Using water-mimic organic compounds to activate guest inclusion by initially dry beta-cyclodextrin

Askar K. Gatiatulin,[a] Marat A. Ziganshin,[a] Goulshat F. Yumaeva,[a] Aidar T. Gubaidullin,[b] Kinga Suwińska,[a c] Valery V. Gorbatchuk*[a]

[a] A. M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya 18, 420008 Kazan, Russia

[b] A. E. Arbuzov Institute of Organic and Physical Chemistry, Akad. Arbuzova, 8, 420088 Kazan, Russia

[c] Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszynski University in Warsaw, K. Woycickiego 1/3, 01-938 Warszawa, Poland

Electronic Supporting Information

Table of Contents

Equation used for calculation of formation Gibbs energy for an inclusion compound formed in two steps 2

Description of fitting procedure used for sorption isotherms in binary systems 2

Data of TG/DSC/MS analysis for bCD hydrates prepared at different humidities P/P_0, T=25°C 3

Data of TG/MS analysis for clathrates prepared by equilibration of dried bCD in binary systems with saturated guest vapors , T=25°C 3

Data of TG/MS analysis for bCD clathrates prepared by solid-phase exchange of THF in the initial bCD•1.0THF•1.0H2O clathrate for **Guest 2** at 25°C 4

Curves of simultaneous thermal analysis for bCD clathrates with HFIP, butanone, dichloromethane; for bCD hydrates prepared at various water activities P/P_0 4

Pictures of initial dried bCD and its samples equilibrated with saturated vapor of ethanol and vapors of HFIP and pyridine 9

X-ray powder diffractograms 11

Curves of thermal analysis for bCD clathrates prepared by simultaneous sorption of ethanol and benzene, simultaneous sorption acetonitrile and benzene; for clathrates prepared by solid-phase exchange of ethanol, acetonitrile and THF 13

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

$$\Delta G_c = (A_1 \cdot \Delta G_{c1} + A_2 \cdot \Delta G_{c2}) / (A_1 + A_2), \tag{S1}$$

where ΔG_{ci} is Gibbs energy of clathrate formation at i-th inclusion step, A_i — guest mole number sorbed in the i-th inclusion step.

Description of fitting procedure used for sorption isotherms in binary systems

Sorption isotherms in binary systems were fitted by minimizing a standard deviation δ of experimental points (A_{exp}, $(P/P_0)_{\text{exp}}$) from the isotherm calculated by equation (1) in the main text of the paper:

$$\delta = (\Sigma\{[(P/P_0)_{\text{calc}} - (P/P_0)_{\text{exp}}]^2 + [(A_{\text{calc}} - A_{\text{exp}})/S]^2\}/(n-2))^{1/2} \tag{S2}$$

where P/P_0 is guest thermodynamic activity, A— guest uptake, S — stoichiometry of a saturated clathrate, n – number of experimental points. In the fitting procedure, points (A_{calc}, $(P/P_0)_{\text{calc}}$) are found on the calculated sorption isotherm having the shortest distances from each experimental point in normalized coordinates A/S *vs.* P/P_0.

Table S1. Data of TG/DSC/MS analysis for bCD hydrates prepared at different humidities P/P_0, T=25°C.

P/P_0	Δm, %	A, mol per mol bCD	T_{max}, °C [b]	ΔH_{dehydr}, kJ/mol
0.10	0.7	0.5	83	51±6
0.20	3.4	2.2	81	45±4
0.25	6.7	4.5 [a]	84	49±4
0.30	8.6	6.0	92	49±3
0.33	8.7	6.0	100	47±3
0.40	10.8	7.6	109	50±3
0.50	10.1	7.1 [a]	102	47±3
0.60	11.9	8.5	110	50±2
0.70	12.5	9.0	110	51±2
0.85	12.6	9.1 [a]	112	47±2
0.90	12.4	9.0	104	48±2
1.00	15.1	11.2 [a]	145	48±2

[a] data from Ref. 1; [b] T_{max} is determined with an error of ±4°C.

Table S2. Data of TG/MS analysis for clathrates prepared by equilibration of dried bCD in binary systems with saturated guest vapors, T=25°C.

Clathrate	Δm, % [a]	T_{max} [b]
bCD·4.1MeOH [c]	10.3	94
bCD·2.6 EtOH [c]	9.6 (4.3)	104; 202
bCD·2.1MeCN [c]	7.1	103
bCD·2.0$MeNO_2$	9.8 (5.6)	84; 213
bCD·1.0$(CH_3)_2CO$ [c]	5.2	121; 225
bCD·(~1.7)HFIP [d]	16.6 (7.9) [e]	108; >250
bCD·6.5C_5H_5N	31.0	115

[a] total mass loss of guest; in brackets, mass loss is given on the second step of clathrate decomposition; [b] T_{max} is a temperature of guest peak on MS curve; [c] data from Ref. 1; [d] the guest content includes ~0.4 mol estimated from MS curve above the onset point of host thermal destruction, T_{onset}= 260°C, Figure S1; [e] Δm is mass loss below T_{onset}= 260°C.

Table S3. Data of TG/MS analysis for bCD clathrates prepared by solid-phase exchange of THF in the initial bCD·1.0THF·1.0H_2O clathrate for **Guest 2** at 25°C. [a]

Guest 2	Clathrate	Δm, %	T_{max} (Guest2), °C	T_{max} (THF), °C
MeOH	bCD·2.9MeOH	7.6	95	-
i-PrOH	bCD·1.1*i*-PrOH·0.2THF·1.0H_2O	8.1	215	217
n-BuOH	bCD·0.8THF·2.9H_2O	8.7	-	240
MeCN	bCD·2.4MeCN	7.8	111	-
THF [b]	bCD·1.2THF·0.9H_2O	8.2	-	241
cyclohexane	bCD·0.9THF·1.3H_2O	7.1	-	228

[a] Experimental procedures of THF exchange and preparation of the initial clathrate were described in Ref. 2.

[b] product of additional THF inclusion by initial bCD·1.0THF·1.0H_2O clathrate.

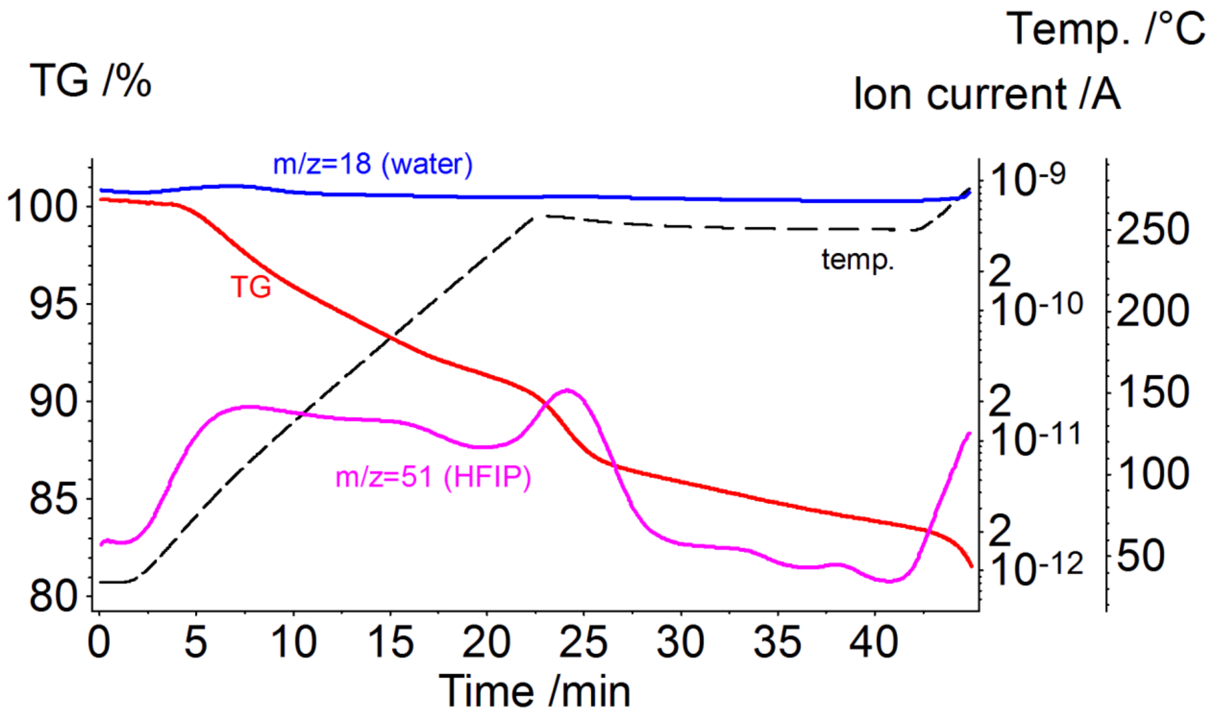

Figure S1. Curves of simultaneous TG/MS analysis for bCD·(~1.7)HFIP clathrate formed by saturation of dry bCD with HFIP vapors (T = 25°C).

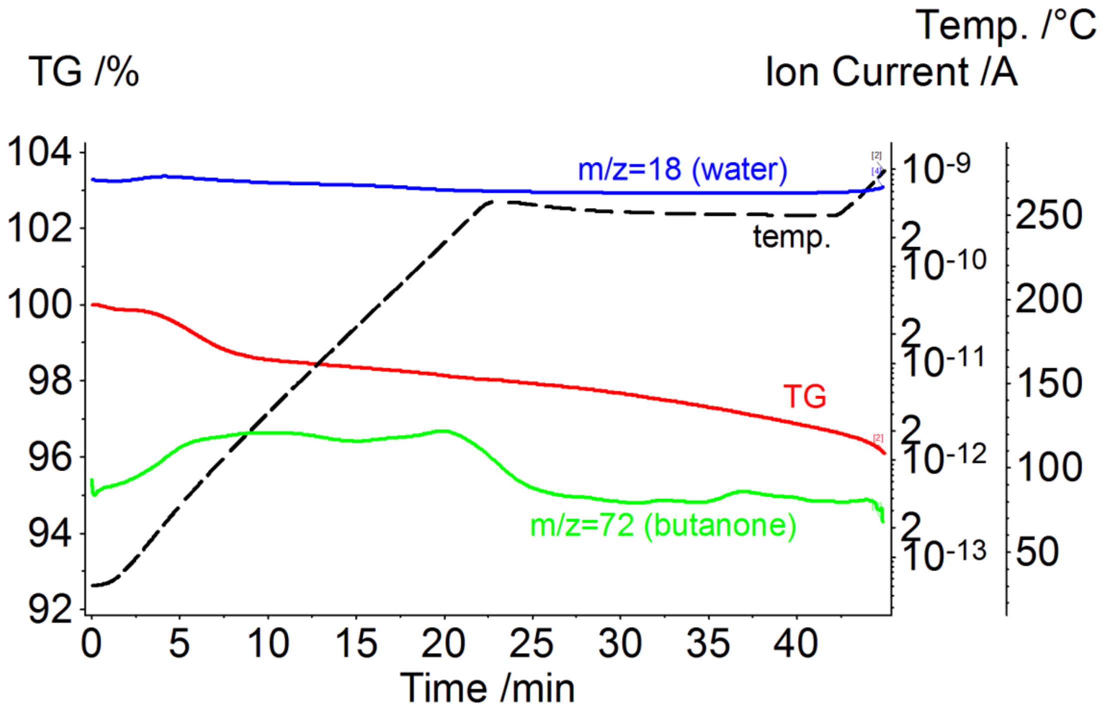

Figure S2. Curves of simultaneous TG/MS analysis for bCD·0.3C_4H_8O clathrate formed by saturation of dry bCD with 2-butanone vapors ($P/P_0 = 1$, $T = 25$°C).

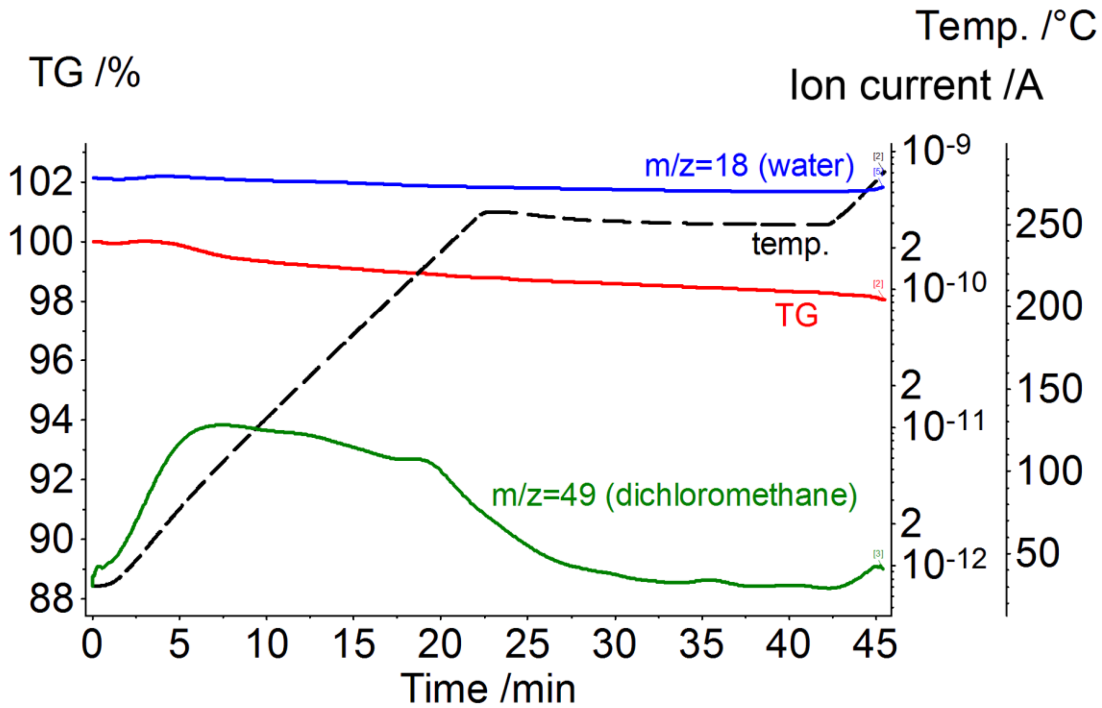

Figure S3. Curves of simultaneous TG/MS analysis for bCD·0.2CH_2Cl_2 clathrate formed by saturation of dry bCD with dichloromethane vapors ($P/P_0 = 1$, $T = 25$°C).

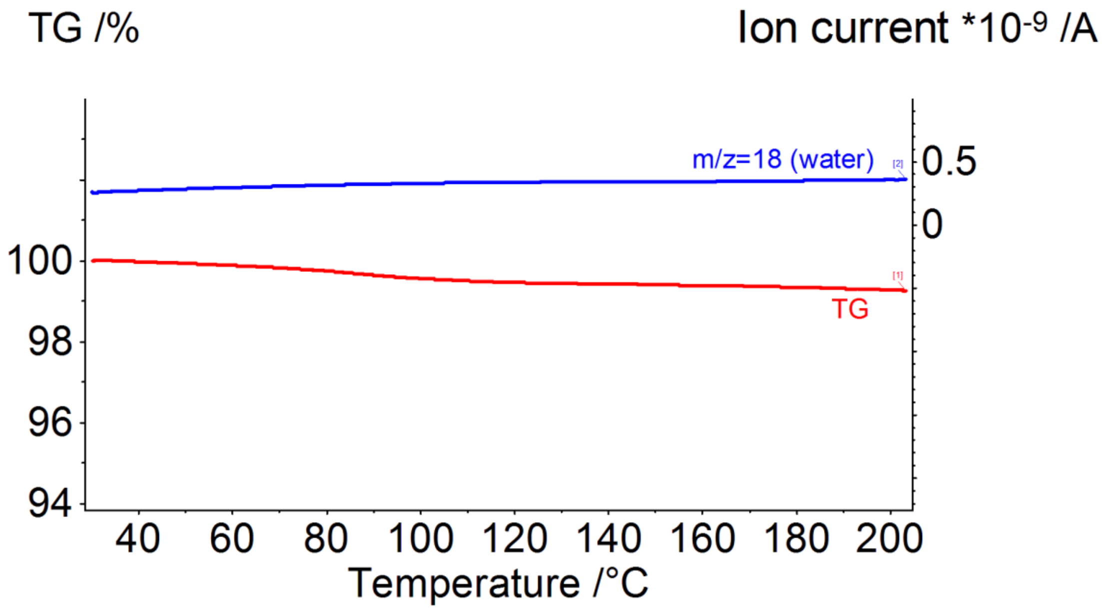

Figure S4. Curves of simultaneous TG/MS analysis for bCD·0.5H_2O clathrate formed by saturation of dry bCD with water vapors at activity $P/P_0 = 0.10$ (T = 25°C).

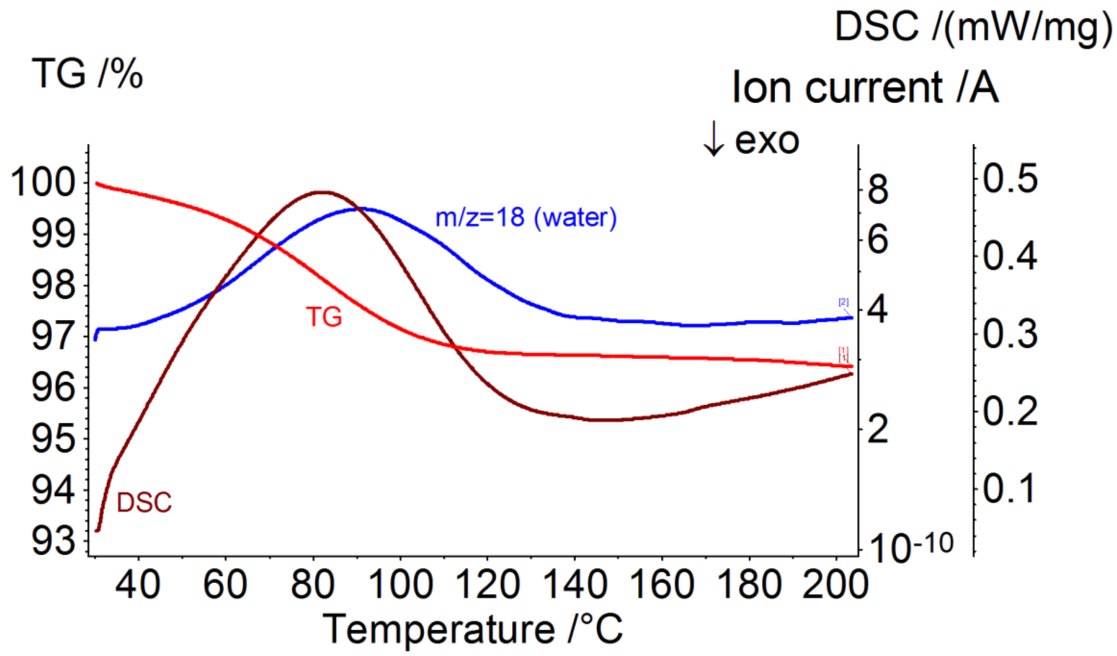

Figure S5. Curves of simultaneous TG/MS analysis for bCD·2.2H_2O clathrate formed by saturation of dry bCD with water vapors at activity $P/P_0 = 0.20$ (T = 25°C).

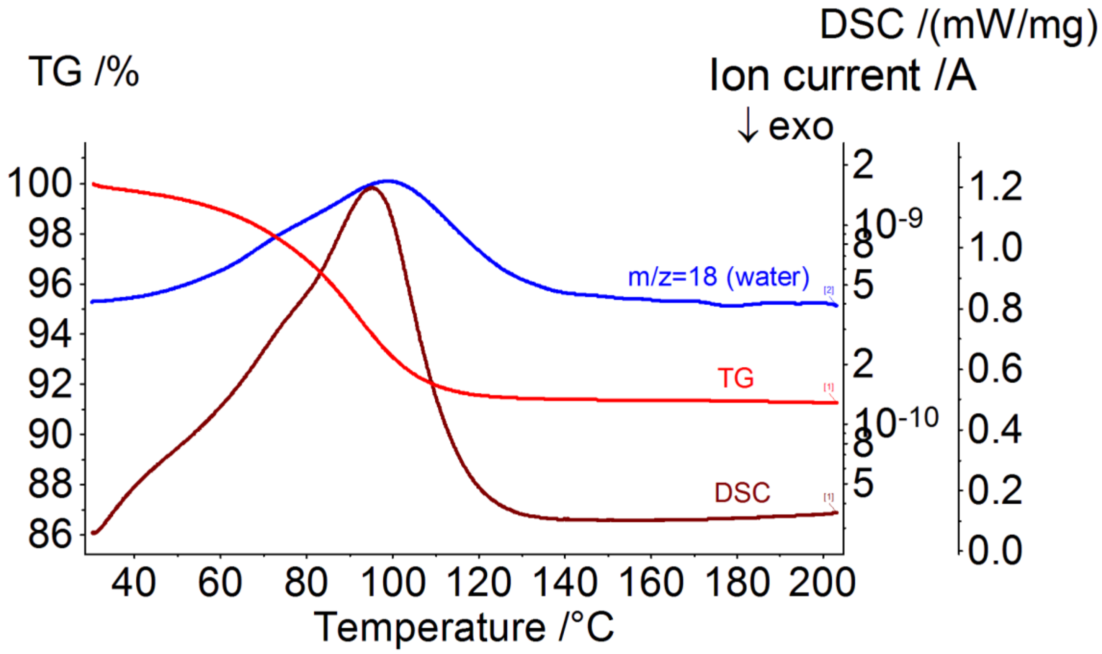

Figure S6. Curves of simultaneous TG/MS analysis for bCD·6.0H_2O clathrate formed by saturation of dry bCD with water vapors at activity $P/P_0 = 0.30$ (T = 25°C).

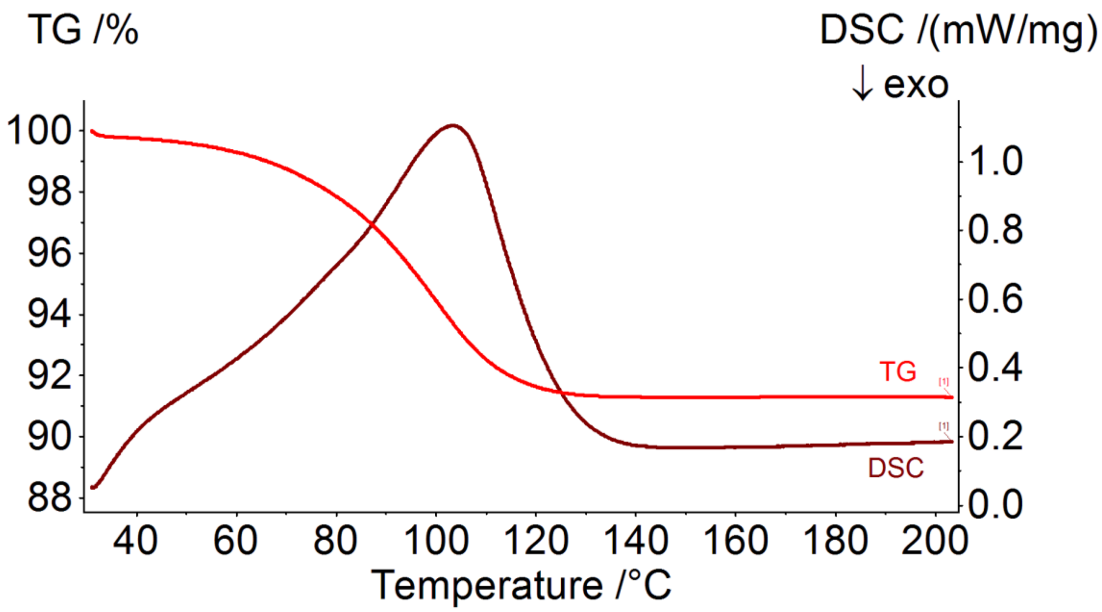

Figure S7. Curves of simultaneous TG/MS analysis for bCD·6.0H_2O clathrate formed by saturation of dry bCD with water vapors at activity $P/P_0 = 0.33$ (T = 25°C).

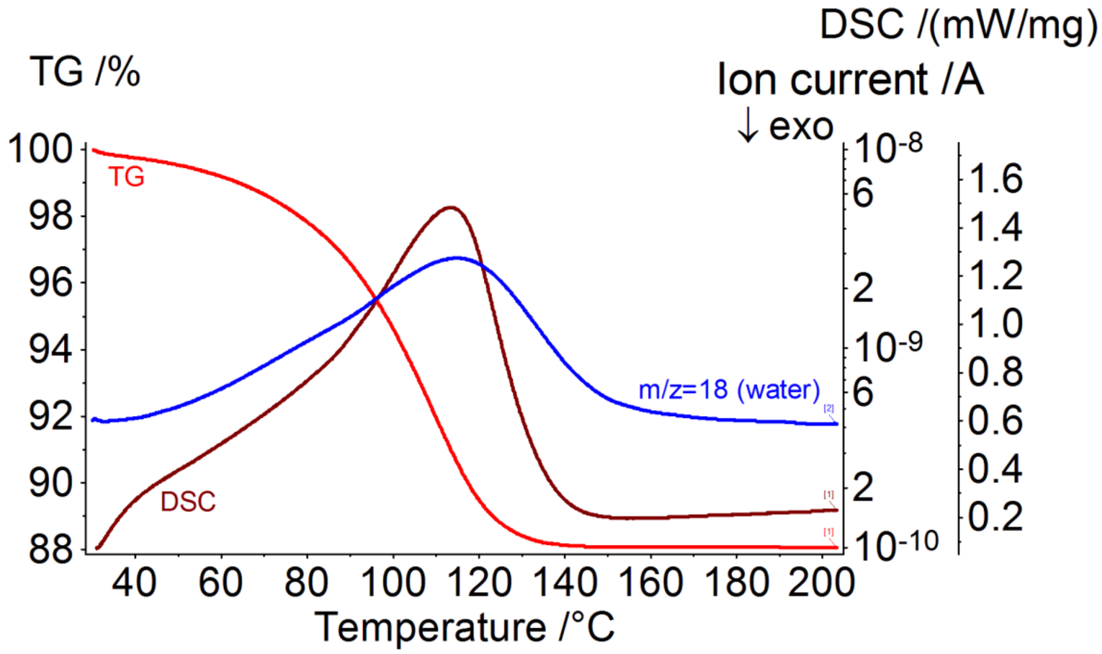

Figure S8. Curves of simultaneous TG/MS analysis for bCD·8.5H_2O clathrate formed by saturation of dry bCD with water vapors at activity $P/P_0 = 0.60$ ($T = 25$°C).

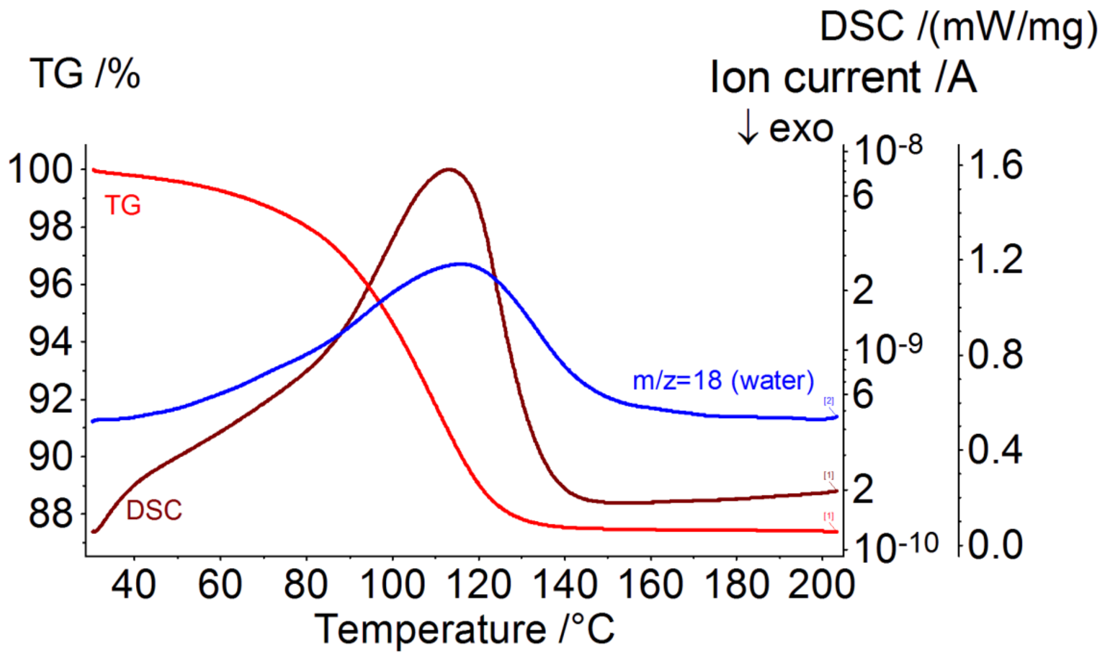

Figure S9. Curves of simultaneous TG/MS analysis for bCD·9.0H_2O clathrate formed by saturation of dry bCD with water vapors at activity $P/P_0 = 0.70$ ($T = 25$°C).

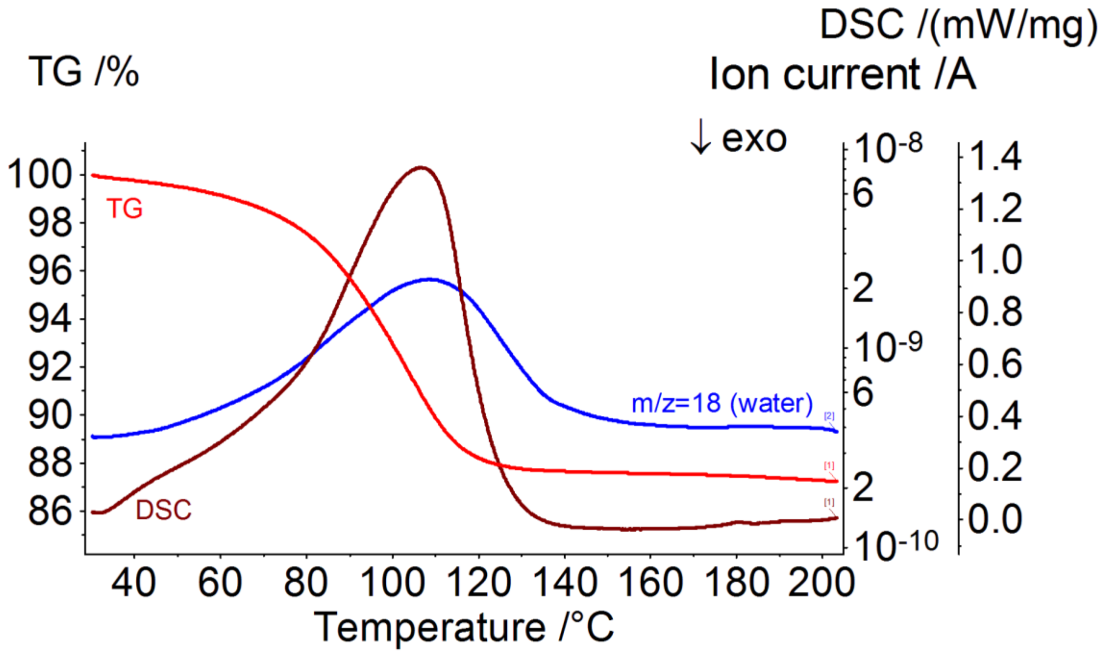

Figure S10. Curves of simultaneous TG/MS analysis for bCD·9.0H_2O clathrate formed by saturation of dry bCD with water vapors at activity P/P_0 = 0.90 (T = 25°C).

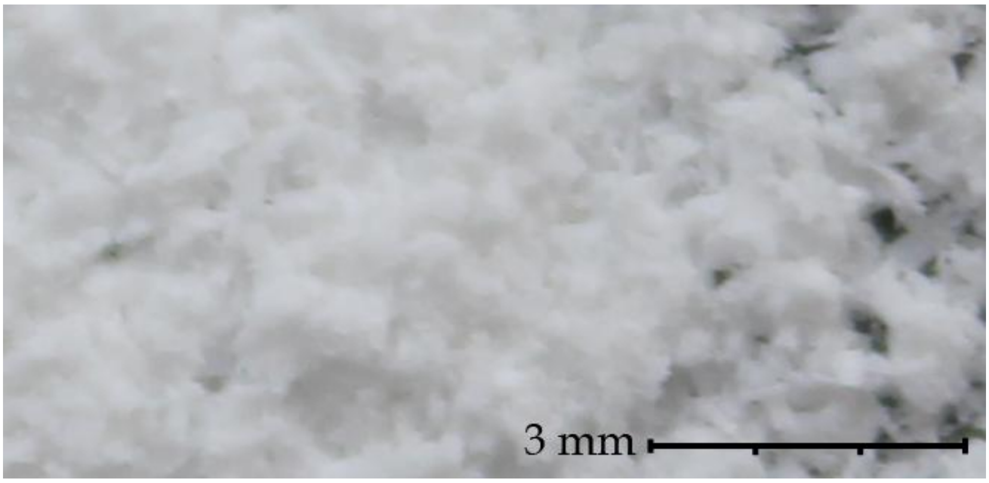

Figure S11. Anhydrous bCD.

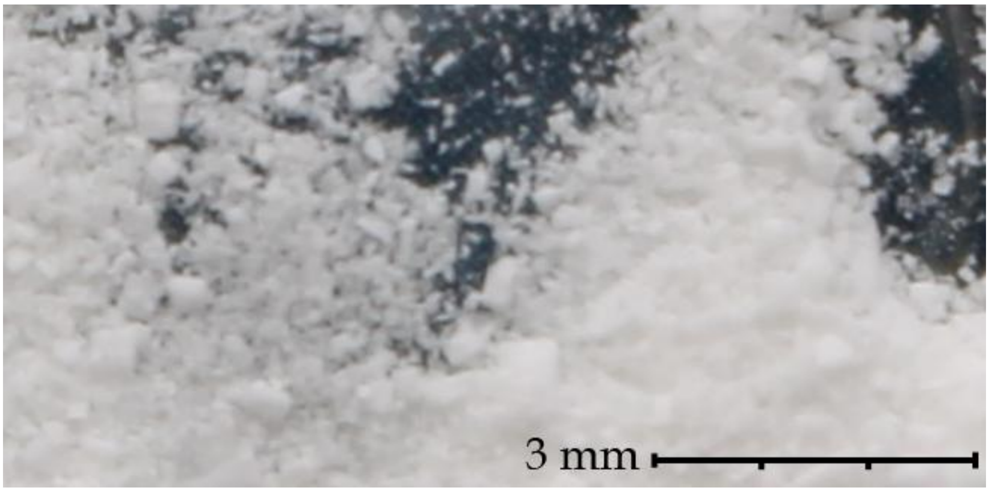

Figure S12. Anhydrous bCD equilibrated with saturated ethanol vapor for 72 hours ($P/P_0 = 1$, $T = 25°C$).

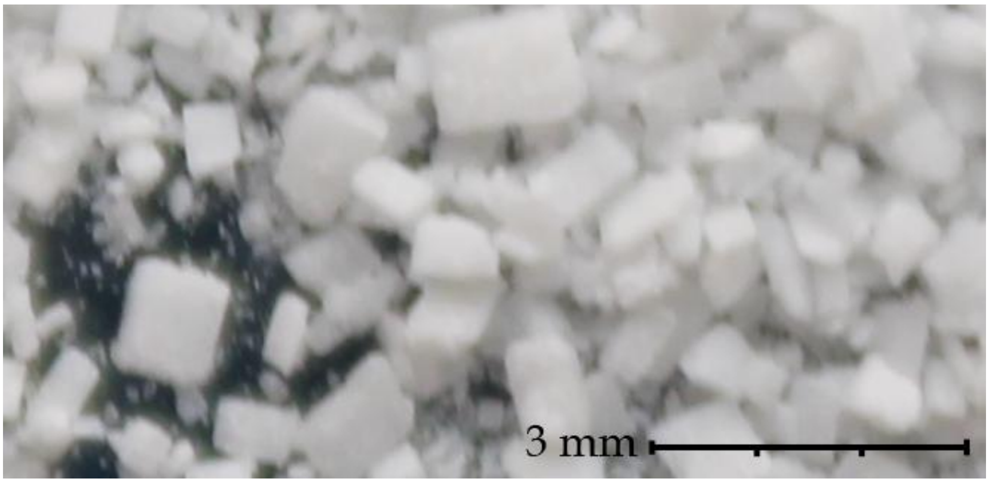

Figure S13. Anhydrous bCD equilibrated with pyridine vapor taken in 6:1 (Guest : Host) molar ratio for 72 hours ($T = 25°C$).

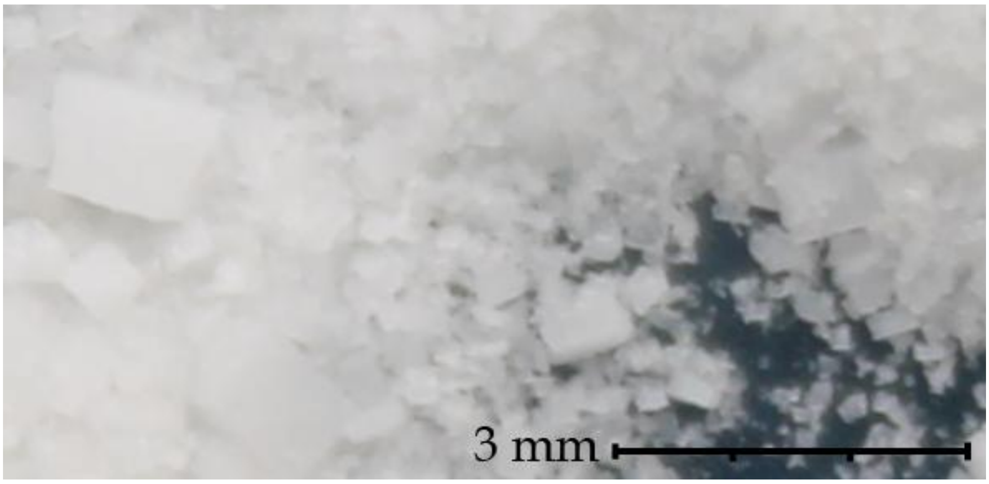

Figure S14. Anhydrous bCD equilibrated with saturated HFIP vapor for 72 hours (P/P_0=0.49, $T = 25°C$).

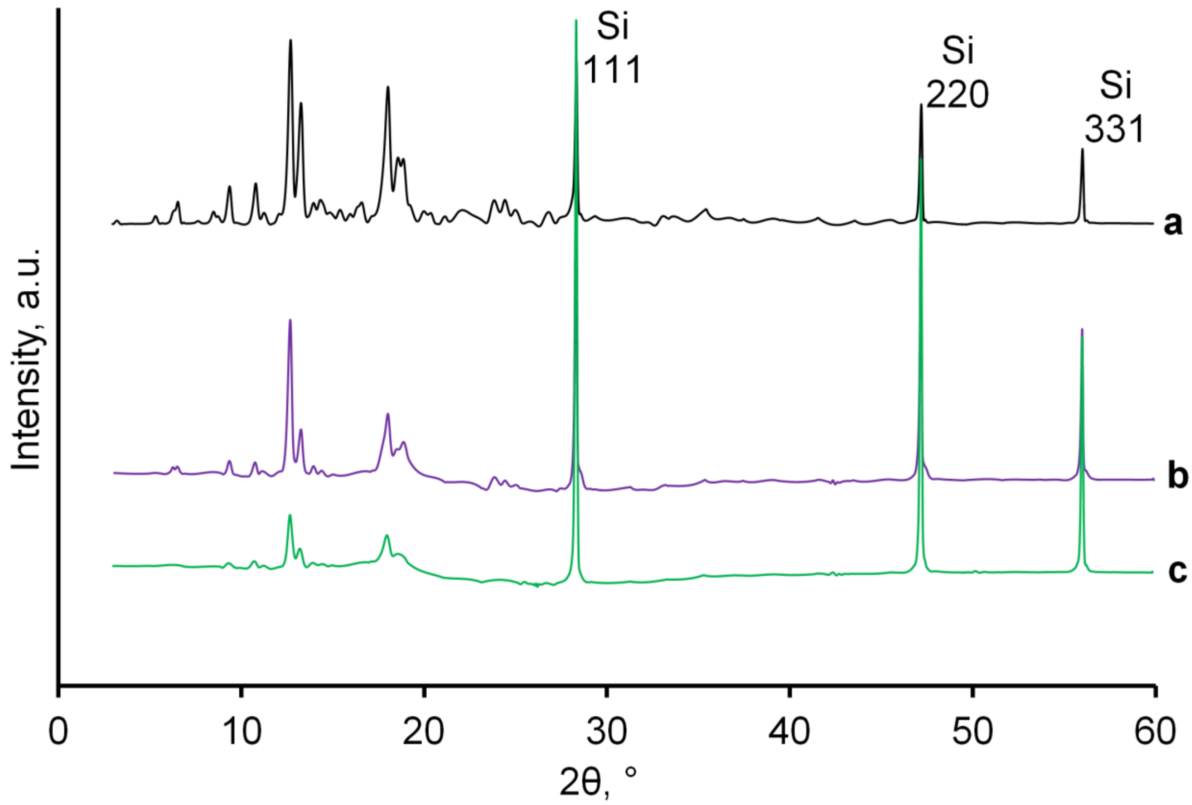

Figure S15. X-ray powder diffractograms of anhydrous bCD (a) and clathrates: (b) bCD·6.5C_5H_5N, (c) bCD·(~1.7)HFIP with addition of standard silicon powder SRM 640d.

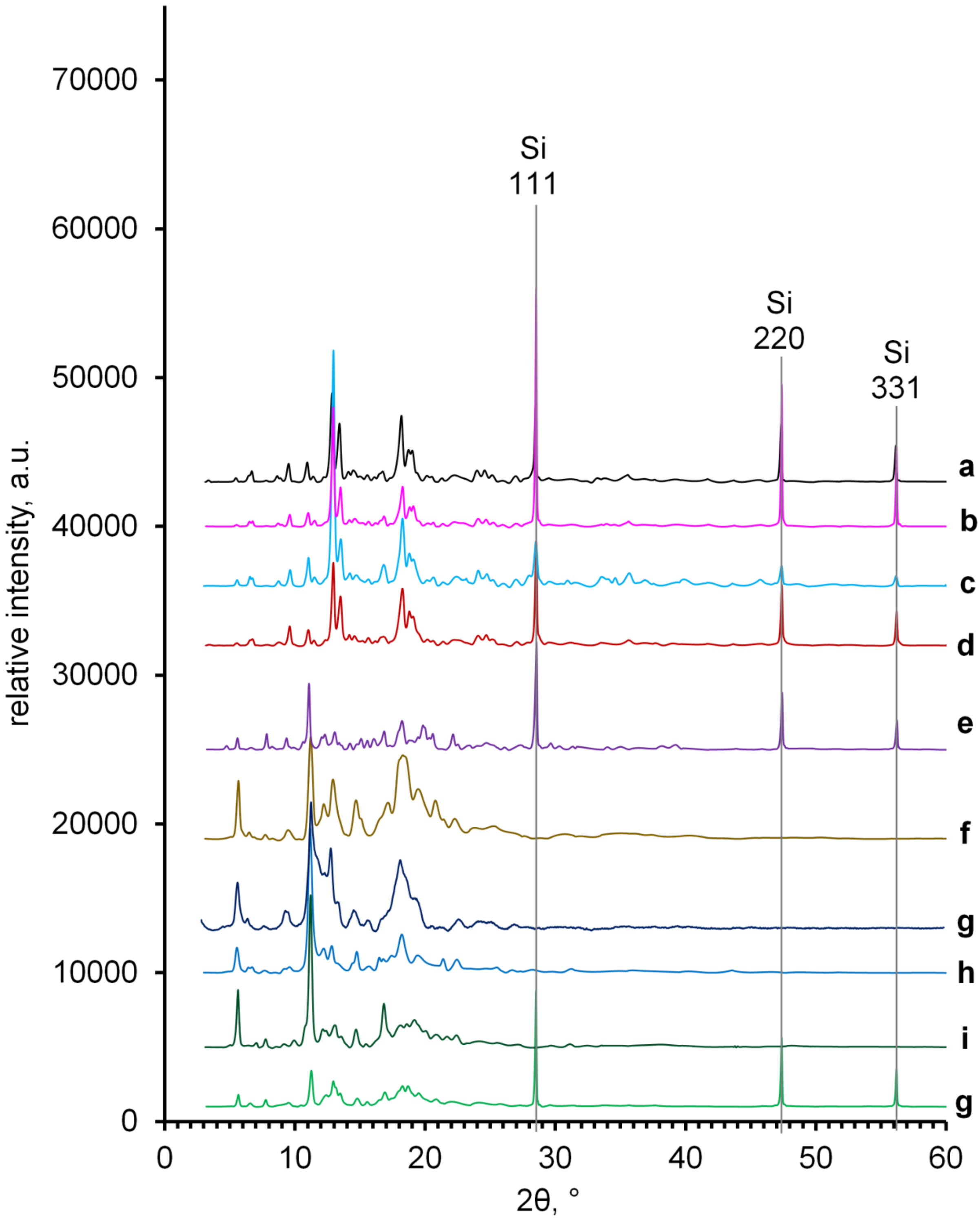

Figure S16. X-ray powder diffractograms for bCD and its clathrates formed by equilibration of dried bCD in binary or ternary systems with guest vapors at various activities P/P_0: (a) dried bCD; (b) bCD·0.6MeOH at P/P_0=0.07; (c) bCD·0.6MeCN at P/P_0=0.33; (d) bCD·1.0Me_2CO at P/P_0=1; (e) bCD·3.8MeOH at P/P_0=0.29; (f) bCD·2.0$MeNO_2$ at P/P_0=1; (g) bCD·1.9MeCN·0.1C_6H_6 at P/P_0=0.48 (MeCN) and P/P_0=0.06 (C_6H_6); (h) bCD·2.1MeCN at P/P_0=1; (i) bCD·2.6EtOH·0.2C_6H_6 at P/P_0=0.69 (EtOH) and P/P_0=0.04 (C_6H_6); (g) bCD·2.6EtOH at P/P_0=1. Diffractograms a-e, g were determined with addition of standard silicon powder SRM 640d.

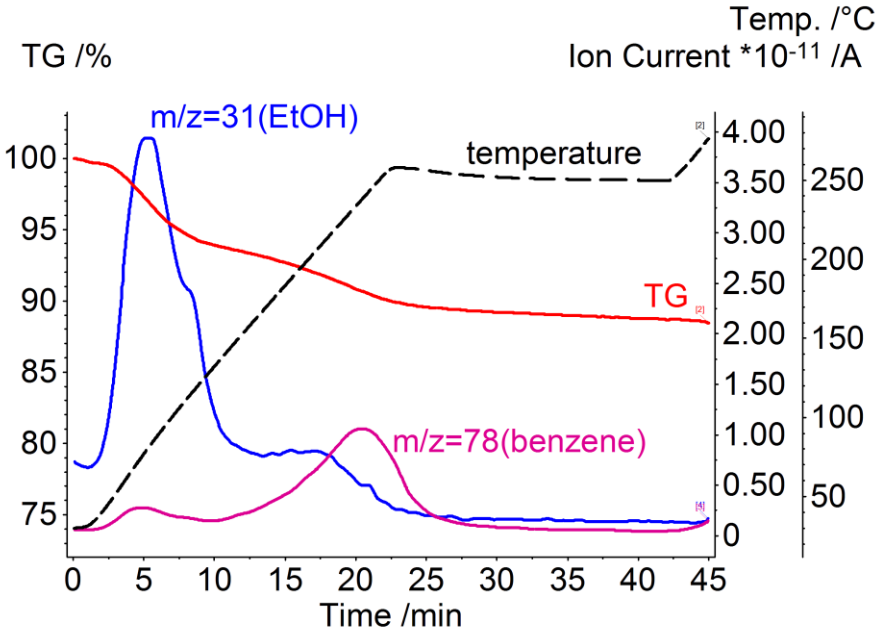

Figure S17. Curves of simultaneous TG/MS analysis for the bCD·2.6EtOH·0.2C_6H_6 clathrate prepared by simultaneous sorption of ethanol and benzene at constant benzene/ethanol molar ratio 1:14 (T = 25°C, ethanol activity P/P_0 = 0.68). MS curve of ethanol has higher level at start due to ethanol evaporation from clathrate at temperature less than 30°C.

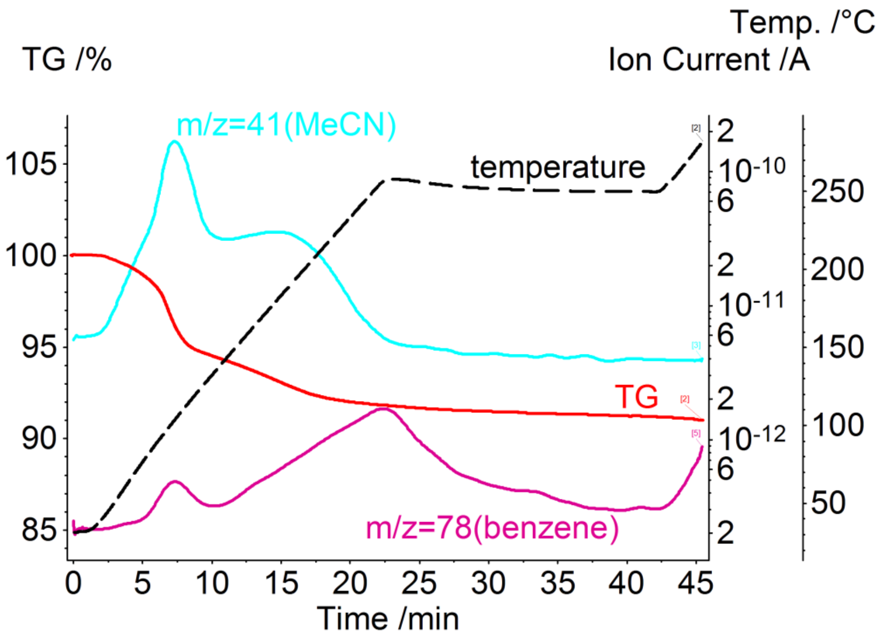

Figure S18. Curves of simultaneous TG/MS analysis for bCD·2.2MeCN·0.1C_6H_6 clathrate prepared by simultaneous sorption of acetonitrile and benzene at constant benzene/acetonitrile molar ratio 1:15 (T = 25°C, acetonitrile activity P/P_0 = 0.80).

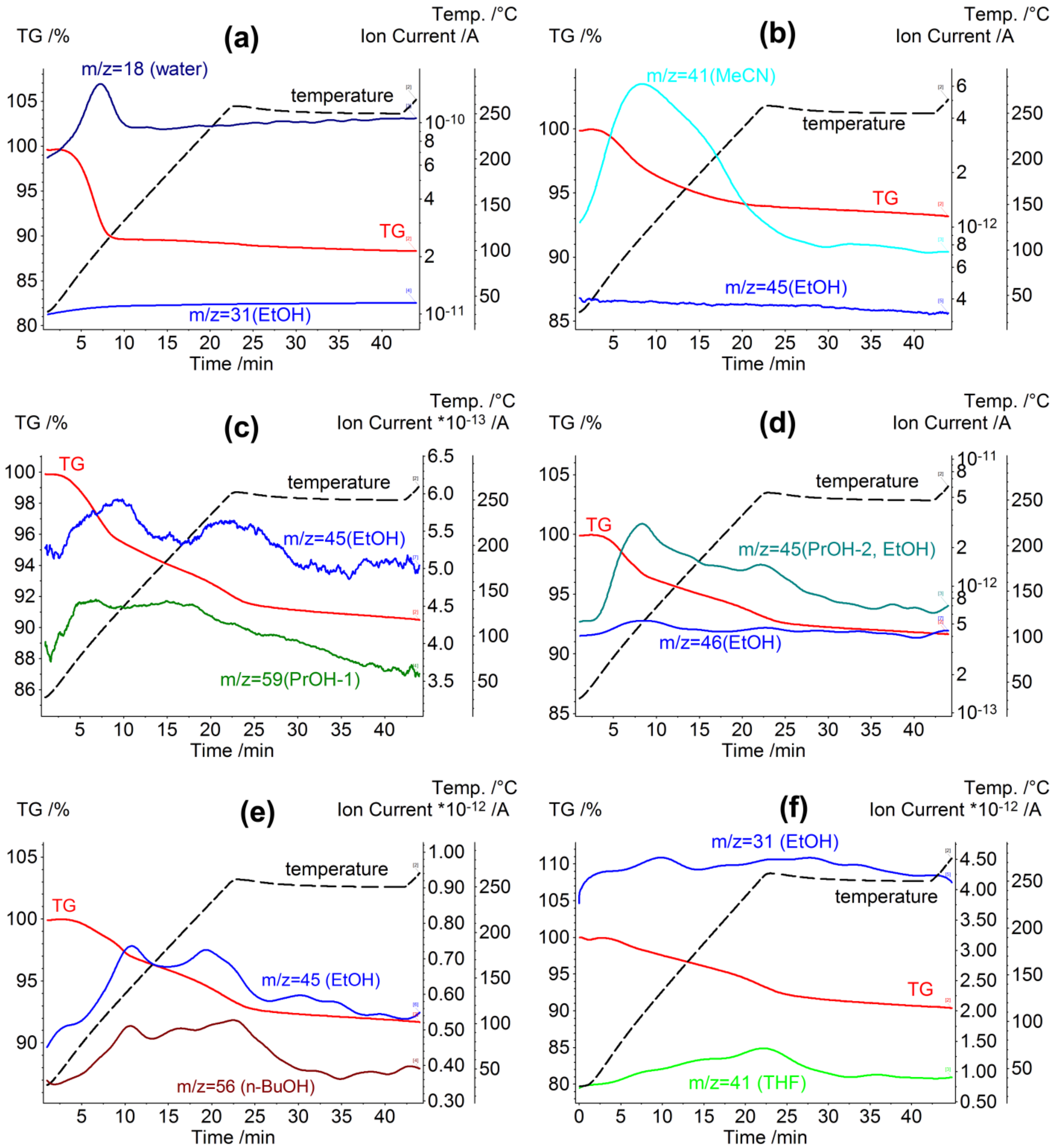

Figure S19. Curves of simultaneous TG/MS analysis for clathrates prepared by ethanol exchange for: (a) water; (b) acetonitrile; (c) 1-propanol; (d) 2-propanol; (e) 1-butanol; (f) tetrahydrofuran.

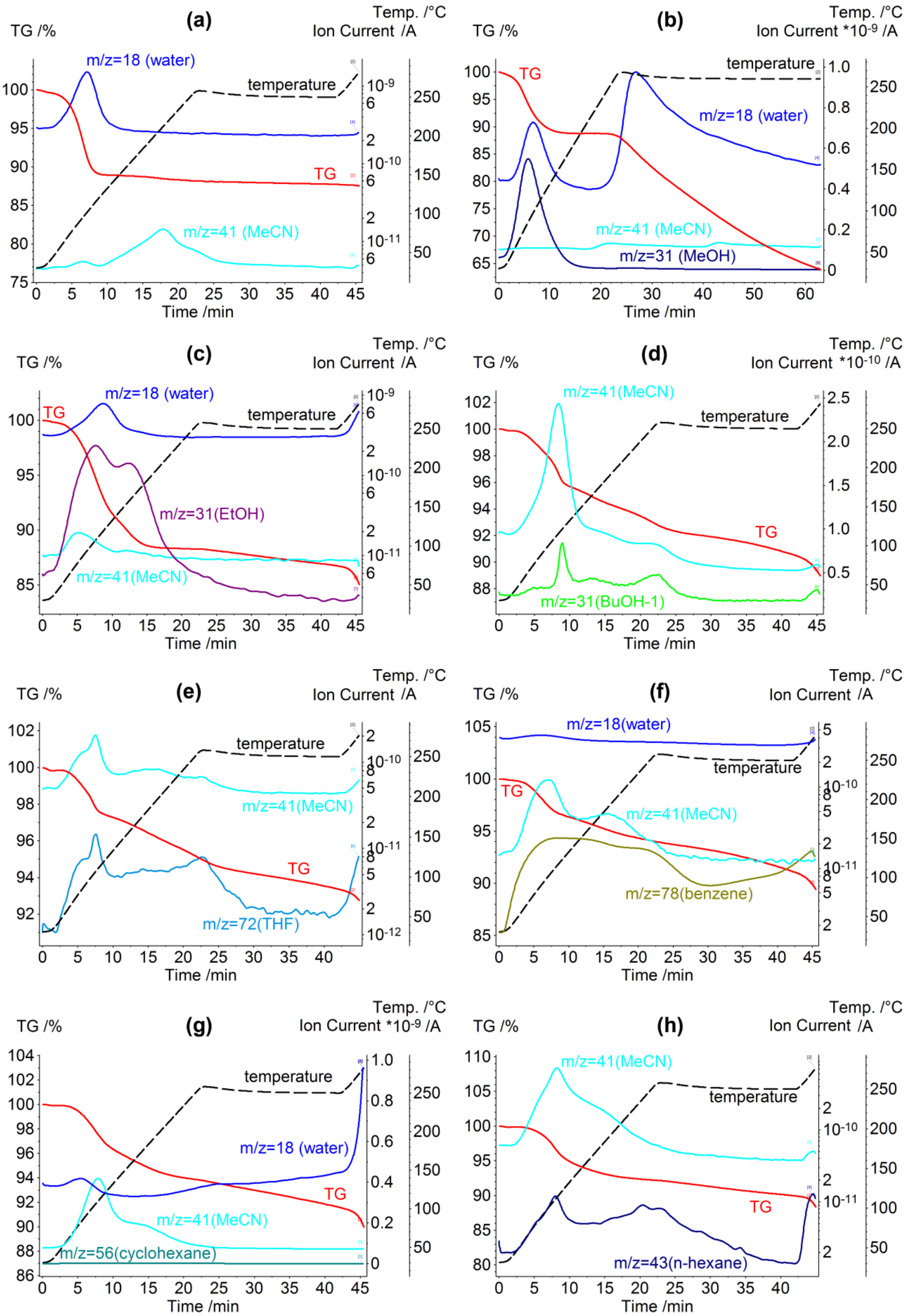

Figure S20. Curves of simultaneous TG/MS analysis for clathrates prepared by acetonitrile exchange for: (a) water; (b) methanol; (c) ethanol; (d) 1-butanol; (e) tetrahydrofuran; (f) benzene; (g) cyclohexane; (h) *n*-hexane.

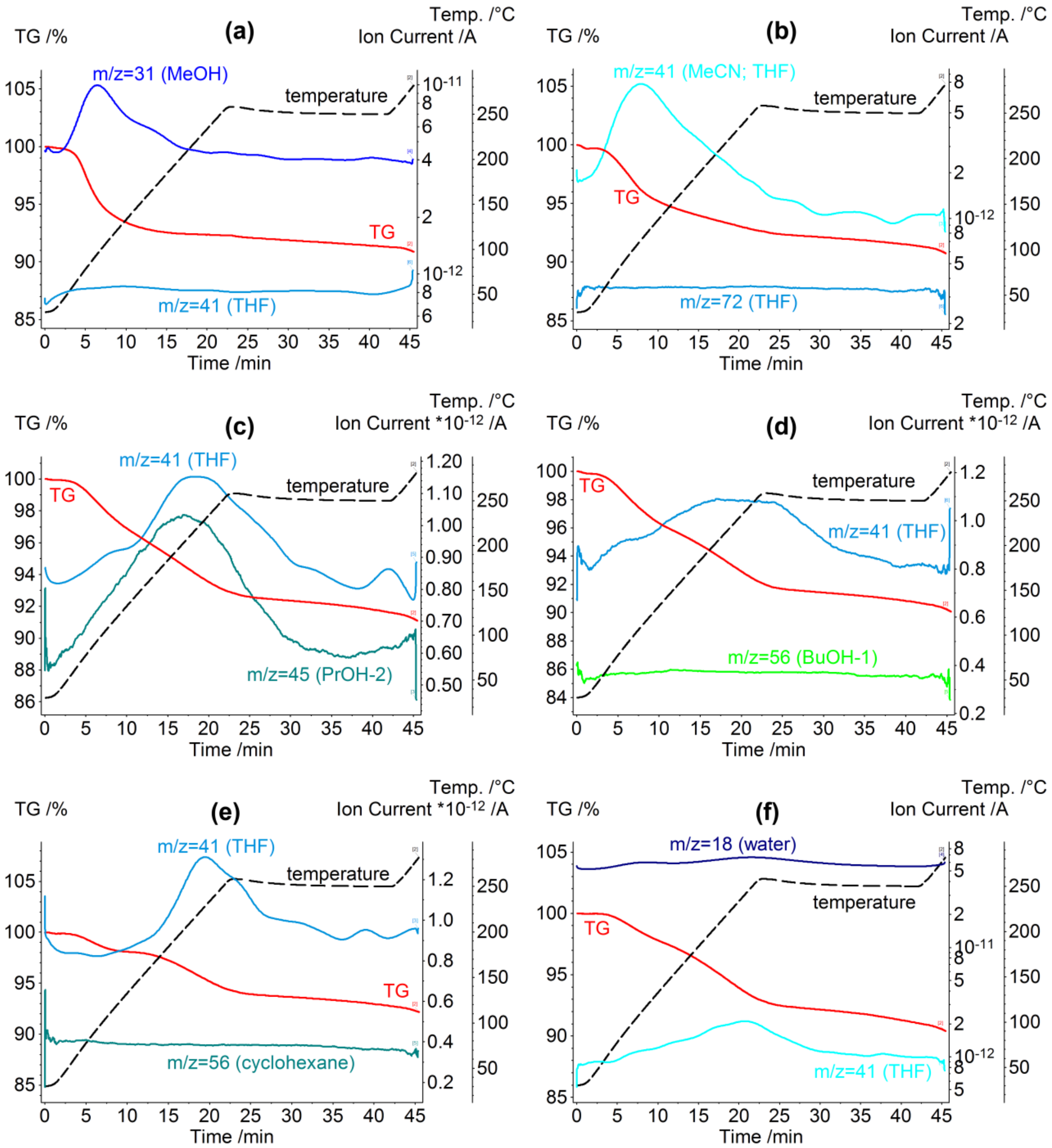

Figure S21. Curves of simultaneous TG/MS analysis for clathrates prepared by THF exchange initial bCD·1.0THF·1.0H_2O clathrate for: (a) methanol; (b) acetonitrile; (c) propanol-1; (d) butanol-1; (e) cyclohexane; (f) additional sorption of THF. Experimental procedure was described elsewhere.[2]

References:

1 V. V. Gorbatchuk, A. K. Gatiatulin, M. A. Ziganshin, A. T. Gubaidullin and L. S. Yakimova, *J. Phys. Chem. B*, 2013, **117**, 14544–14556.

2 A. K. Gatiatulin, M. A. Ziganshin and V. V. Gorbatchuk, *J. Therm. Anal. Calorim.*, 2014, **118(2**), 987–992.