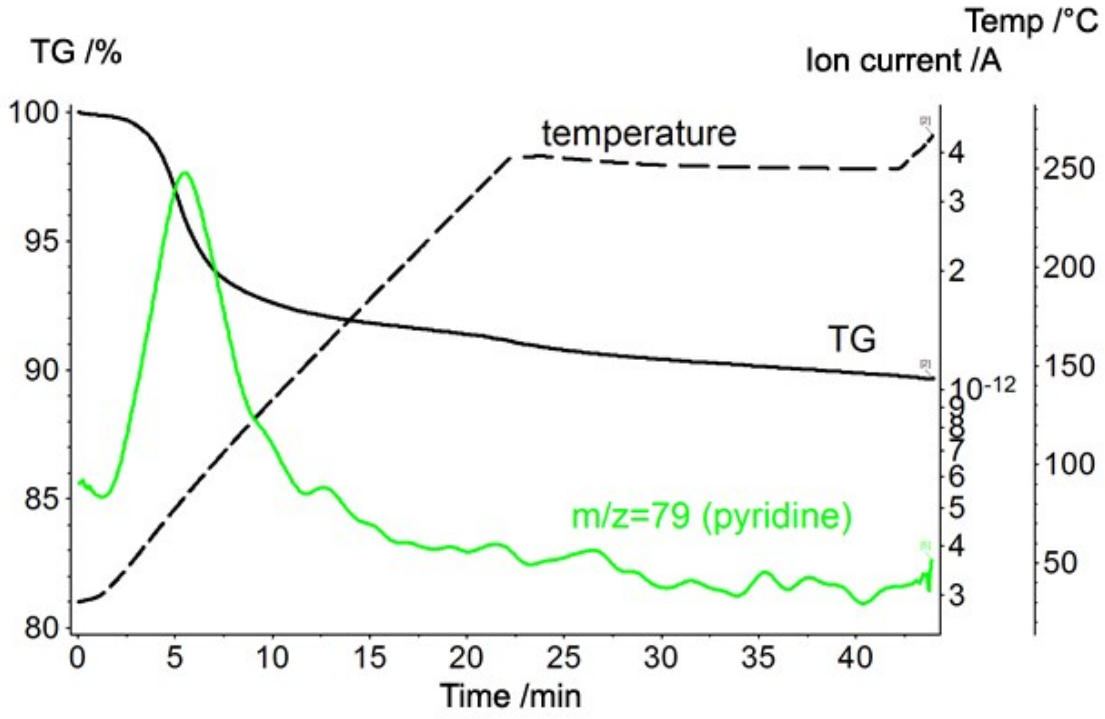

Figure S11. Curves of simultaneous TG/MS analysis for aCD·0.9C_5H_5N clathrate prepared by equilibration of anhydrous aCD with saturated pyridine vapors at 298 K.

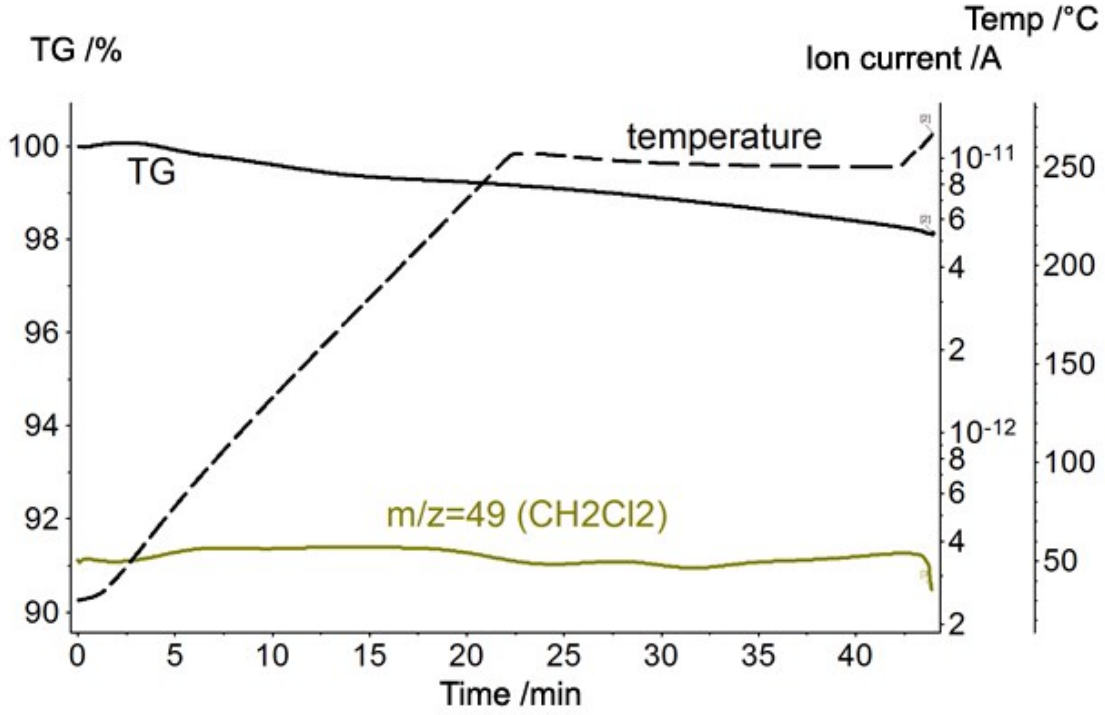

Figure S12. Curves of simultaneous TG/MS analysis for aCD·0.1CH_2Cl_2 clathrate prepared by equilibration of anhydrous aCD with saturated CH_2Cl_2 vapors at 298 K.

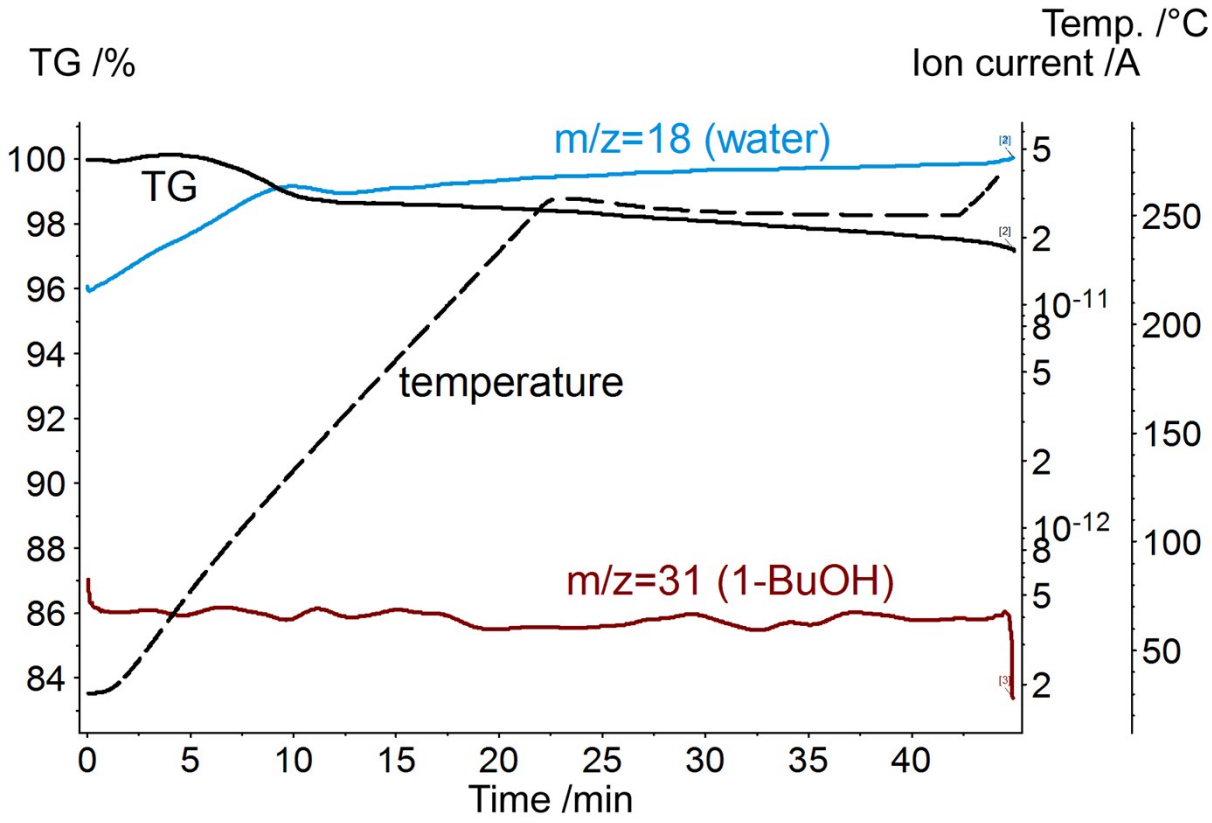

Figure S13. Curves of simultaneous TG/MS analysis for equilibration product of anhydrous aCD with saturated 1-BuOH vapors at 298 K. No 1-BuOH inclusion is observed.

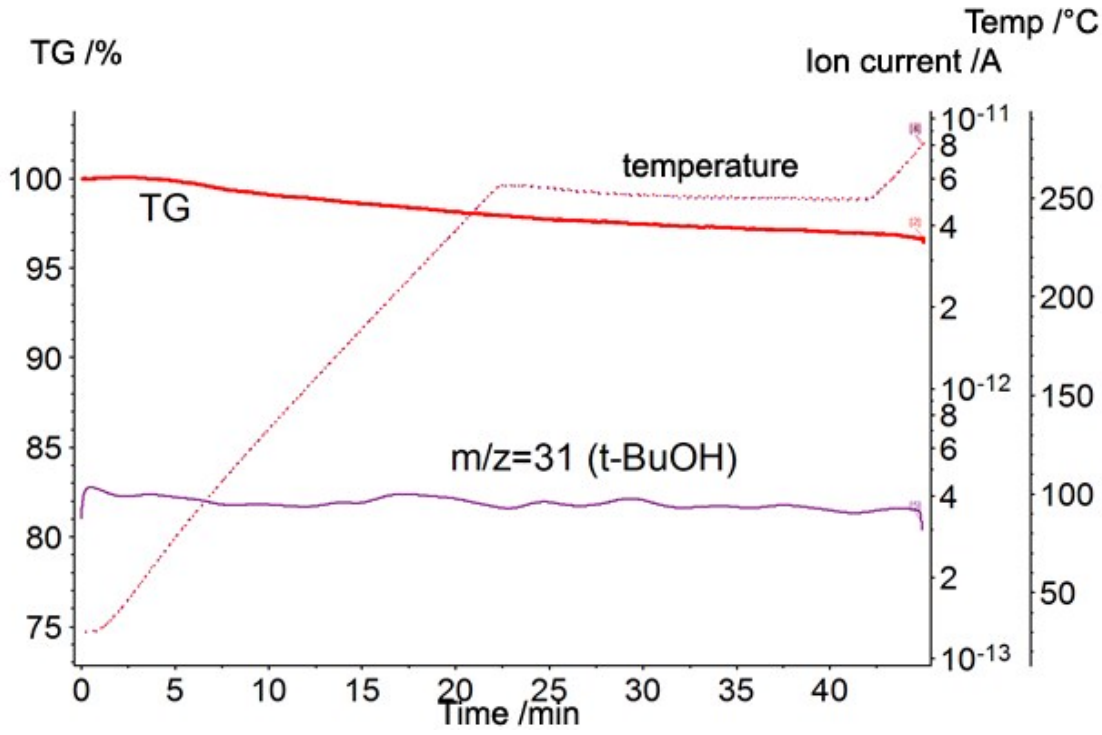

Figure S14. Curves of simultaneous TG/MS analysis for equilibration product of anhydrous aCD with saturated *t*-BuOH vapors at 298 K. No *t*-BuOH inclusion is observed.

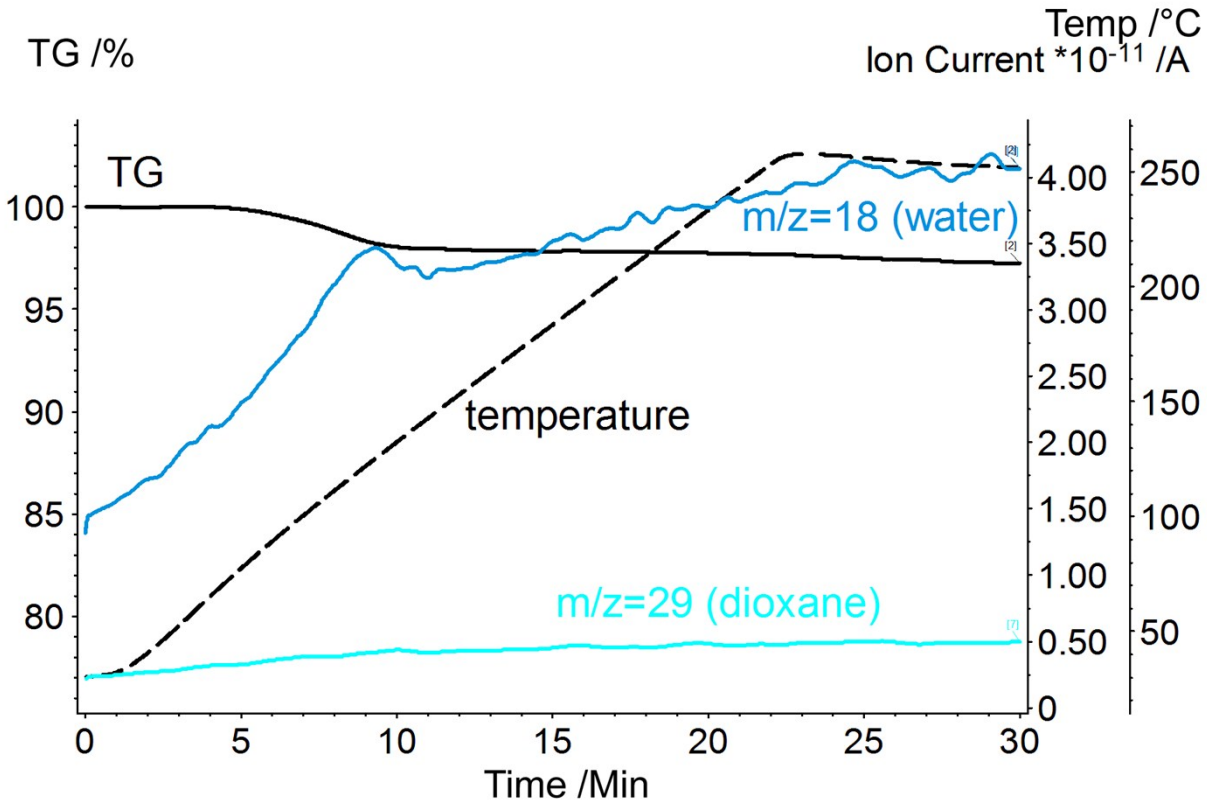

Figure S15. Curves of simultaneous TG/MS analysis for equilibration product of anhydrous aCD with saturated *1,4*-dioxane vapors at 298 K. No dioxane inclusion is observed.

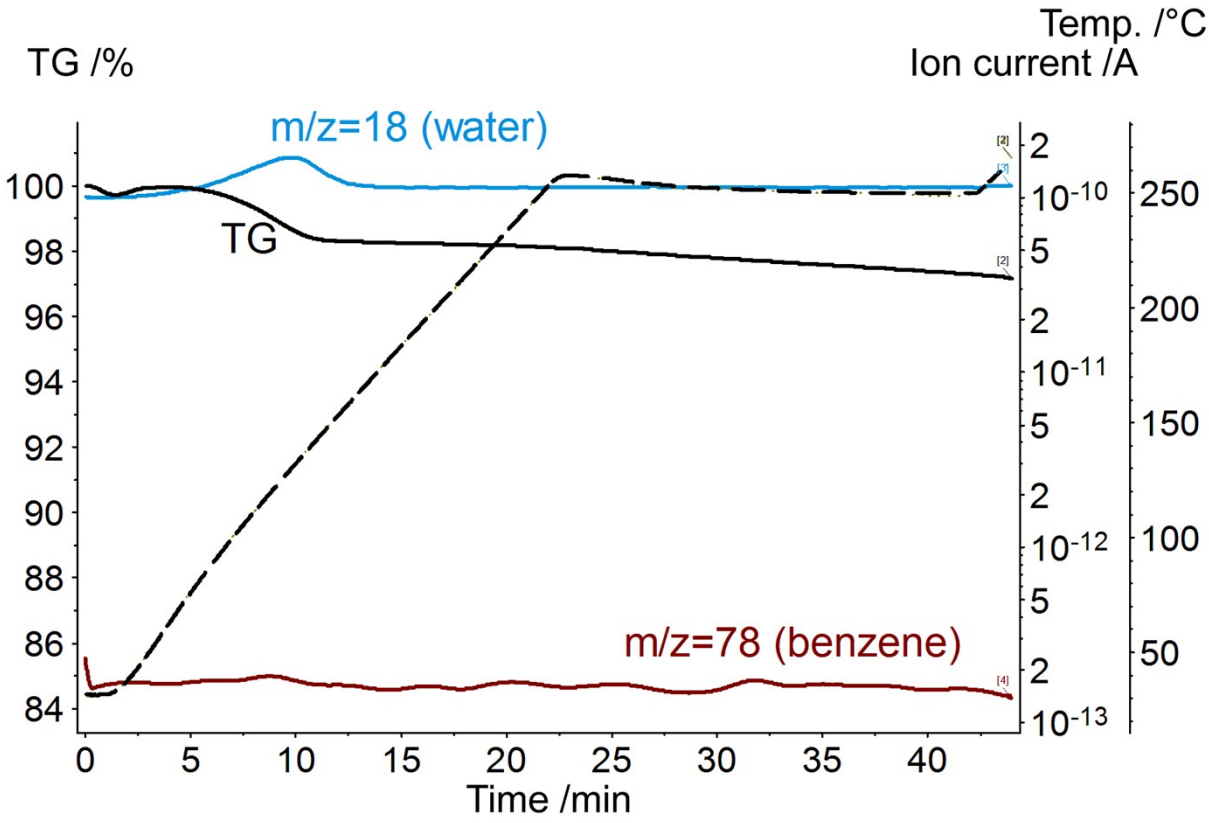

Figure S16. Curves of simultaneous TG/MS analysis for equilibration product of anhydrous aCD with saturated benzene vapors at 298 K. No benzene inclusion is observed.

Powder diffractograms of dried aCD and its saturated hydrates

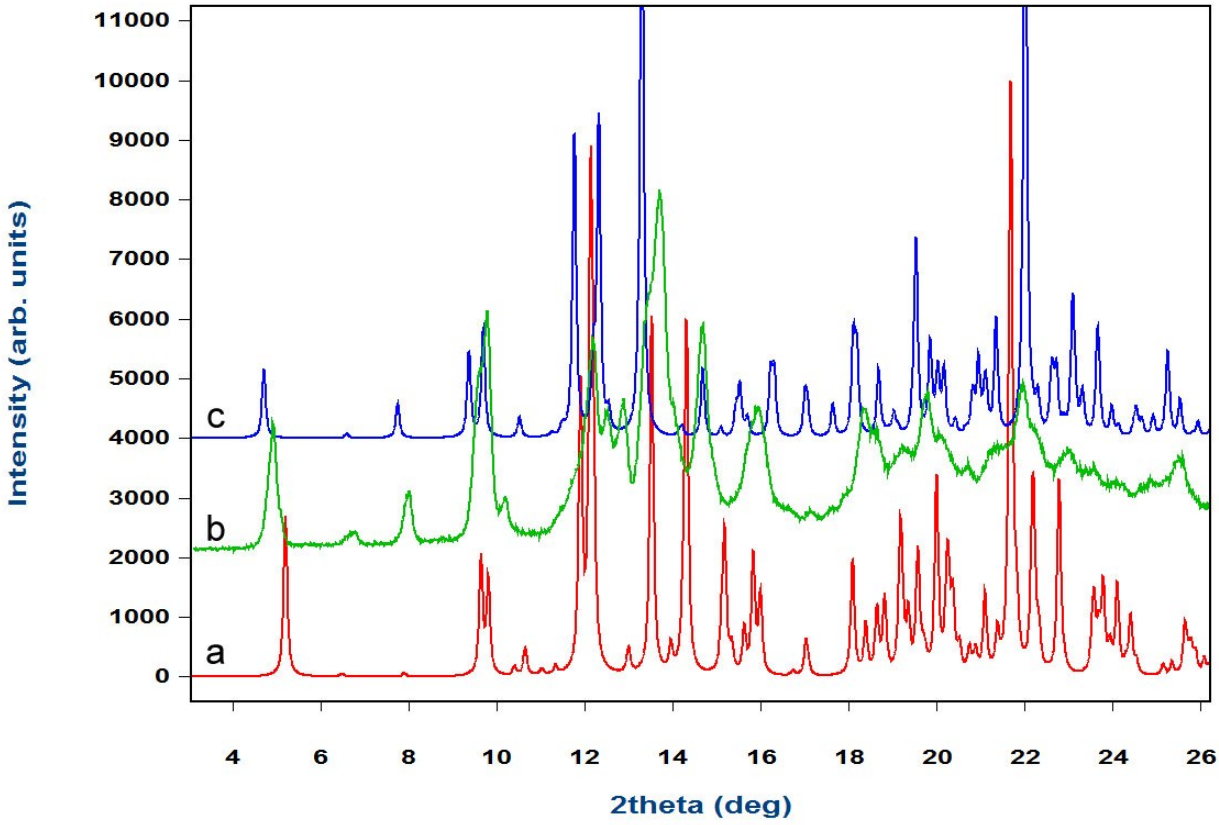

Figure S17. Powder diffractograms of (a) hydrate aCD·6H_2O simulated from SCXRD data [2], (b) anhydrous aCD, (c) hydrate aCD·7.57H_2O simulated from SCXRD data [3].

Powder diffractograms of aCD clathrates with MeCN

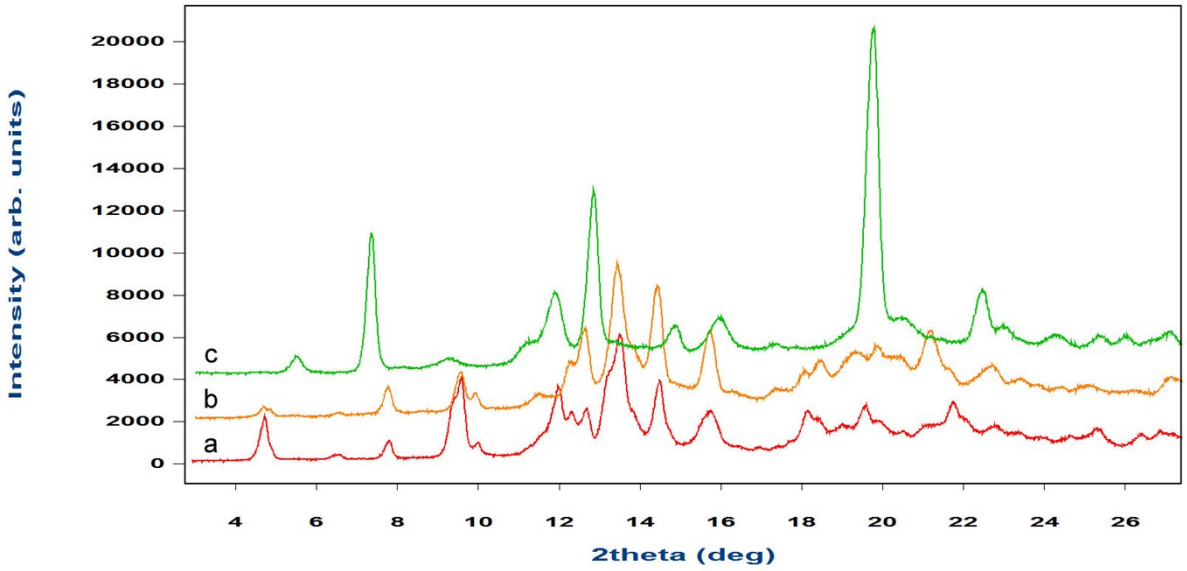

Figure S18. Powder diffractograms of (a) dry aCD, (b) intermediate aCD·1.0MeCN clathrate prepared at MeCN activity $P/P_0 = 0.31$, (c) saturated aCD·1.9MeCN clathrate prepared at MeCN activity $P/P_0 = 1$.

Powder diffractograms of aCD clathrates with MeOH

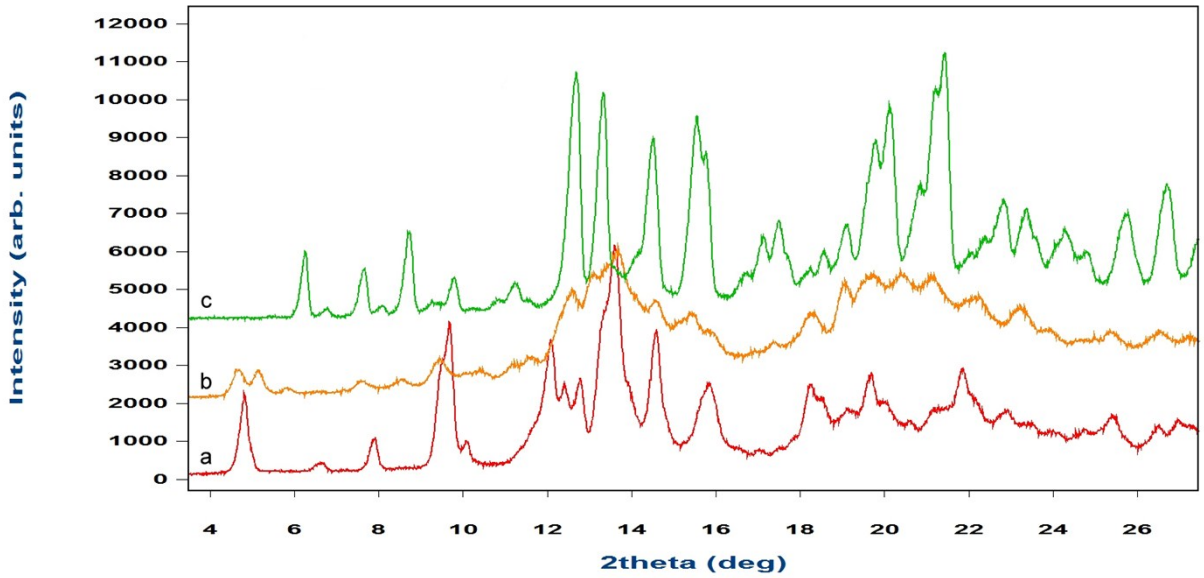

Figure S19. Powder diffractograms of (a) dry aCD, (b) intermediate aCD·3.2MeOH clathrate prepared at MeOH activity $P/P_0 = 0.22$, (c) saturated aCD·3.3MeOH clathrate prepared at MeOH activity $P/P_0 = 1$.

XRPD data tables

In this chapter, the following powder X-ray diffraction data is given: peak positions (2θ), estimated standard deviation (ESD) of peak position, corresponding interplanar distances, full width at half maximum (FWHM) of peaks, relative height. Peaks of a silicon powder diffraction standard reference are marked in notes.

Table S3. PXRD data on dried aCD.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	4.930	0.003	17.910	0.2749	15.15	
2	6.759	0.016	13.067	0.2515	1.56	
3	8.022	0.005	11.012	0.2151	6.62	
4	9.581	0.005	9.224	0.2095	10.14	
5	9.809	0.003	9.010	0.2913	30.16	
6	10.221	0.005	8.647	0.1951	4.34	
7	12.227	0.006	7.233	0.4904	17.01	
8	12.505	0.014	7.073	0.4577	15.74	
9	12.891	0.007	6.861	0.2648	16.66	
10	13.435	0.009	6.585	0.8222	30.13	
11	13.748	0.006	6.436	0.2378	21.99	
12	14.645	0.005	6.043	0.3615	23.22	
13	15.955	0.008	5.550	0.5968	15.12	
14	18.346	0.011	4.832	0.3273	11.04	
15	18.654	0.043	4.753	0.2753	6.38	
16	19.189	0.047	4.622	0.6163	4.28	
17	19.770	0.012	4.487	0.2653	9.78	
18	20.145	0.026	4.404	0.311	4.48	
19	21.304	0.051	4.167	0.6051	2.48	
20	21.962	0.013	4.044	0.2785	10.15	
21	22.277	0.014	3.987	0.2648	4.37	
22	23.010	0.032	3.862	0.3136	2.86	
23	25.551	0.032	3.483	0.3348	4.09	
24	26.596	0.035	3.349	0.204	2.65	
25	27.084	0.038	3.290	0.5169	3.21	
26	28.441	0.001	3.136	0.1772	100	Si(111)

27	29.140	0.039	3.062	1.0561	1.13	
28	31.364	0.032	2.850	0.5275	3.13	
29	33.121	0.030	2.702	0.2823	2.18	
30	33.889	0.025	2.643	0.3069	2.73	
31	34.580	0.028	2.592	0.3643	2.38	
32	37.055	0.013	2.424	0.3039	1.39	
33	39.973	0.035	2.254	1.6962	0.8	

Table S4. PXRD data on aCD·5.9H_2O hydrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	5.200	0.003	16.981	0.1712	4.71	
2	7.740	0.040	11.413	1.8261	0.14	
3	9.611	0.005	9.194	0.2838	4.3	
4	10.412	0.009	8.489	0.2815	0.62	
5	11.873	0.006	7.448	0.229	11.91	
6	12.085	0.005	7.317	0.2403	18.65	
7	13.451	0.003	6.577	0.2226	11.74	
8	13.550	0.091	6.529	2.0747	1.31	
9	14.128	0.017	6.263	0.2187	3.36	
10	14.277	0.004	6.199	0.2102	18.1	
11	15.094	0.007	5.865	0.2697	7.1	
12	15.583	0.025	5.682	0.0781	1.85	
13	15.779	0.010	5.612	0.4216	7.43	
14	16.984	0.022	5.216	0.2695	1.36	
15	18.016	0.019	4.920	0.195	3.62	
16	18.305	0.052	4.843	0.1923	1.26	
17	18.643	0.028	4.756	0.3144	2.31	
18	19.085	0.016	4.646	0.279	6.93	
19	19.485	0.026	4.552	0.2388	3.35	
20	19.929	0.014	4.452	0.2302	8.07	
21	20.206	0.024	4.391	0.1983	4.19	
22	21.594	0.006	4.112	0.2871	24.23	

23	22.086	0.012	4.021	0.2697	7.39	
24	22.689	0.011	3.916	0.2224	6.77	
25	23.510	0.015	3.781	0.3703	5.28	
26	24.063	0.010	3.695	0.589	4.04	
27	25.600	0.017	3.477	0.3726	3.85	
28	27.248	0.024	3.270	0.3636	4.39	
29	27.680	0.046	3.220	0.3559	2.33	
30	28.441	0.002	3.136	0.0964	100	Si(111)
31	30.221	0.044	2.955	0.76	2.25	
32	31.733	0.052	2.817	0.4028	1.44	
33	32.295	0.027	2.770	0.3825	1.45	
34	32.899	0.036	2.720	0.3749	2.49	
35	33.222	0.012	2.695	0.25	2.4	
36	35.082	0.024	2.556	0.3292	3.63	
37	35.481	0.031	2.528	0.2511	1.59	
38	36.110	0.034	2.485	0.2188	0.99	
39	36.992	0.024	2.428	0.5376	2.44	
40	37.505	0.021	2.396	0.3339	0.96	
41	38.621	0.015	2.329	0.3957	2.7	
42	39.610	0.022	2.273	0.3956	2.27	
43	41.144	0.015	2.192	1.1486	0.88	
44	42.658	0.013	2.118	0.4835	0.85	
45	44.506	0.028	2.034	0.3177	0.96	
46	47.292	0.001	1.920	0.0955	72.43	Si(220)
47	53.456	0.025	1.713	0.5954	0.36	
48	56.113	0.001	1.638	0.0986	42.01	Si(311)

Table S5. PXRD data on aCD·3.3MeOH clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	6.439	0.003	13.715	0.1874	15.68	
2	6.968	0.010	12.676	0.1824	2.05	

3	7.809	0.004	11.312	0.22	11.46	
4	8.251	0.012	10.707	0.2409	2.85	
5	8.897	0.003	9.932	0.2379	20.56	
6	9.496	0.024	9.305	0.3498	2.09	
7	9.957	0.006	8.876	0.2129	7.67	
8	10.969	0.035	8.060	0.2548	2.53	
9	11.372	0.019	7.774	0.2756	5.44	
10	12.884	0.003	6.865	0.3067	61.13	
11	13.491	0.004	6.558	0.2736	53.08	
12	14.667	0.004	6.035	0.2987	48.29	
13	15.665	0.009	5.652	0.342	39.91	
14	15.955	0.011	5.550	0.2094	25.8	
15	17.262	0.019	5.133	0.2658	10.7	
16	17.636	0.016	5.025	0.314	15.49	
17	18.688	0.029	4.744	0.2035	3.87	
18	19.229	0.012	4.612	0.2492	11.54	
19	19.900	0.007	4.458	0.3181	30.42	
20	20.282	0.007	4.375	0.318	39.52	
21	20.942	0.013	4.238	0.2705	13.71	
22	21.308	0.026	4.166	0.3128	15.42	
23	21.592	0.006	4.112	0.349	54.89	
24	23.008	0.019	3.862	0.3836	12.67	
25	23.493	0.018	3.784	0.3284	13.31	
26	24.387	0.031	3.647	0.4659	7.08	
27	25.885	0.013	3.439	0.3251	15.53	
28	26.848	0.010	3.318	0.314	24.19	
29	27.672	0.017	3.221	0.2569	10.63	
30	28.441	0.003	3.136	0.1259	100	Si(111)
31	29.650	0.013	3.010	0.2999	10.36	
32	32.211	0.043	2.777	0.4518	5.11	
33	33.266	0.023	2.691	0.4433	10.29	
34	34.757	0.036	2.579	0.331	4.55	

35	35.788	0.028	2.507	0.2659	5.21	
36	36.937	0.034	2.432	0.2505	4.89	
37	39.729	0.026	2.267	0.5796	2.06	
38	43.933	0.027	2.059	0.3635	4.7	
39	47.304	0.003	1.920	0.1121	69.8	Si(220)
40	49.090	0.043	1.854	0.4801	2.85	
41	55.319	0.017	1.659	0.4255	1.41	
42	56.125	0.002	1.637	0.1131	42.23	Si(311)

Table S6. PXRD data on aCD·2.2EtOH clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	5.680	0.011	15.547	0.2182	2.52	
2	6.812	0.011	12.965	0.28	1.29	
3	7.315	0.006	12.074	0.2274	4.31	
4	8.276	0.004	10.675	0.2217	6.52	
5	8.924	0.017	9.901	0.1953	3.46	
6	9.268	0.010	9.534	0.2144	7	
7	10.964	0.013	8.063	0.2748	9.61	
8	11.396	0.007	7.758	0.2715	30.6	
9	11.727	0.019	7.540	0.1522	4.67	
10	12.624	0.005	7.006	0.3268	38.51	
11	13.464	0.009	6.571	0.2487	12.26	
12	13.862	0.006	6.383	0.3355	31.12	
13	14.676	0.005	6.031	0.3269	30.66	
14	15.130	0.010	5.851	0.1982	3.12	
15	17.117	0.011	5.176	0.3831	26.63	
16	17.910	0.007	4.948	0.2227	8.14	
17	19.417	0.013	4.568	0.286	20.08	
18	19.802	0.028	4.480	0.3174	13.87	
19	20.244	0.010	4.383	0.3058	31.88	
20	20.791	0.028	4.269	0.2945	8.12	
21	21.579	0.015	4.115	0.4185	21.82	

22	22.071	0.011	4.024	0.2895	25.94	
23	22.734	0.008	3.908	0.4117	38.29	
24	23.482	0.011	3.785	0.2842	19.66	
25	24.140	0.054	3.684	0.2002	2.54	
26	24.856	0.064	3.579	0.2763	1.96	
27	26.097	0.024	3.412	0.2011	2.65	
28	26.697	0.019	3.336	0.2565	4.01	
29	28.441	0.004	3.136	0.1231	100	Si(111)
30	29.626	0.039	3.013	0.3181	4.2	
31	30.216	0.019	2.955	0.2369	2.54	
32	30.902	0.013	2.891	0.255	3.8	
33	33.326	0.012	2.686	0.3699	3.28	
34	34.190	0.060	2.620	0.6161	2.84	
35	34.949	0.021	2.565	0.3736	6.81	
36	37.443	0.053	2.400	0.3187	1.24	
37	38.238	0.031	2.352	0.315	2.24	
38	38.962	0.132	2.310	0.5862	0.63	
39	40.050	0.024	2.249	0.4712	3.42	
40	41.379	0.015	2.180	0.3417	1.54	
41	43.126	0.074	2.096	0.5999	1.11	
42	47.303	0.001	1.920	0.1089	66.12	Si(220)
43	49.128	0.017	1.853	0.7884	1.14	
44	52.179	0.074	1.752	1.1243	0.93	
45	56.125	0.001	1.637	0.1082	39.44	Si(311)

Table S7. PXRD data on aCD·1.0*n*-PrOH clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	4.935	0.009	17.891	0.3207	16.69	
2	6.743	0.012	13.097	0.3091	6.35	
3	8.011	0.003	11.027	0.2332	28.8	
4	9.668	0.007	9.141	0.4049	45.47	
5	10.158	0.005	8.701	0.1913	13.96	

6	12.213	0.010	7.241	0.5021	34.2	
7	12.504	0.014	7.073	0.3821	38.45	
8	12.879	0.008	6.868	0.469	75.59	
9	13.361	0.015	6.621	0.4477	64.53	
10	13.689	0.007	6.464	0.4508	100	
11	14.093	0.020	6.279	0.1415	13.94	
12	14.683	0.005	6.028	0.2833	66.72	
13	15.910	0.018	5.566	0.4306	48.07	
14	18.262	0.032	4.854	0.2338	16.07	
15	18.661	0.053	4.751	0.3252	15.4	
16	19.240	0.032	4.609	0.4662	10.85	
17	19.920	0.052	4.454	1.0101	25.25	
18	21.313	0.043	4.166	0.5212	23.1	
19	21.905	0.032	4.054	0.4766	25.26	
20	25.416	0.030	3.502	0.3857	11.35	
21	27.233	0.056	3.272	1.4293	15.69	
22	28.441	0.006	3.136	0.2337	94.86	Si(111)
23	29.170	0.155	3.059	1.2241	3.79	
24	33.878	0.062	2.644	0.3241	4.02	
25	34.459	0.053	2.601	0.3571	3.71	
26	47.285	0.005	1.921	0.2464	44.48	Si(220)
27	56.115	0.004	1.638	0.2236	21.6	Si(311)

Table S8. PXRD data on aCD·1.2*i*-PrOH clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	4.875	0.027	18.110	0.2462	4.26	
2	6.640	0.156	13.300	1.2444	2.08	
3	7.961	0.016	11.097	0.4189	7.78	
4	8.990	0.062	9.828	0.3304	4.2	
5	9.522	0.037	9.281	0.2526	10.76	
6	9.780	0.019	9.036	0.2327	11.88	
7	11.821	0.040	7.480	0.5049	15.9	

8	12.518	0.080	7.066	0.4341	16.44	
9	12.840	0.022	6.889	0.3207	33.34	
10	13.572	0.032	6.519	0.6477	41.39	
11	14.125	0.052	6.265	0.328	12.17	
12	14.626	0.018	6.051	0.3356	28.48	
13	15.948	0.039	5.553	0.7071	17.99	
14	18.262	0.032	4.854	0.3529	7.56	
15	19.609	0.022	4.523	0.4736	20.12	
16	20.124	0.024	4.409	0.5152	14.49	
17	21.629	0.041	4.105	0.8525	9.93	
18	22.912	0.026	3.878	0.4598	11.13	
19	27.082	0.039	3.290	0.6295	6.86	
20	28.441	0.004	3.136	0.1315	100	Si(111)
21	28.676	0.039	3.111	0.5962	12.86	
22	33.126	0.029	2.702	0.5831	1.94	
23	34.991	0.059	2.562	0.7087	1.11	
24	47.298	0.001	1.920	0.1118	64.83	Si(220)
25	47.543	0.014	1.911	0.3902	10.09	
26	56.111	0.003	1.638	0.1274	39.63	Si(311)

Table S9. PXRD data on aCD·1.9MeCN clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	5.621	0.007	15.709	0.251	2.5	
2	7.510	0.001	11.763	0.2008	40.65	
3	8.302	0.003	10.641	0.2395	2.02	
4	8.848	0.021	9.986	0.3366	1.44	
5	11.150	0.020	7.929	0.5122	3.28	
6	12.015	0.008	7.360	0.3709	11.4	
7	13.001	0.002	6.804	0.2399	41.55	
8	13.512	0.021	6.548	0.2065	1.96	
9	13.736	0.018	6.441	0.2163	2.24	
10	14.705	0.010	6.019	0.2176	2.86	

11	15.013	0.003	5.896	0.3203	8.41	
12	16.066	0.022	5.512	0.4107	5.19	
13	17.685	0.028	5.011	0.4638	1.3	
14	19.921	0.003	4.453	0.2871	100	
15	20.517	0.026	4.325	0.582	4.75	
16	21.550	0.029	4.120	0.2678	2.45	
17	22.610	0.006	3.929	0.2936	15.68	
18	23.072	0.038	3.852	0.3863	2.48	
19	23.595	0.013	3.768	0.2438	1.55	
20	24.391	0.047	3.646	0.2579	2.4	
21	26.178	0.029	3.401	0.1956	2.7	
22	27.301	0.011	3.264	0.477	2.27	
23	28.441	0.002	3.136	0.136	59.82	Si(111)
24	28.710	0.013	3.107	0.4614	4.71	
25	33.520	0.020	2.671	0.7615	3.51	
26	38.536	0.025	2.334	0.3649	0.67	
27	39.335	0.016	2.289	0.561	1.64	
28	41.424	0.030	2.178	1.1124	0.53	
29	47.295	0.001	1.920	0.138	43.64	Si(220)
30	50.751	0.058	1.797	0.4961	0.65	
31	56.118	0.001	1.638	0.1339	23.74	Si(311)

Table S10. PXRD data on aCD·0.4EtCN clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	4.895	0.009	18.038	0.2565	7.89	
2	7.526	0.006	11.737	0.4207	4.43	
3	7.961	0.005	11.096	0.1757	11.96	
4	9.557	0.041	9.247	0.2489	20.1	
5	9.763	0.041	9.052	0.2603	18.92	
6	12.365	0.022	7.152	0.9362	24.56	
7	12.910	0.010	6.851	0.183	20.96	

8	13.607	0.008	6.502	0.5246	55.5	
9	14.687	0.008	6.026	0.3301	27.45	
10	15.893	0.015	5.572	0.4812	21.75	
11	18.299	0.018	4.844	0.5066	11.85	
12	19.412	0.087	4.569	0.7778	7.08	
13	19.750	0.012	4.492	0.4248	21.48	
14	21.361	0.020	4.156	0.4479	9.55	
15	21.957	0.018	4.045	0.403	13.71	
16	22.268	0.019	3.989	0.4444	8.53	
17	22.996	0.017	3.864	0.3366	7.64	
18	25.486	0.036	3.492	0.4496	5.03	
19	27.124	0.036	3.285	0.6346	4.66	
20	28.441	0.003	3.136	0.1819	100	Si(111)
21	34.475	0.067	2.599	2.4786	1.43	
22	43.452	0.070	2.081	0.4987	1.23	
23	47.300	0.001	1.920	0.1491	53.6	Si(220)
24	56.124	0.002	1.637	0.1306	29.53	Si(311)

Table S11. PXRD data on aCD·1.8$MeNO_2$ clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height
1	4.611	0.011	19.149	0.2813	34.74
2	4.869	0.031	18.135	0.2717	20.51
3	6.561	0.145	13.461	1.4753	3.07
4	8.061	0.031	10.960	0.3489	12.39
5	9.838	0.023	8.983	0.2884	18.22
6	10.625	0.010	8.319	0.2063	14.79
7	11.746	0.027	7.528	0.7479	19.63
8	13.100	0.025	6.753	0.6319	64.07
9	13.633	0.014	6.490	0.5392	100
10	14.727	0.009	6.010	0.376	71.18
11	15.961	0.007	5.548	0.3918	54.94
12	18.592	0.026	4.769	0.3979	30

13	19.277	0.036	4.600	0.3511	28.23
14	19.764	0.046	4.488	0.378	34.33
15	20.139	0.033	4.406	0.4851	41.65
16	20.643	0.093	4.299	0.3317	26.55
17	21.411	0.014	4.147	0.4861	86.21
18	22.744	0.054	3.907	0.9904	24.78
19	27.350	0.049	3.258	0.8476	18.08
20	31.870	0.025	2.806	0.8572	10.58
21	33.732	0.043	2.655	0.4318	7.91
22	35.552	0.012	2.523	0.4787	23.2
23	36.868	0.105	2.436	1.9919	2.42
24	43.810	0.040	2.065	0.6822	5.34

Table S12. PXRD data on aCD·0.6$(CH_3)_2CO$ clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height	note
1	4.923	0.005	17.936	0.2329	18.21	
2	5.710	0.029	15.465	0.3218	1	
3	6.807	0.010	12.975	0.3372	2.64	
4	7.477	0.005	11.814	0.3715	8.16	
5	8.049	0.003	10.976	0.1882	14.81	
6	9.618	0.025	9.188	0.2079	24.22	
7	9.780	0.009	9.037	0.2091	46.76	
8	12.357	0.056	7.157	0.8528	16.2	
9	12.519	0.012	7.065	0.1699	9.85	
10	12.955	0.013	6.828	0.2254	27.38	
11	13.378	0.033	6.613	0.2451	20.52	
12	13.686	0.014	6.465	0.3336	62.01	
13	14.696	0.004	6.023	0.2671	50.97	
14	15.948	0.010	5.553	0.3799	28.03	
15	18.335	0.017	4.835	0.3743	16.31	
16	18.670	0.017	4.749	0.2175	9.84	
17	19.321	0.027	4.590	0.4583	10.57	

18	19.768	0.015	4.487	0.3506	22.85	
19	20.131	0.030	4.407	0.3383	11.43	
20	21.392	0.020	4.150	0.3301	10.08	
21	21.954	0.031	4.045	0.173	5.6	
22	22.329	0.013	3.978	0.5704	7.96	
23	22.977	0.023	3.868	0.36	8.84	
24	25.492	0.022	3.491	0.2722	4.59	
25	28.441	0.006	3.136	0.1649	100	Si(111)
26	29.371	0.050	3.038	0.8951	2.45	
27	33.936	0.042	2.639	0.4781	2.47	
28	34.559	0.037	2.593	0.4454	2.72	
29	37.089	0.028	2.422	0.2967	1.17	
30	47.308	0.001	1.920	0.1621	61.35	Si(220)
31	56.131	0.001	1.637	0.1594	33.38	Si(311)

Table S13. PXRD data on aCD·1.8HFIP clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height
1	4.861	0.003	18.165	0.2158	8.43
2	6.760	0.011	13.066	0.3118	3.87
3	8.012	0.002	11.026	0.2362	25.82
4	9.783	0.005	9.034	0.3756	23.85
5	12.644	0.024	6.995	1.4409	31.94
6	12.942	0.002	6.835	0.1777	28.65
7	13.665	0.004	6.475	0.3684	100
8	14.696	0.003	6.023	0.3099	59.68
9	15.951	0.014	5.552	0.4059	39.44
10	18.282	0.026	4.849	0.2702	14.37
11	18.583	0.036	4.771	0.6206	14.12
12	19.367	0.044	4.579	0.5693	17.41
13	19.870	0.061	4.465	0.6758	15.81
14	20.138	0.018	4.406	0.1918	8.95
15	21.455	0.016	4.138	0.4117	24.62

16	22.852	0.068	3.888	0.4401	5.83
17	31.907	0.104	2.802	0.7966	4.52
18	39.131	0.082	2.300	1.2143	2.25

Table S14. PXRD data on $0.9C_5H_5N$ clathrate.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height
1	5.024	0.006	17.573	0.2767	8.48
2	6.894	0.005	12.811	0.4583	3.83
3	8.128	0.003	10.869	0.2526	22.79
4	9.772	0.008	9.044	0.4161	36.62
5	12.297	0.016	7.192	0.5311	31.95
6	12.585	0.018	7.028	0.3817	36
7	12.995	0.018	6.807	0.4371	48.22
8	13.599	0.047	6.506	0.488	100
9	13.775	0.034	6.423	0.4562	51.83
10	14.761	0.006	5.996	0.4622	60.58
11	16.107	0.014	5.498	0.5271	38.03
12	18.529	0.041	4.785	0.5536	21.76
13	19.899	0.050	4.458	0.7728	24.61
14	21.460	0.038	4.137	0.3852	16.46
15	22.046	0.015	4.029	0.4434	23.87
16	23.077	0.014	3.851	0.2196	6.97
17	25.632	0.012	3.472	0.3952	12.22
18	27.284	0.054	3.266	1.1184	11.89
19	34.778	0.033	2.577	1.1077	3.48
20	37.120	0.016	2.420	0.289	3.74
21	39.994	0.045	2.252	1.2081	1.91

Table S15. PXRD data on aCD·3.2MeOH clathrate prepared at MeOH activity $P/P_0 = 0.22$.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height
1	4.654	0.008	18.973	0.3323	31.52
2	5.143	0.008	17.167	0.2554	28.38
3	5.829	0.018	15.151	0.222	6.73
4	7.551	0.013	11.698	0.3677	12.67
5	8.559	0.016	10.323	0.2581	8.42
6	9.413	0.029	9.388	0.3299	24.28

7	12.459	0.030	7.099	0.7642	75.15
8	13.088	0.023	6.759	0.5399	61.68
9	13.671	0.169	6.472	0.6251	100
10	14.566	0.029	6.077	0.8036	57.89
11	15.378	0.024	5.757	0.7569	40.94
12	19.009	0.024	4.665	0.2626	44.21
13	19.654	0.069	4.513	0.7548	48.12
14	20.424	0.041	4.345	0.4844	37.31
15	21.128	0.053	4.202	0.5269	32.69
16	23.208	0.045	3.829	0.2077	11.08
17	26.539	0.071	3.356	0.6118	19.31
18	27.282	0.071	3.266	0.5364	15.7
19	28.235	0.039	3.158	0.7828	15.17
20	32.977	0.029	2.714	0.2795	4.36
21	35.186	0.020	2.548	0.7374	6.08
22	39.030	0.178	2.306	0.7431	1.62
23	43.234	0.089	2.091	0.7594	3.12

Table S16. PXRD data on intermediate aCD·1.0MeCN clathrate prepared at MeCN activity P/P_0 = 0.31.

Peak No.	2θ, °	ESD, °	d, Å	FWHM, °	Rel. height
1	4.845	0.008	18.223	0.3159	7.93
2	6.526	0.018	13.533	0.2169	2
3	7.787	0.003	11.344	0.2382	21.57
4	9.551	0.007	9.253	0.2707	22.43
5	9.929	0.009	8.901	0.2523	15.23
6	11.488	0.016	7.696	0.8568	7.27
7	12.299	0.013	7.191	0.3606	30.43
8	12.614	0.006	7.012	0.3091	46.64
9	13.514	0.004	6.547	0.4314	100
10	13.893	0.007	6.369	0.3662	32.51

11	14.425	0.004	6.136	0.2844	80.01
12	15.719	0.016	5.633	0.3479	43.02
13	18.467	0.027	4.801	0.3073	14
14	19.266	0.040	4.603	0.5806	18.37
15	19.853	0.031	4.468	0.3801	15.18
16	20.427	0.105	4.344	0.4405	9.46
17	21.132	0.020	4.201	0.4196	25.96
18	22.667	0.071	3.920	0.2676	7.58
19	26.188	0.036	3.400	0.8833	2.16
20	27.162	0.026	3.280	0.6536	11.51
21	28.043	0.036	3.179	0.2509	4.91
22	29.258	0.023	3.050	0.432	7.03
23	32.091	0.012	2.787	0.7289	5.48
24	33.457	0.082	2.676	0.5265	2.49
25	35.680	0.042	2.514	0.4874	4.92

Images of dry aCD samples before and after the saturation with HFIP and pyridine vapors

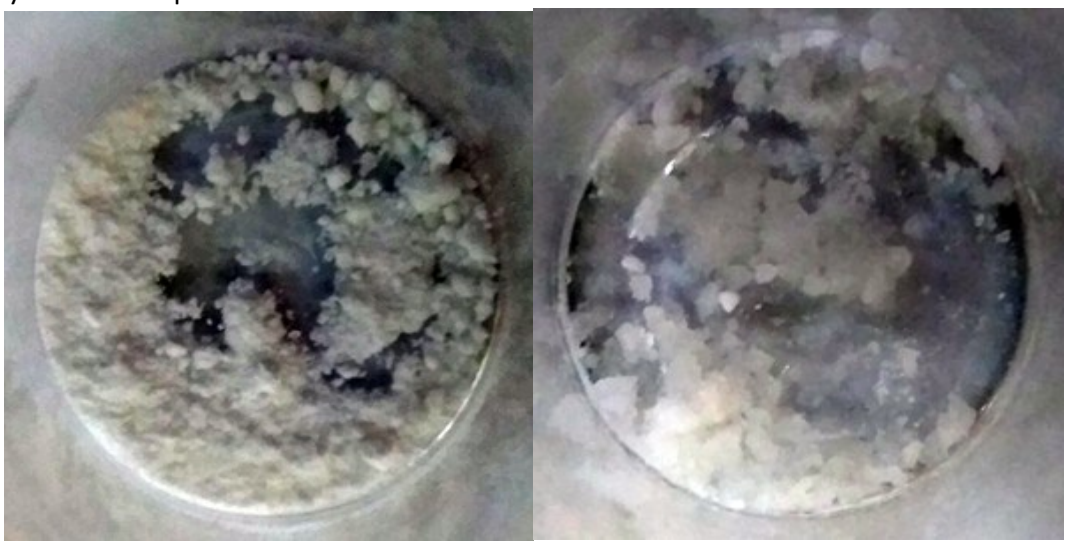

Figure S20. Photos of aCD sample: (left) dried; (right) after equilibration with saturated HFIP vapors.

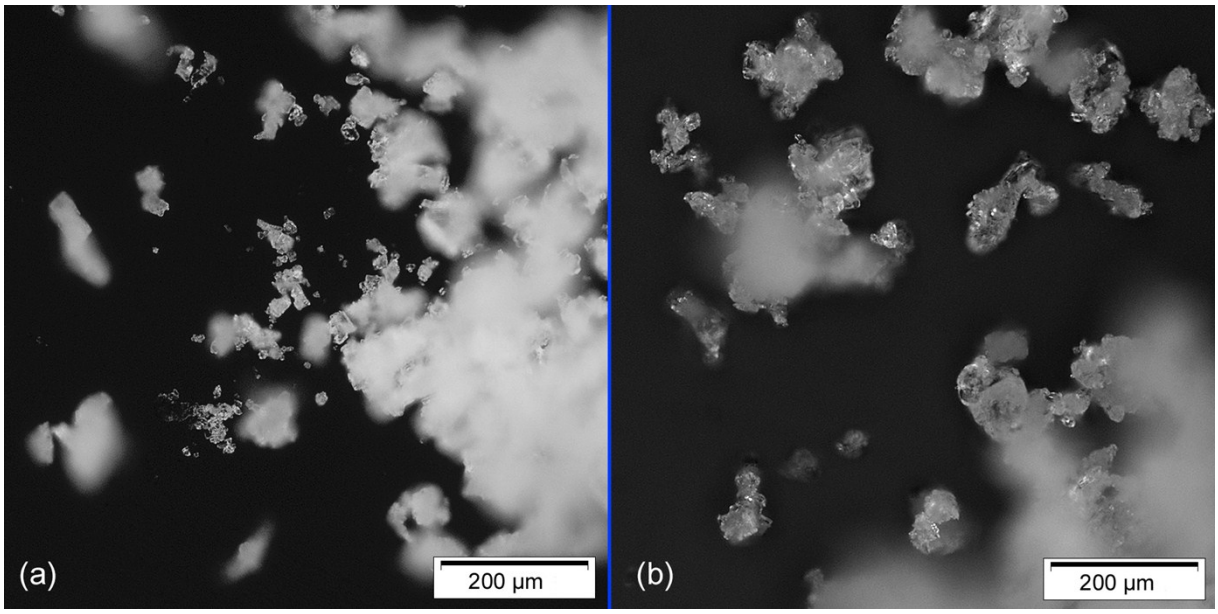

Figure S21. Optical microscopy images (20x) of aCD sample in polarized light: (left) dried; (right) after equilibration with saturated pyridine vapors.

References:

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