Electronic Supplementary Information

Twice as smart behavior of tert-butylthiacalix[4]arene derivative in glassy and crystalline form

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TG/DSC, DSC, TM-DSC and TG/DSC/MS curves for the studied calixarene samples in glassy and crystalline form and TG/DSC/MS curves for the products of their saturation with guest vapors and for metastable $\boldsymbol{\beta}_0$ polymorph formed after guest release; visual changes of glassy calixarene in this process and at the heating; molar enthalpies of fusion and **α→α'** polymorphic transition

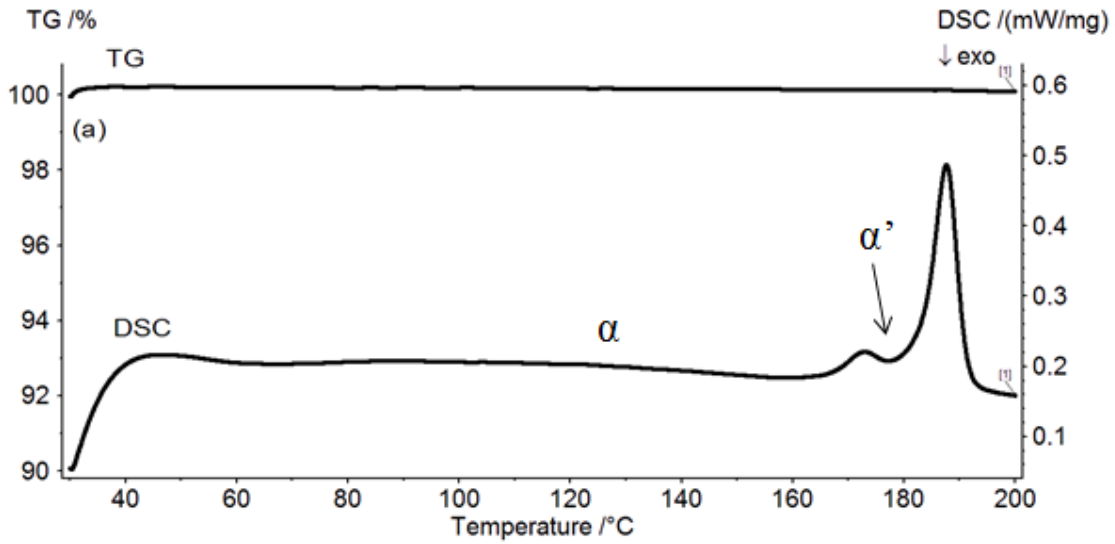

Figure 1S – TG/DSC curves for **1α** sample.

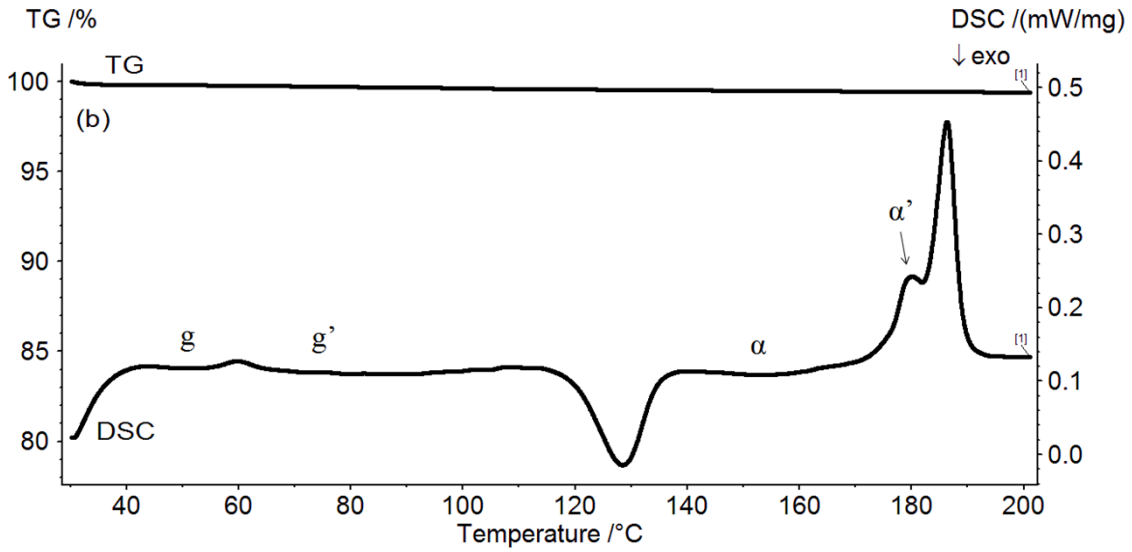

Figure 2S – TG/DSC curves for **1g** sample.

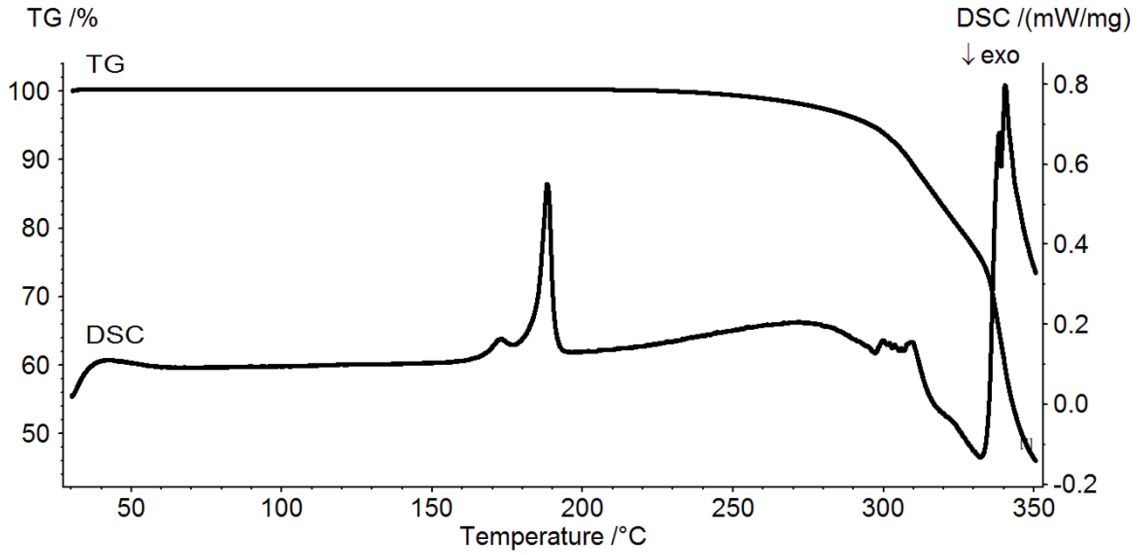

Figure 3S – TG/DSC curves for **1α** sample.

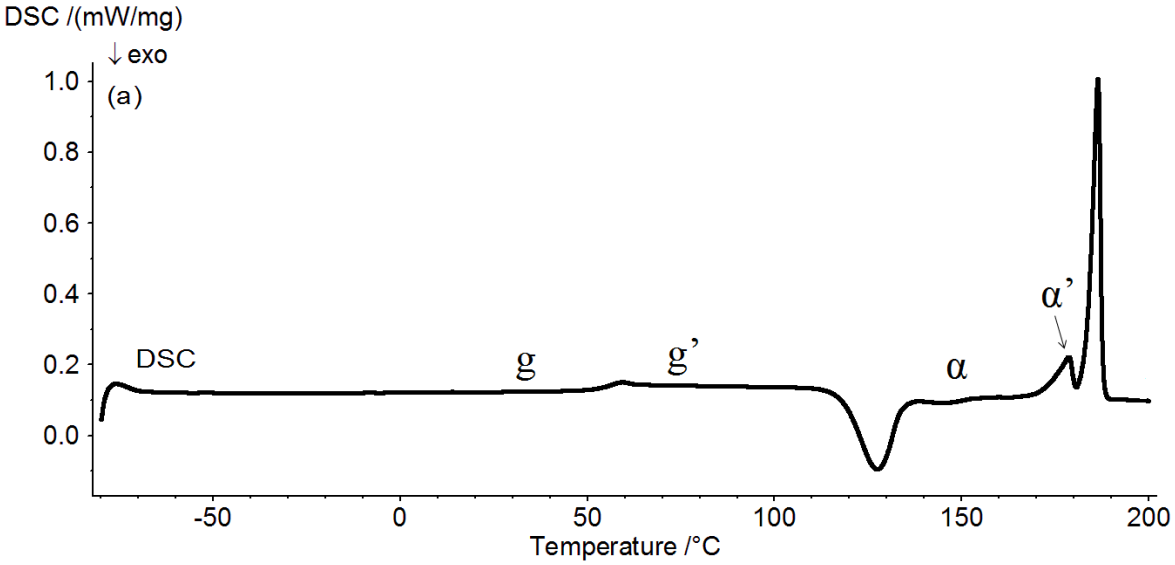

Figure 4S – DSC curves for **1g** sample. Heating rate is 5°C/min.

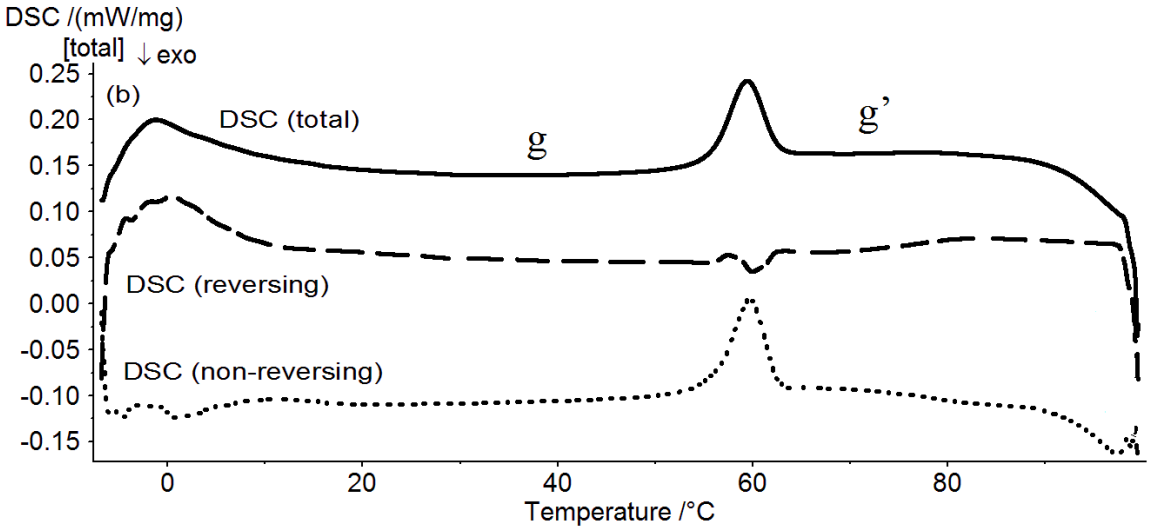

Figure 5S – TM-DSC curves for **1g** sample. Heating rate is 10°C/min.

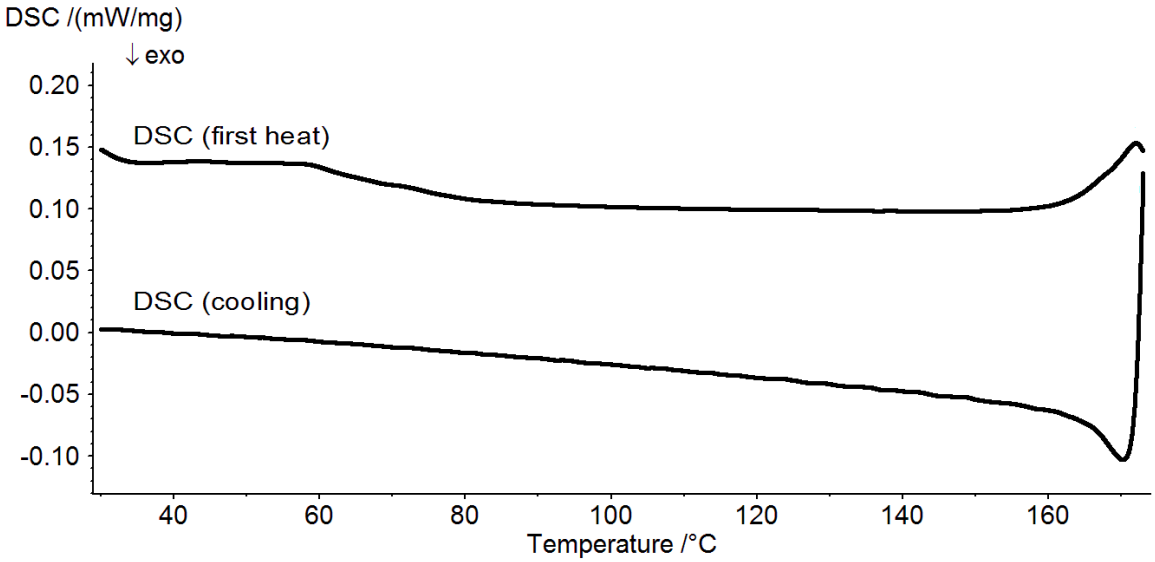

Figure 6S – DSC curves of **1g** heating to 173°C and cooling to 30°C with rate of 4 °C/min.

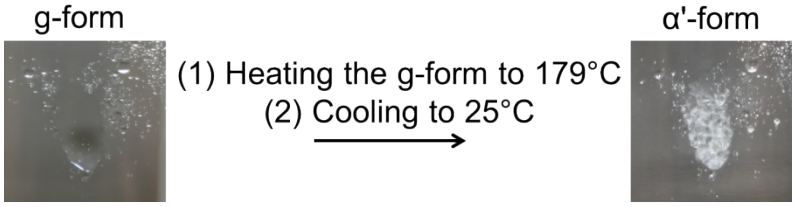

Figure 7S – Visual changes in **1g** sample at the heating to 179°C and cooling to RT of 25°C on the air.

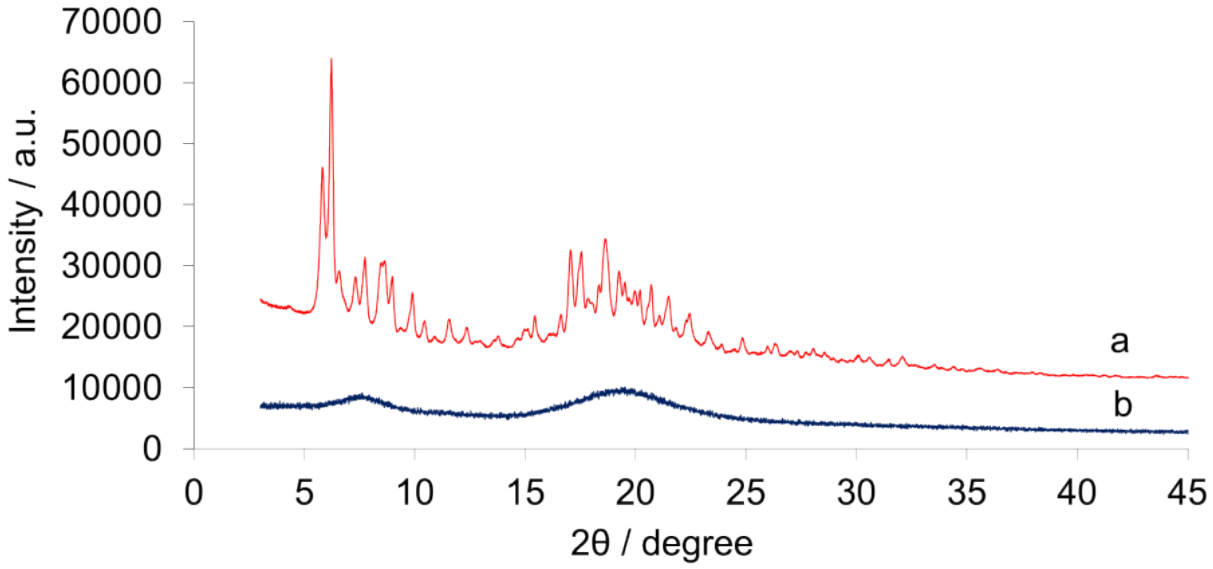

Figure 8S – XRPD data for **1α** prepared by heating of (a) **1g** to 150°C at the heating rate of 10°C/min and immediate cooling to RT on the air; (b) **1g** heated to 80°C and cooled to RT.

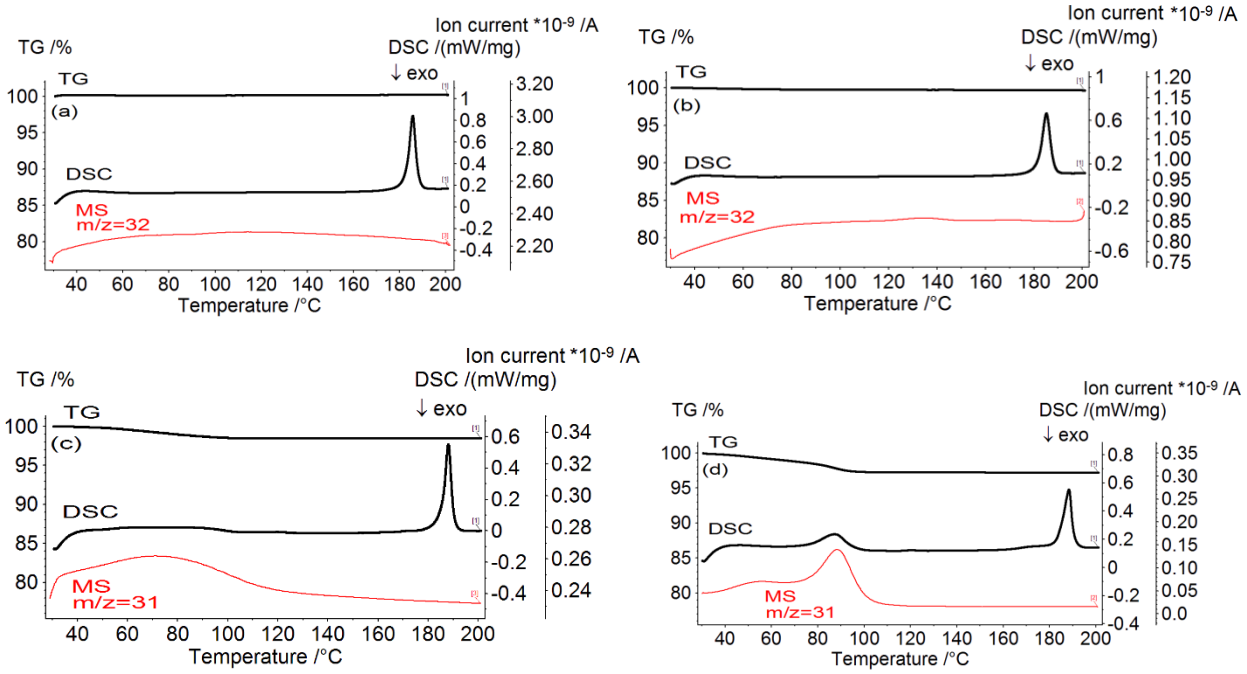

Figure 9S – TG/DSC/MS curves for products of solid calixarene **1** saturation with guest vapors at P/P_0 = 1, T= 25°C, in systems: (a) **1α** + MeOH, (b) **1g** + MeOH, (c) **1α** + EtOH, (d) **1g** + EtOH.

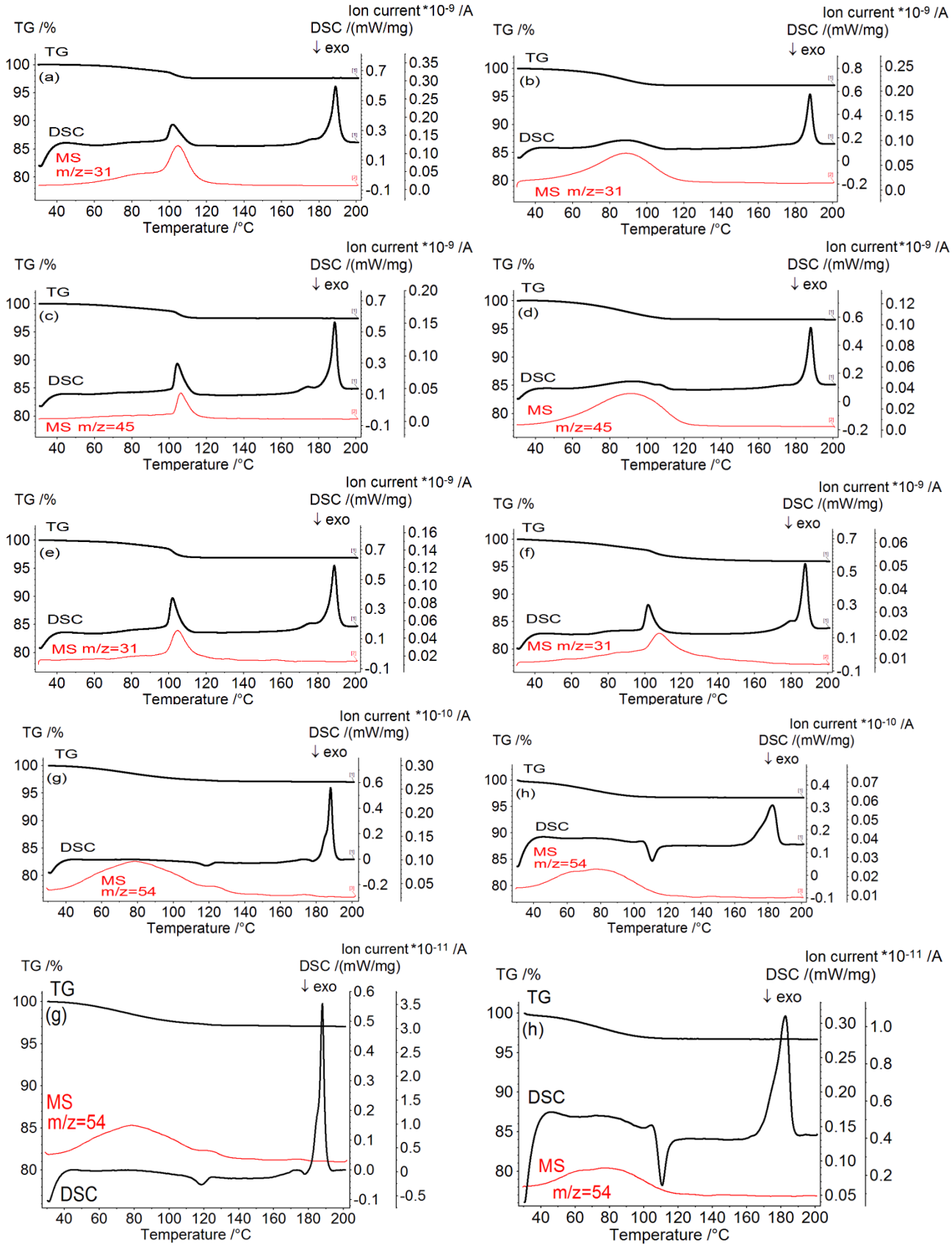

Figure 10S – TG/DSC/MS curves for products of solid calixarene **1** saturation with guest vapors at $P/P_0 = 1$, $T = 25$°C, in systems: (a) **1α** + n-PrOH, (b) **1g** + n-PrOH, (c) **1α** + i-PrOH, (d) **1g** + i-PrOH, (e) **1α** + n-BuOH, (f) **1g** + n-BuOH , (g) **1α** + EtCN, (h) **1g** + EtCN.

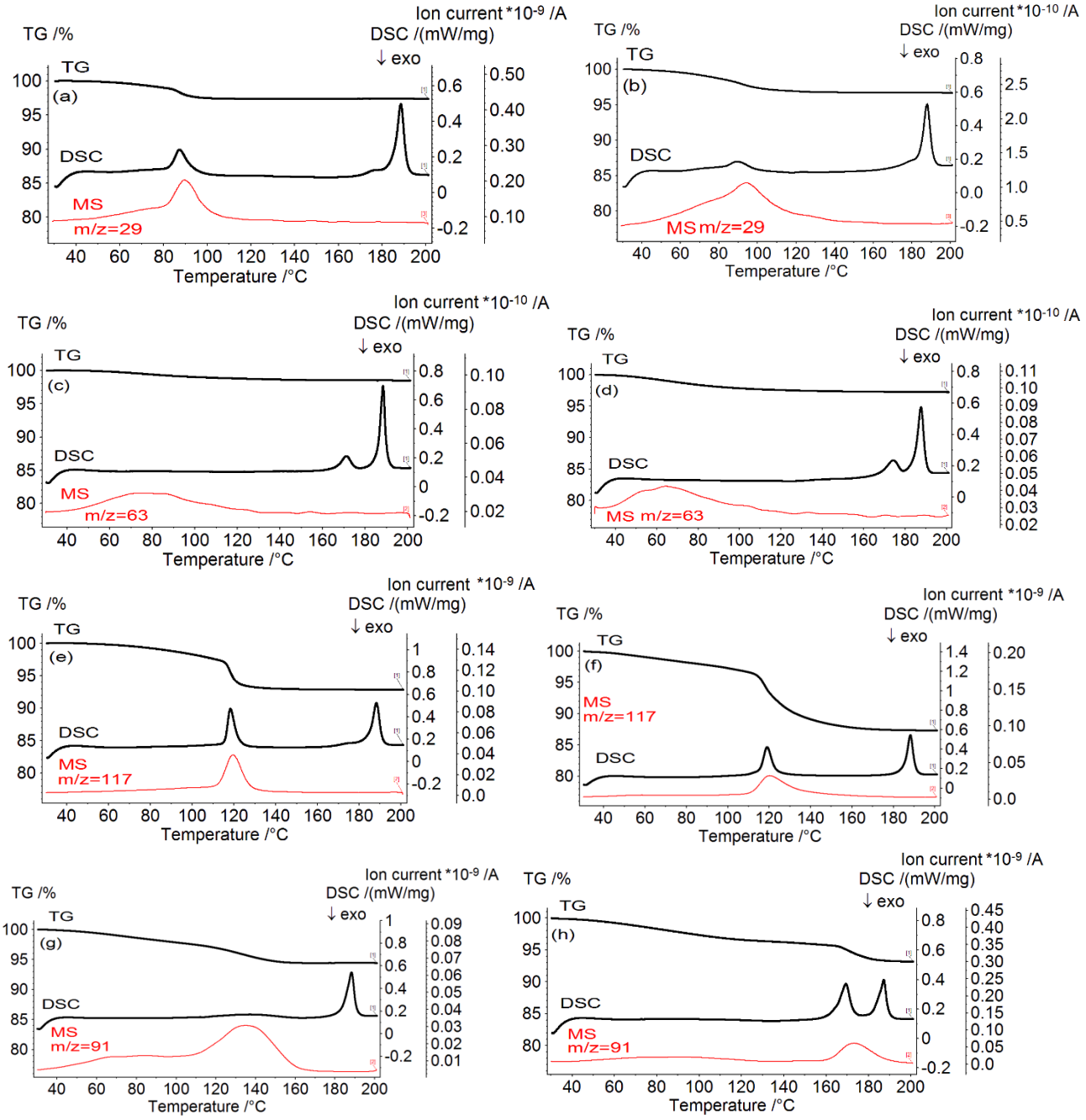

Figure 11S – TG/DSC/MS curves for products of solid calixarene **1** saturation with guest vapors at $P/P_0 = 1$, $T = 25$°C, in systems: (a) **1α** + PrCN, (b) **1g** + PrCN, (c) **1α** + $C_2H_4Cl_2$, (d) **1g** + $C_2H_4Cl_2$, (e) **1α** + CCl_4, (f) **1g** + CCl_4, (g) **1α** + C_6H_5Me, (h). **1g** + C_6H_5Me.

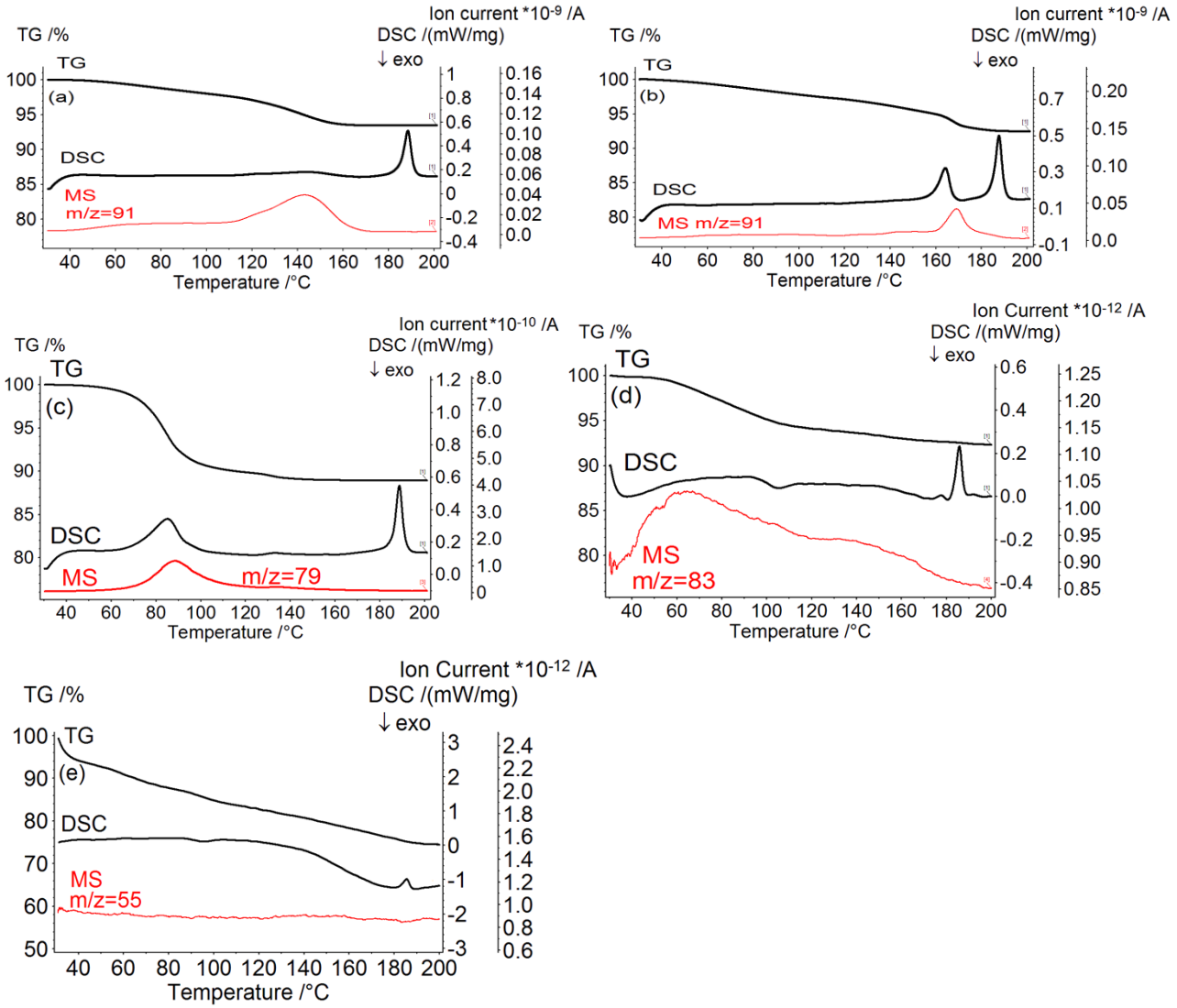

Figure 12S – TG/DSC/MS curves for products of solid calixarene **1** saturation with guest vapors at $P/P_0 = 1$, $T = 25$°C, in systems: (a) **1α** + C_6H_5Et, (b) **1g** + C_6H_5Et, (c) **1α** + C_5H_5N, (d) **1α** + $CHCl_3$, (e) **1α** + HFP.

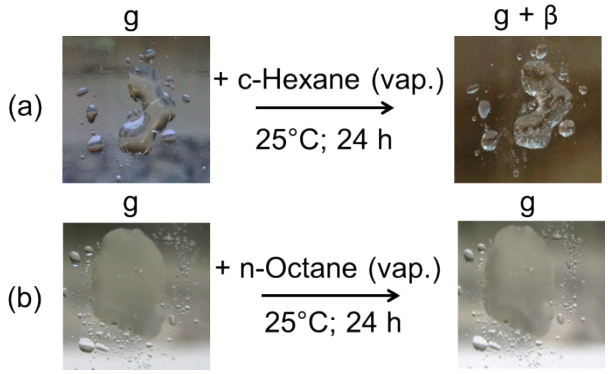

Figure 13S – Visual changes in **1g** sample at the saturation with vapors of (a) cyclohexane, (b) *n*-octane.

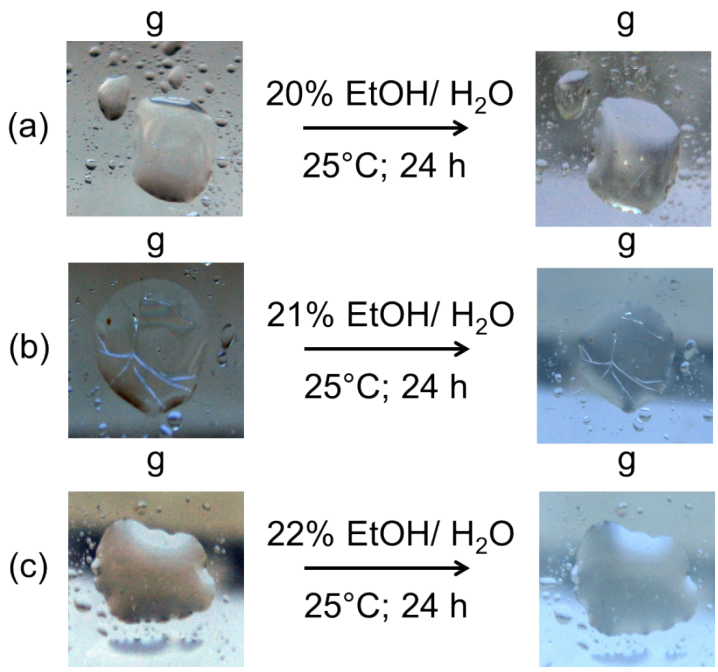

Figure 14S – Visual images of **1g** samples before and after saturation with vapors of binary aqueous mixture having ethanol contents (a) 20 vol. %, (b) 21 vol. %, (c) 22 vol. %; saturation time 24 h, *T*=25°C.

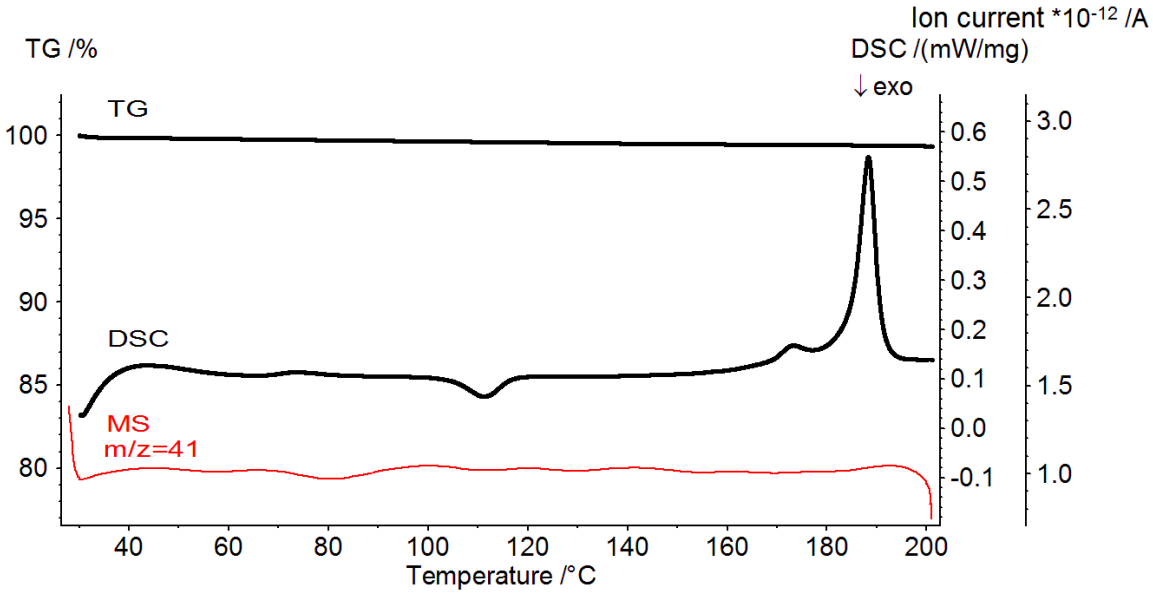

Figure 15S – TG/DSC/MS curves for a sample of β_0 phase prepared from clathrate formed by saturation of **1α** with acetonitrile vapor.

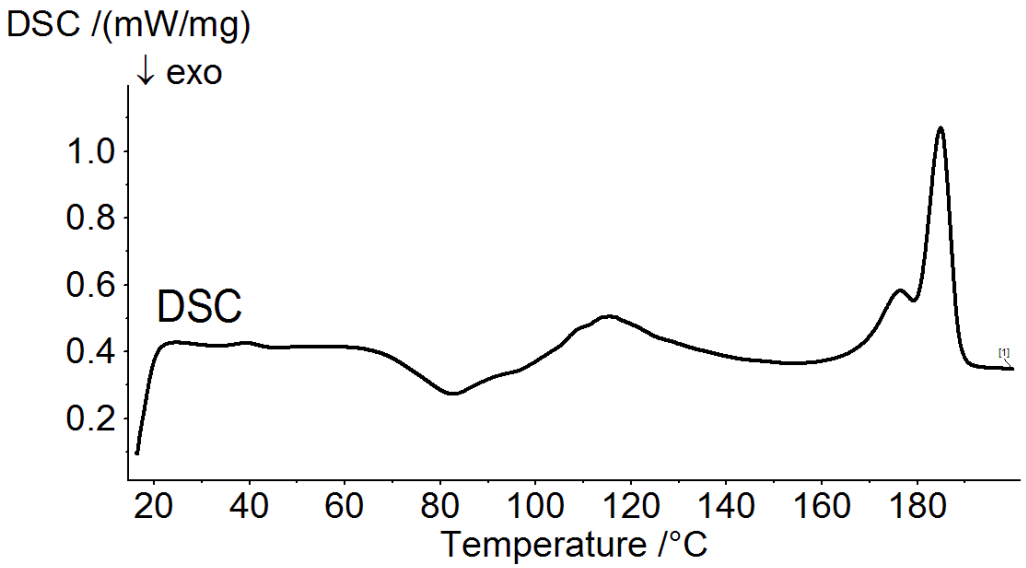

Figure 16S – DSC curve for compact **1g** glass saturated with vapor of liquid aqueous ethanol (25 vol%) for 24 h.

Table 1S. Enthalpies of **α→α'** transition $\Delta H_{\alpha\rightarrow\alpha'}$, fusion ΔH_m, and sum of these two values $\Delta H_\Sigma = \Delta H_{\alpha\rightarrow\alpha'} + \Delta H_m$ for products of **1α** and **1g** saturation with guest vapors from TG/DSC/MS experiment.

Guest	Host					
	1α			**1g**		
	$\Delta H_{\alpha\rightarrow\alpha'}$, kJ/mol	ΔH_m, kJ/mol	ΔH_Σ, kJ/mol	$\Delta H_{\alpha\rightarrow\alpha'}$, kJ/mol	ΔH_m, kJ/mol	ΔH_Σ, kJ/mol
No guest[a]	6	46	52	14	31	45
H_2O	7.2[b]	43.5	50.7	-	34.9	34.9
CH_3OH	-	57.0	57.0	-	52.2	52.2
C_2H_5OH	1.1	44.8	45.9	4.6	42.2	46.9
1-C_3H_7OH	5.0	42.3	47.3	3.0	41.5	44.5
2-C_3H_7OH	5.1[b]	41.0	46.0	3.0	38.6	41.5
1-C_4H_9OH	6.4[b]	43.8	50.3	9.2[b]	37.1	46.3
CH_3CN	3.1[b]	42.8	45.9	4.3	41.6	45.9
C_2H_5CN	3.2[b]	44.7	47.9	-	35.0	35.0
C_3H_7CN	4.6	41.5	46.0	3.2	42.4	45.7
Acetone	4.6[b]	43.8	48.3	3.8	40.1	43.9
Pyridine[c]	3.9	43.1	47.0	-	-	-
$C_2H_4Cl_2$	12.7[b]	40.9	53.6	15.7[b]	38.2	53.9
CCl_4	5.3	41.7	47.0	-	40.9	40.9
$CHCl_3$[c]	1.1	16.4	17.5	-	-	-
Benzene	3.4[b]	41.3	44.7	-	43.9	43.9
Toluene	-	42.7	42.7	-	29.5	29.5
Ethylbenzene	-	41.2	41.2	2	32.2	34.2
Cyclohexane	7.6[b]	44.5	52.1	4.8	41.8	46.6
n-Octane	6.4[b]	44.5	50.9	4.4	39.3	43.8

[a] data for initial **1α** and **1g** samples from TM-DSC experiment; [b] a separate peak of **α→α'** transition is observed, in other cases $\Delta H_{\alpha\rightarrow\alpha'}$ values are for shoulders of fusion peak where observed; [c] data for inclusion compounds from dried **1α** solution in liquid guest formed in vapor sorption process. The values of ΔH_Σ are determined with the error of ±1 kJ/mol.