Electronic supplementary information

# Analysis of guest binary mixtures by *tert*-butylcalix[6]arene using host memory of previously bound guests

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Supplemental TG/DSC/MS data for clathrates of *tert*-butylcalix[6]arene with $CCl_4$, $CHCl_3$, $C_6H_6$, *c*-$C_6H_{12}$ and products of saturation of calixarene **1** powder with headspace of $C_6H_6$ /*c*-$C_6H_{12}$ and $CCl_4$ /$CHCl_3$ mixtures.

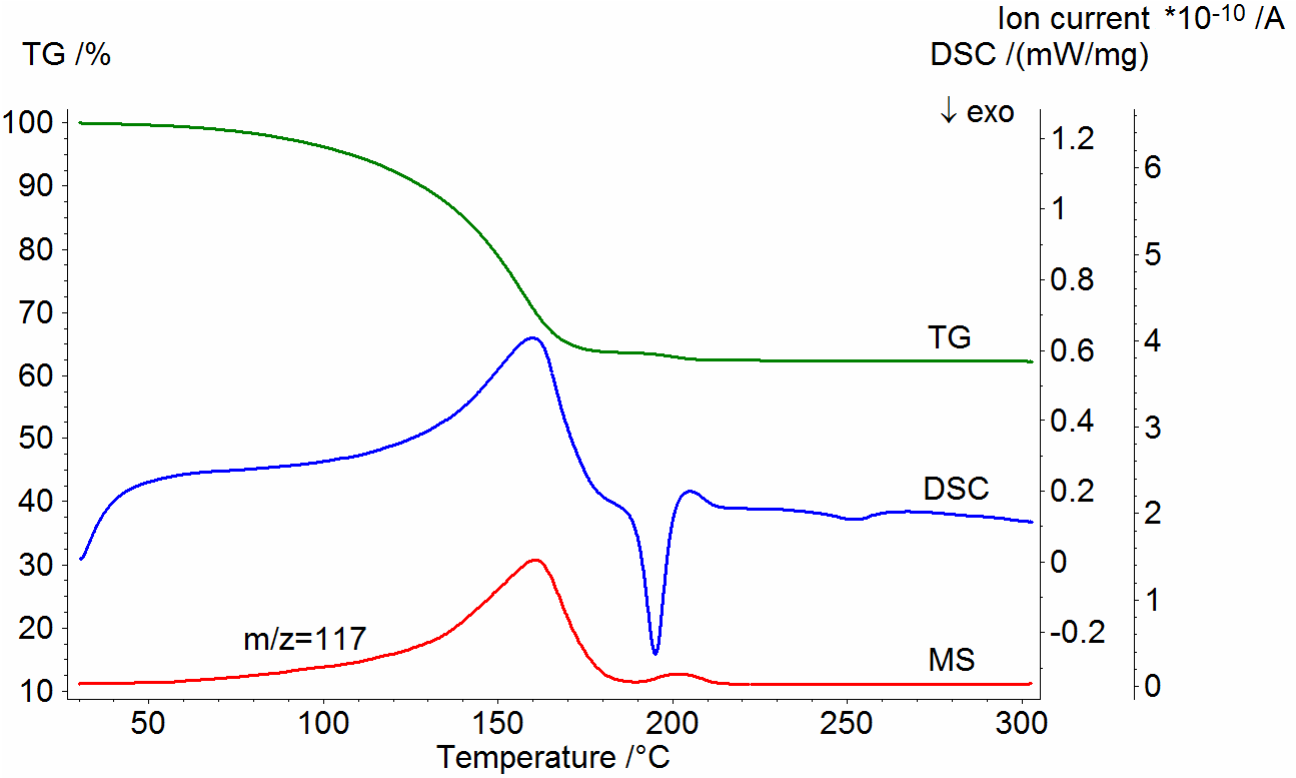


**Fig. S1** The data of TG/DSC/MS analysis of *tert*-butylcalix[6]arene clathrate with $CCl_4$. Heating rate 10 K $min^{-1}$.

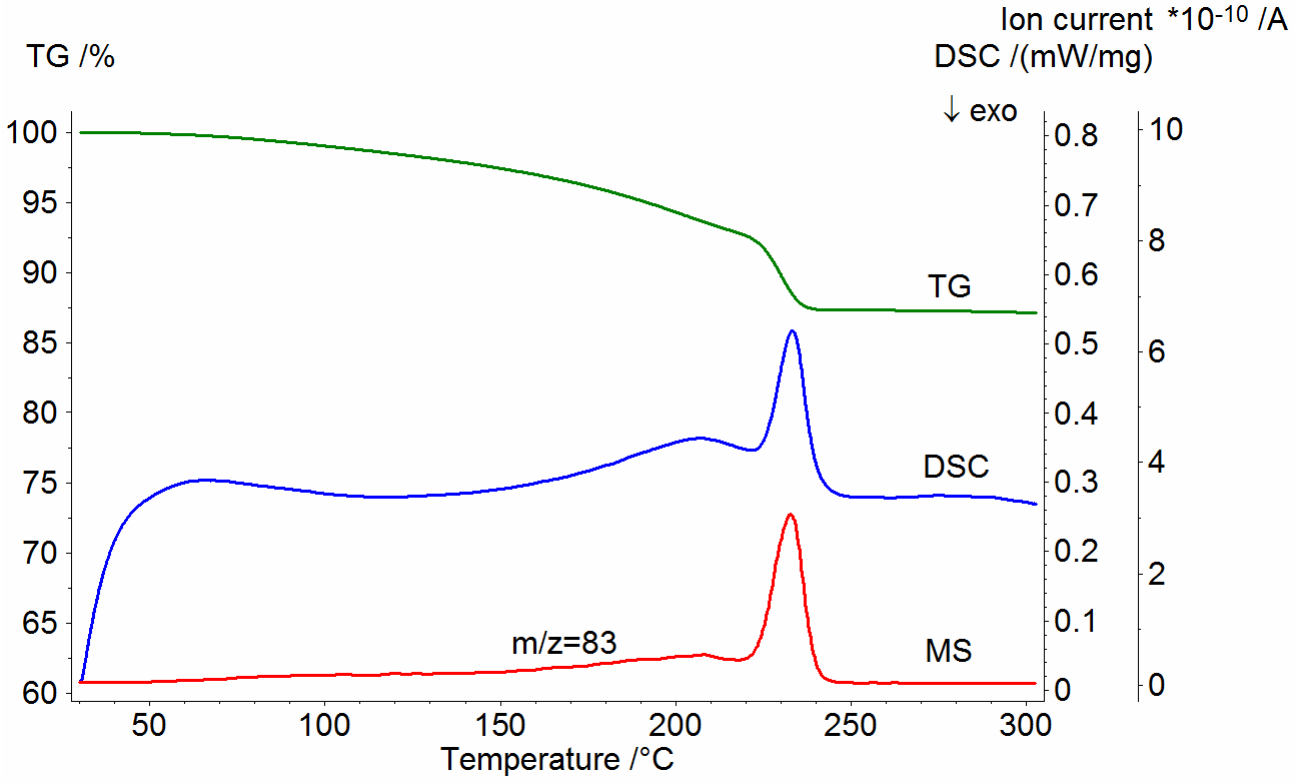


**Fig. S2** The data of TG/DSC/MS analysis of *tert*-butylcalix[6]arene clathrate with $CHCl_3$. Heating rate 10 K $min^{-1}$.

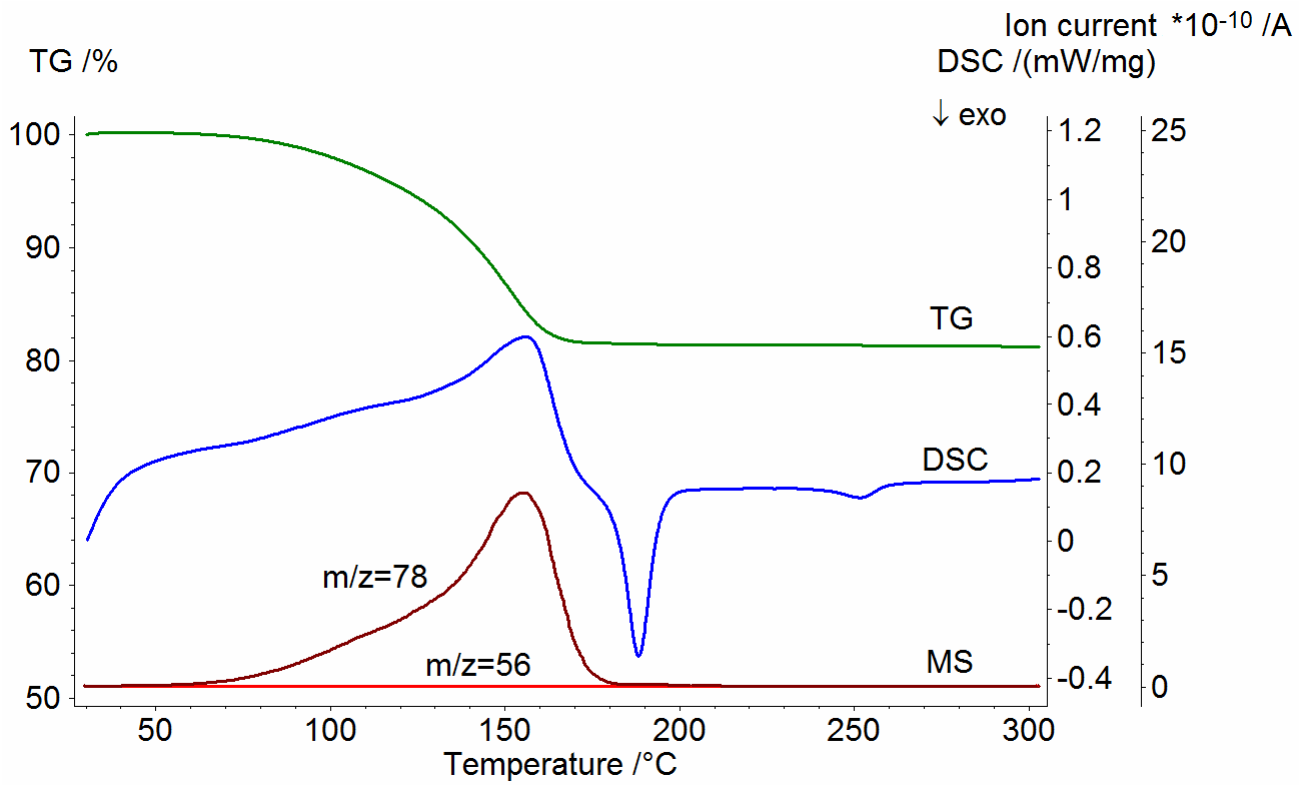


**Fig. S3** The data of TG/DSC/MS analysis of *tert*-butylcalix[6]arene clathrate with $C_6H_6$. Heating rate 10 K $min^{-1}$.

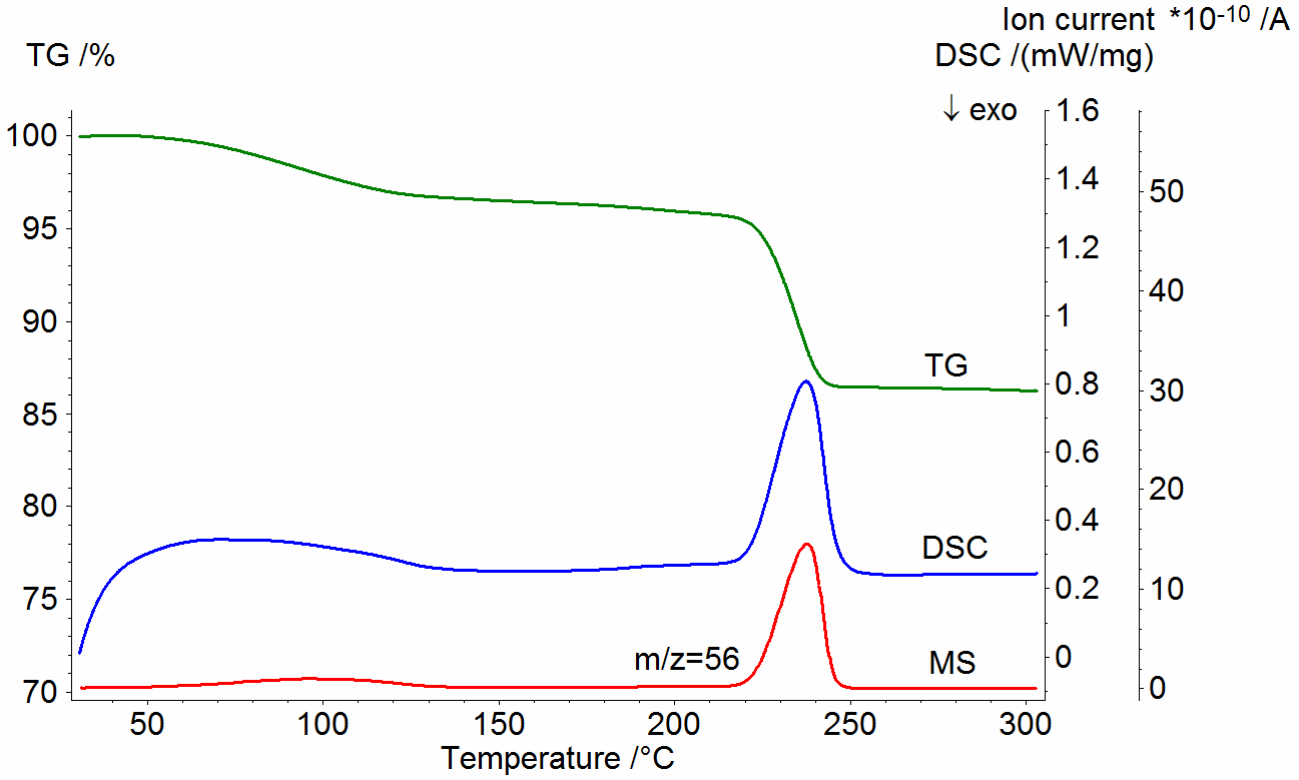


**Fig. S4** The data of TG/DSC/MS analysis of *tert*-butylcalix[6]arene clathrate with *c*-$C_6H_{12}$. Heating rate 10 K $min^{-1}$.

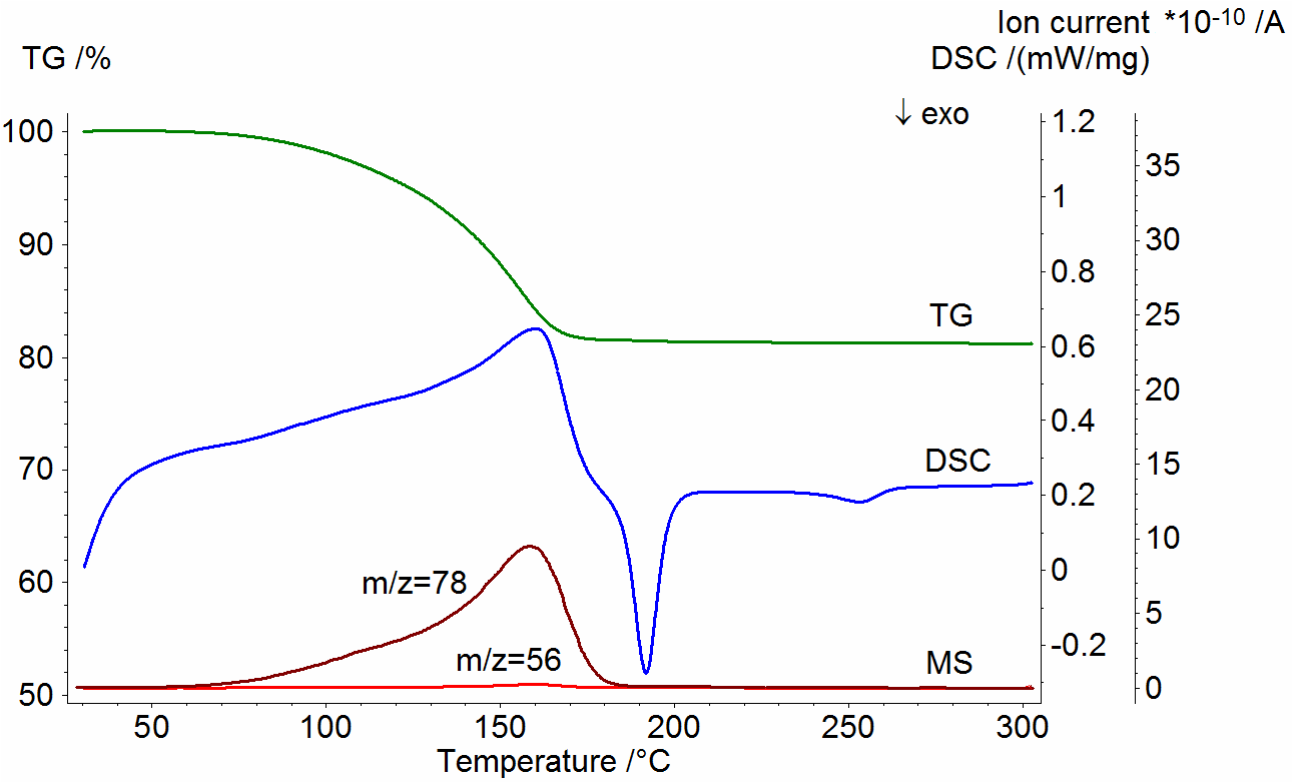


**Fig. S5** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (2 vol.%) in benzene at 25°C. Heating rate 10 K $min^{-1}$.

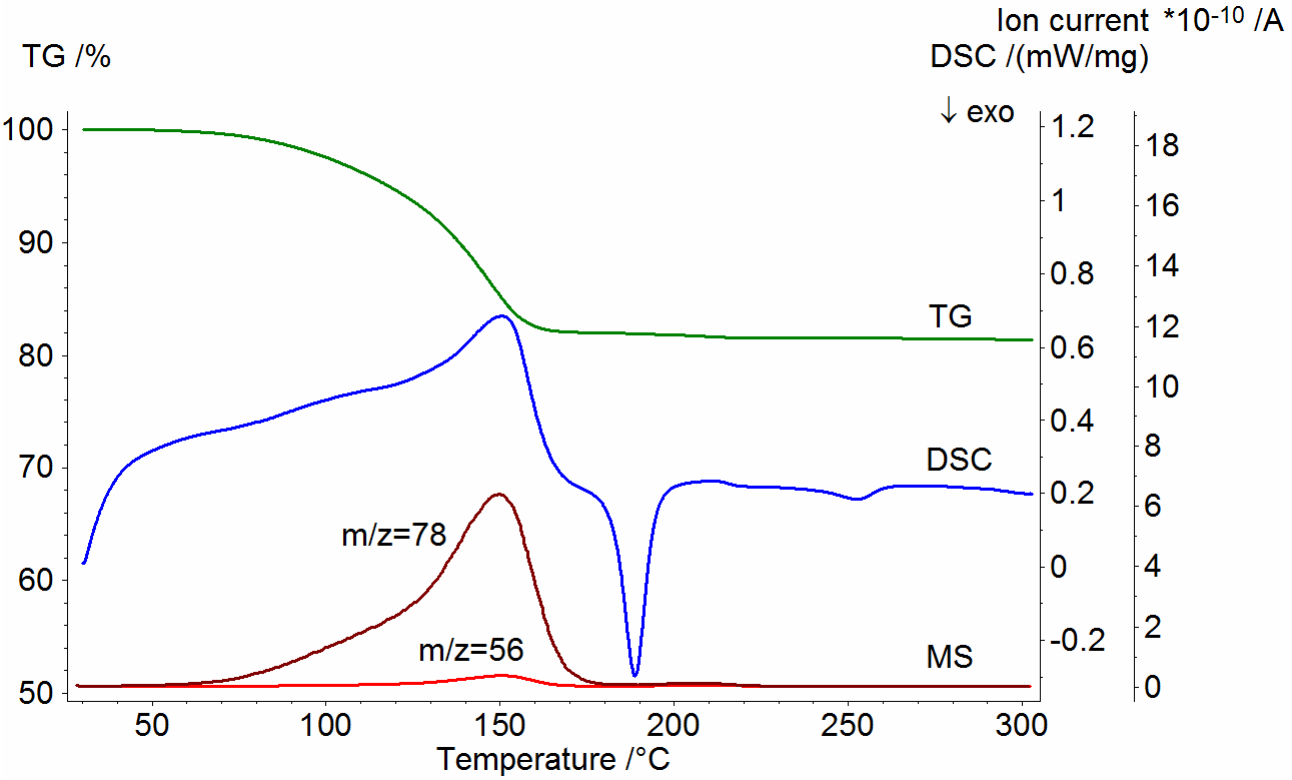


**Fig. S6** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (5 vol.%) in benzene at 25°C. Heating rate 10 K $min^{-1}$.

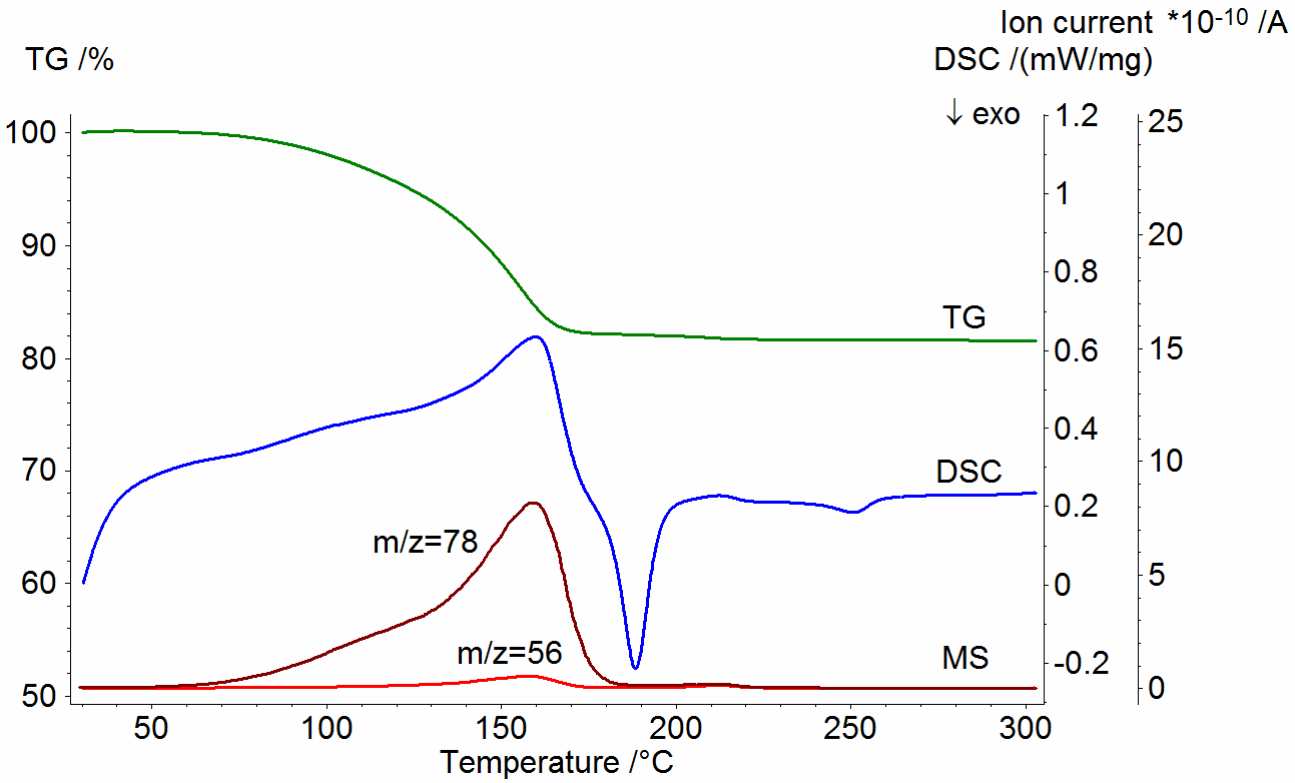


**Fig. S7** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (6 vol.%) in benzene at 25°C. Heating rate 10 K $min^{-1}$.

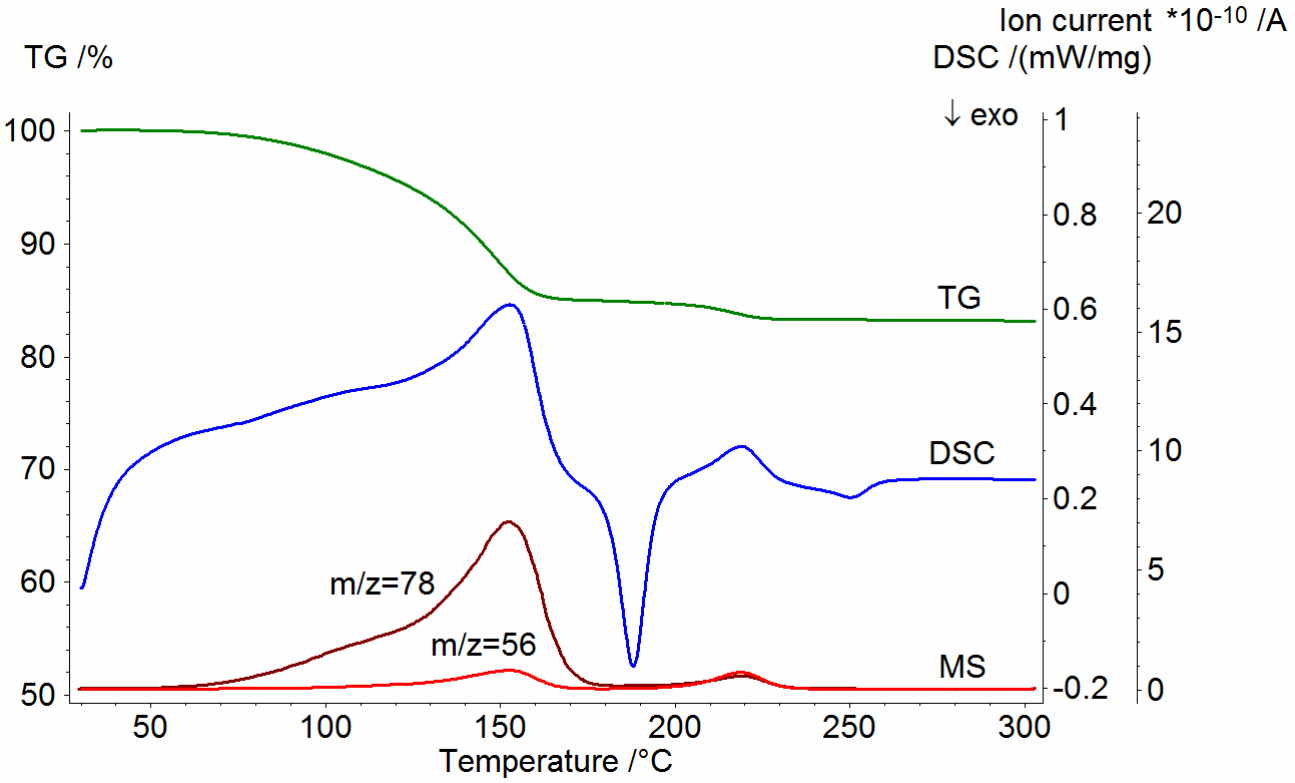


**Fig. S8** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (10 vol.%) in benzene at 25°C. Heating rate 10 K $min^{-1}$.

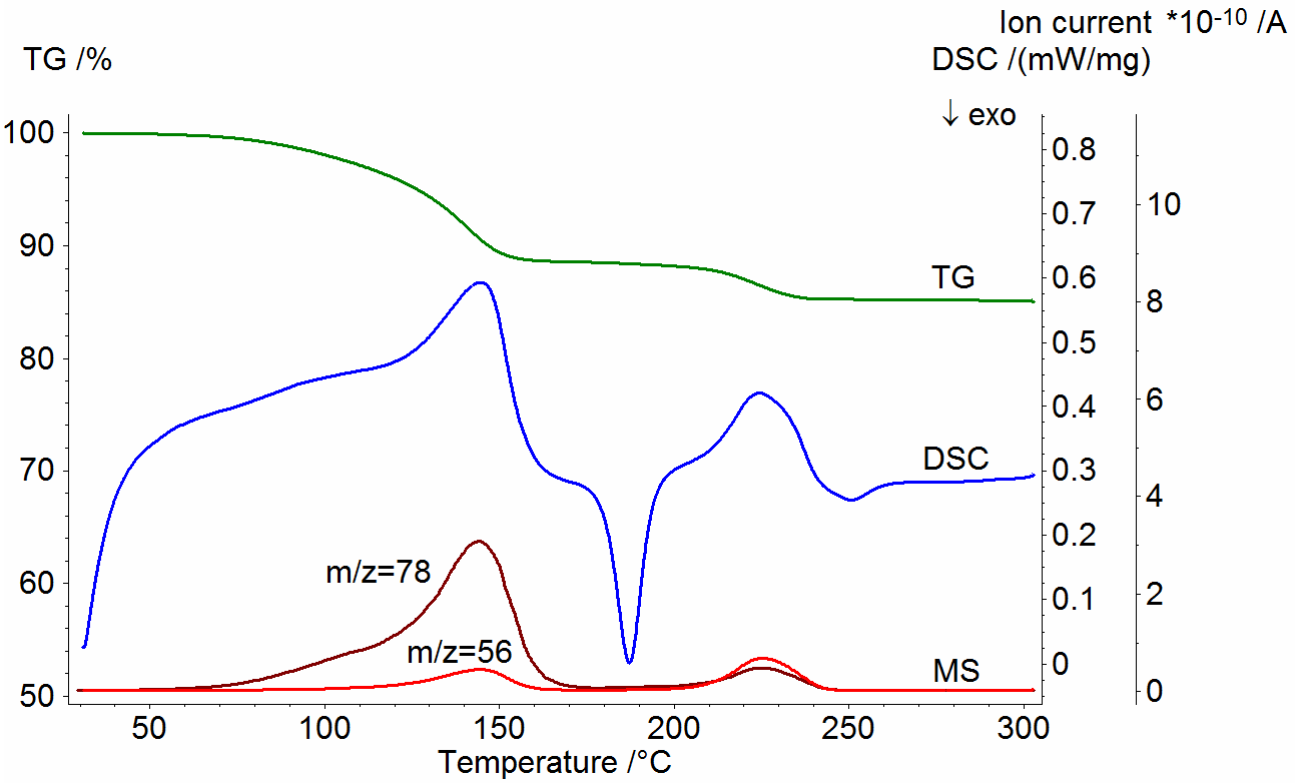


**Fig. S9** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (14 vol.%) in benzene at 25°C. Heating rate 10 K $min^{-1}$.

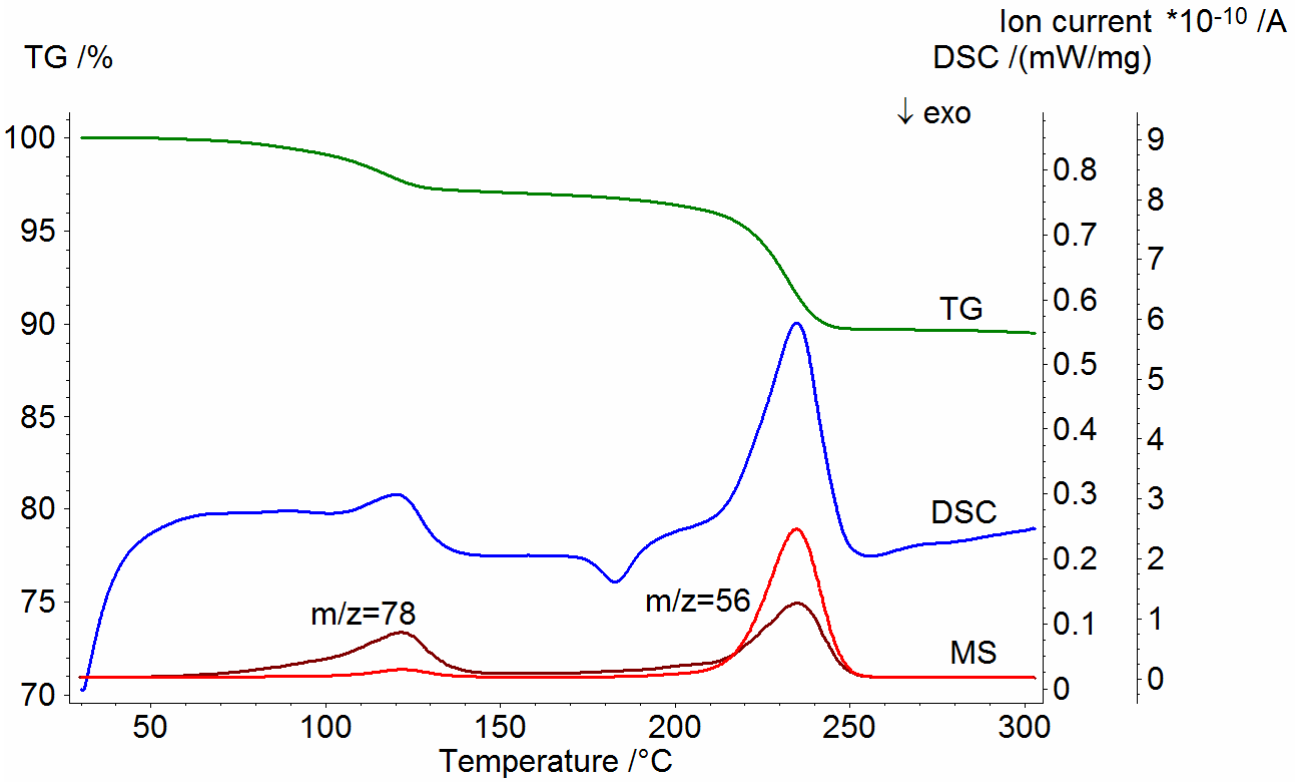


**Fig. S10** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (18 vol.%) in benzene at 25°C. Heating rate 10 K $min^{-1}$.

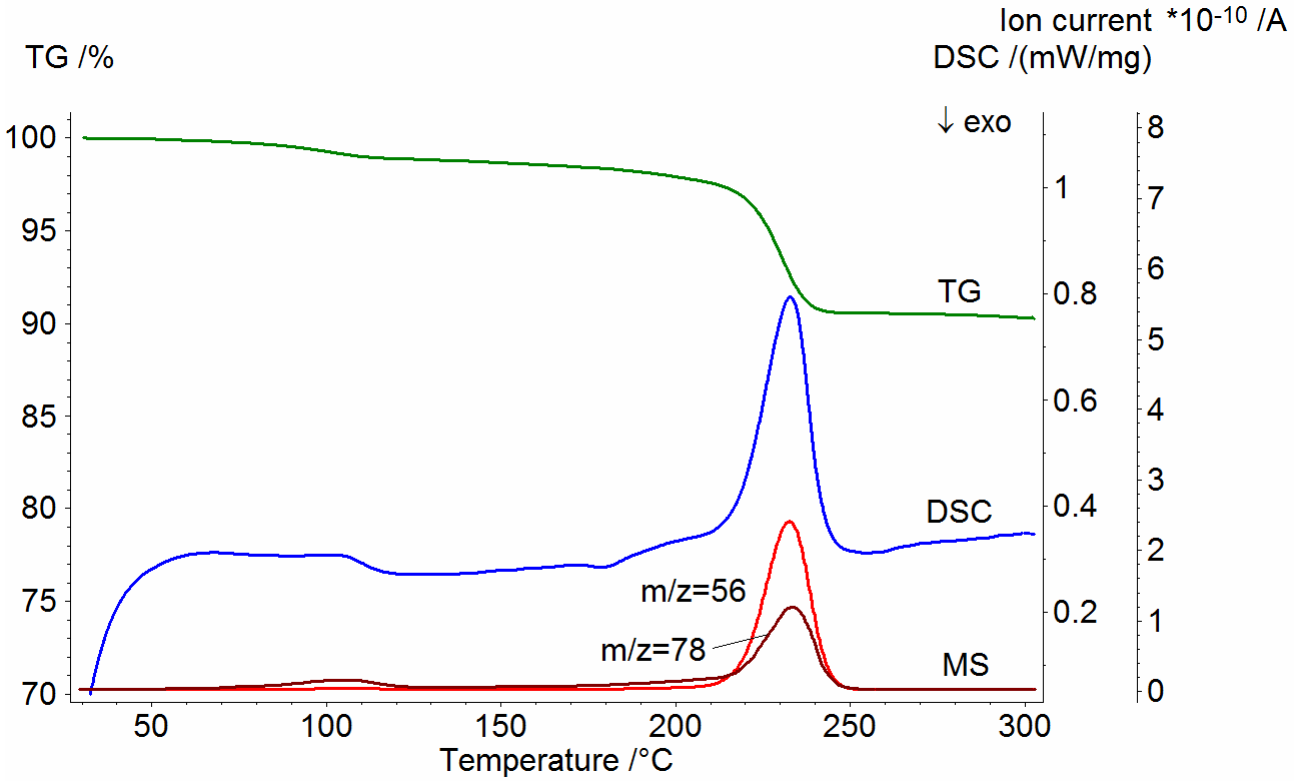


**Fig. S11** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (20 vol.%) in benzene at 25°C. Heating rate 10 K min$^{-1}$.

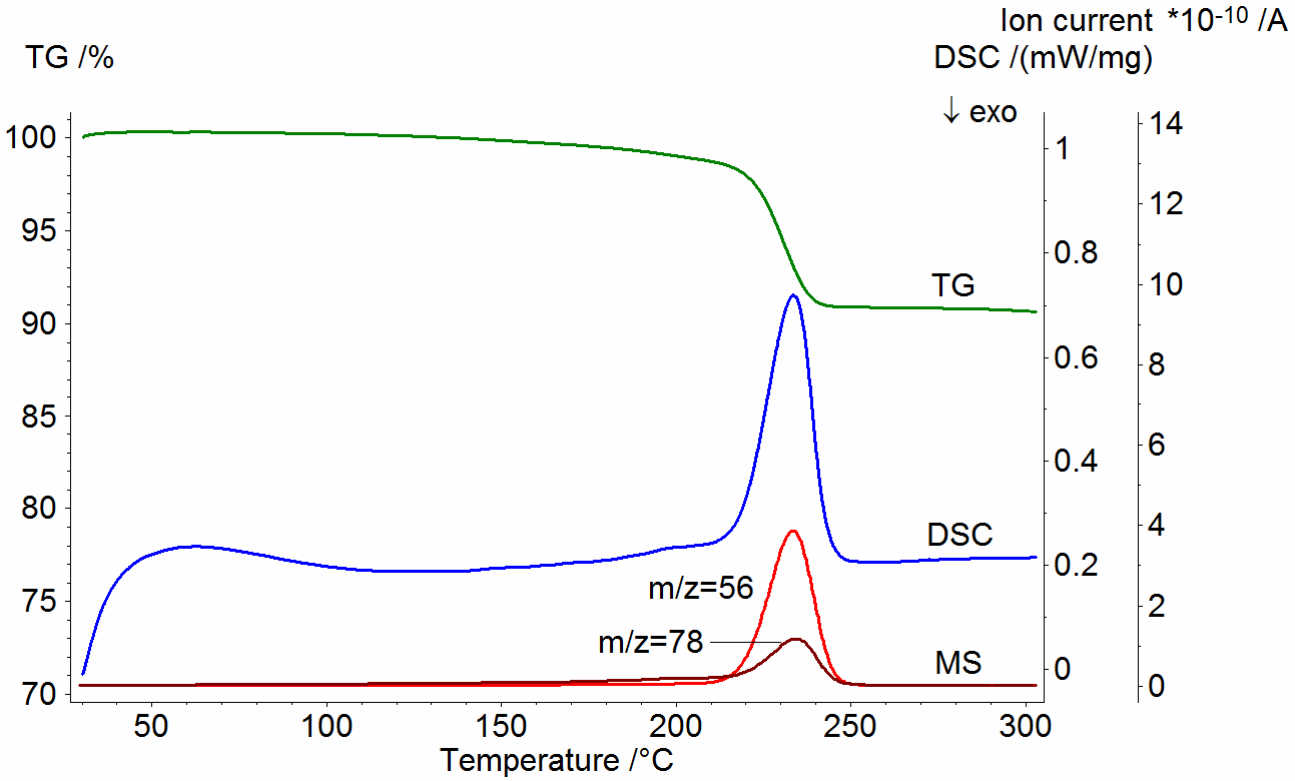


**Fig. S12** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of cyclohexane solution (28 vol.%) in benzene at 25°C. Heating rate 10 K min$^{-1}$.

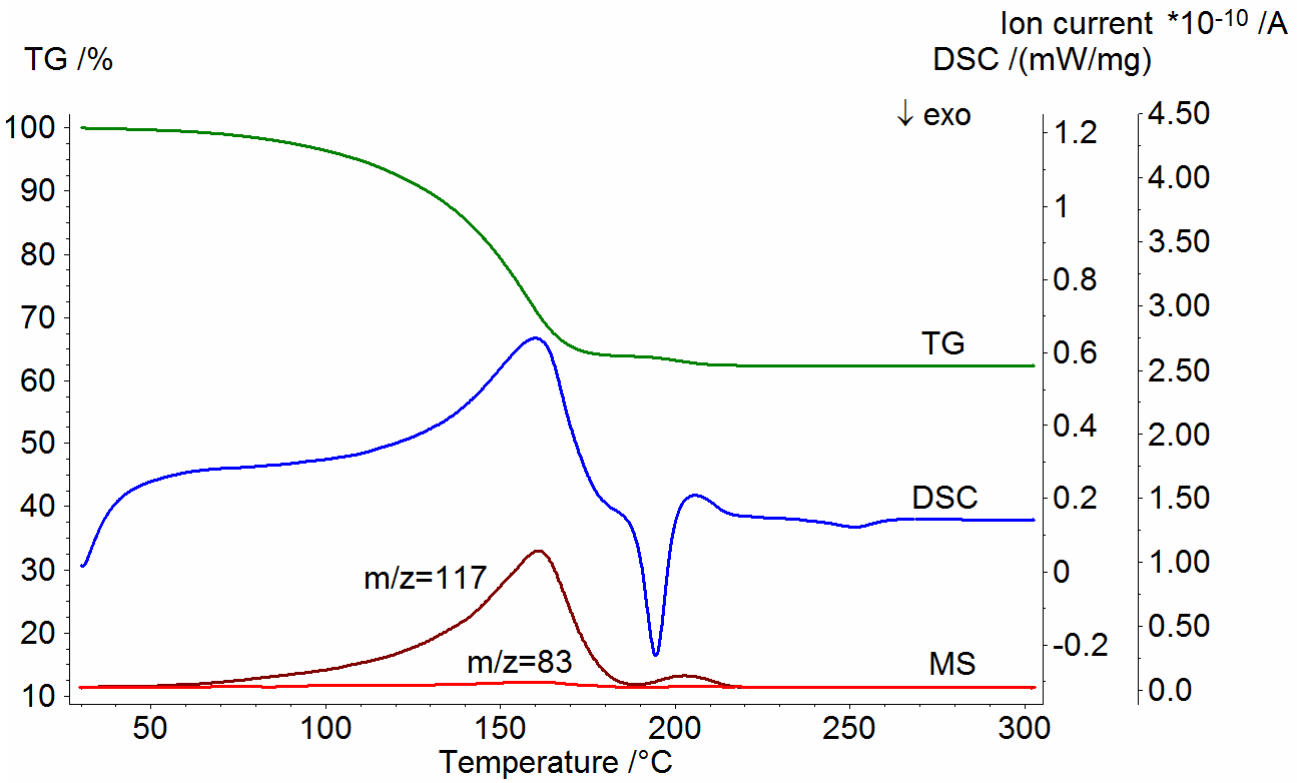


**Fig. S13** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of chloroform solution (2 vol.%) in tetrachloromethane at 25°C. Heating rate 10 K $min^{-1}$.

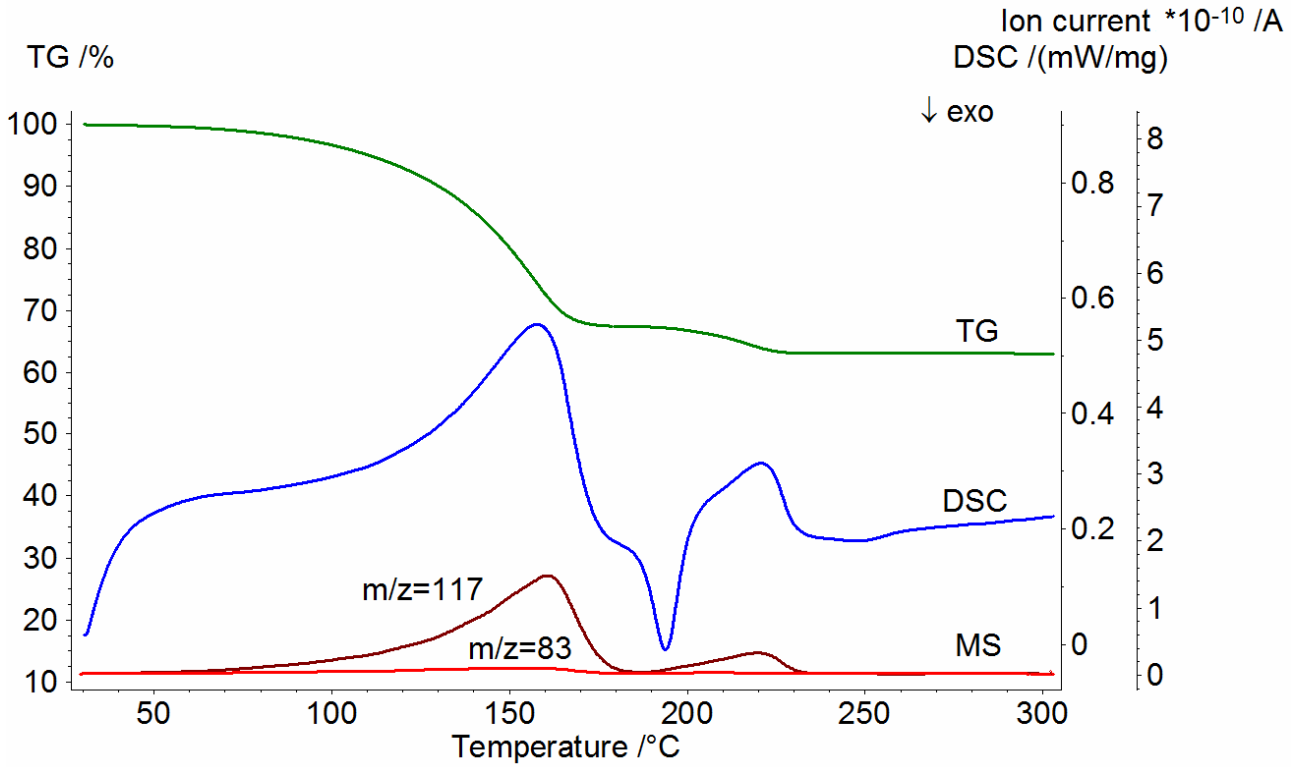


**Fig. S14** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of chloroform solution (6 vol.%) in tetrachloromethane at 25°C. Heating rate 10 K $min^{-1}$.

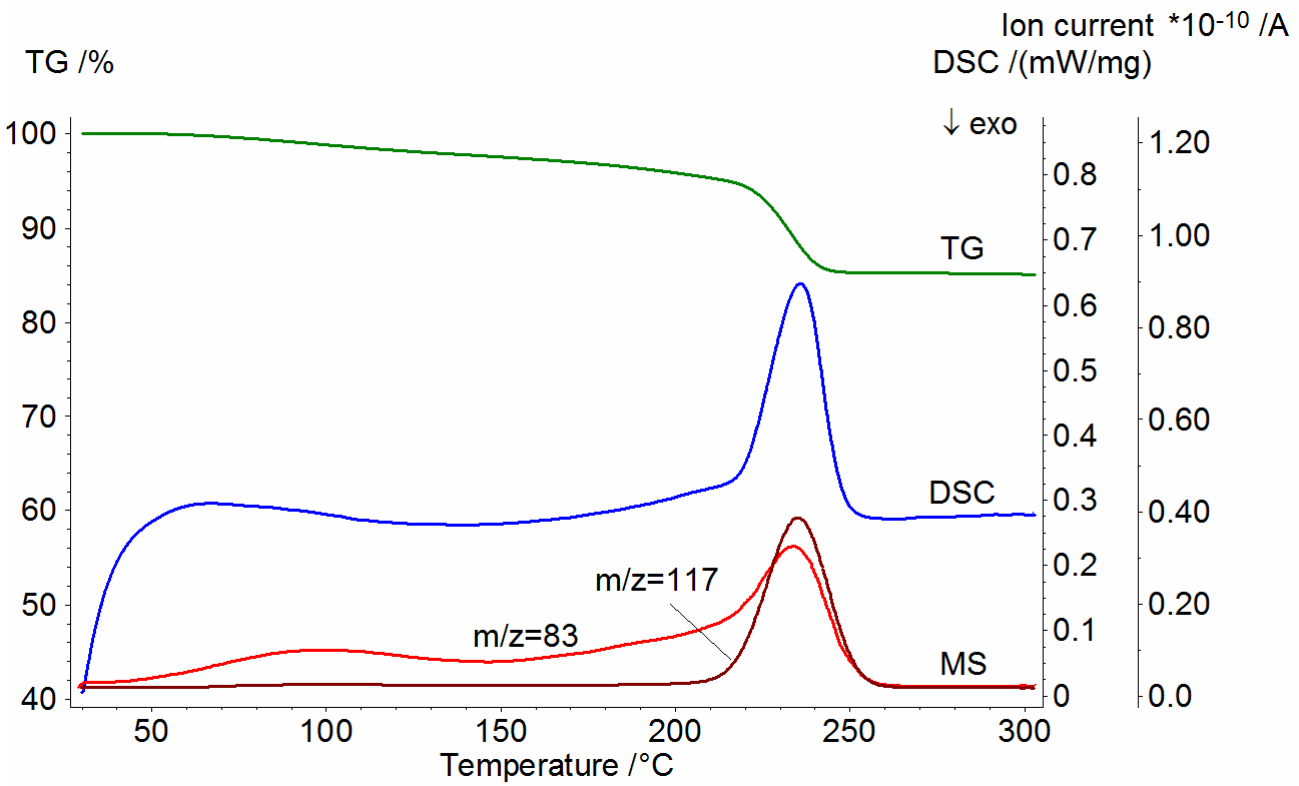


**Fig. S15** The data of TG/DSC/MS analysis for product of *tert*-butylcalix[6]arene saturation by headspace of chloroform solution (70 vol.%) in tetrachloromethane at 25°C. Heating rate 10 K min$^{-1}$.

**Table 1S.** End points of the first decomposition step ($T_{end}^{(1)}$), temperatures of DTG-peaks ($T_{max}^{(1)}$, $T_{max}^{(2)}$) and the enthalpy of second exothermic peak ($\Delta H_{col}^{(2)}$) of decomposition of clathrates prepared by saturation of *tert*-butylcalix[6]arene with vapors of individual and mixed cyclohexane and benzene.

| $\varphi$ ($c$-$C_6H_{12}$), vol.% | $T_{end}^{(1)}$,°C | $T_{max}^{(1)}$,°C | $T_{max}^{(2)}$, °C | $\Delta H_{col}^{(2)}$, kJ mol$^{-1}$ |
|---|---|---|---|---|
| 0 | 163 | 152 | - | -3 |
| 2 | 168 | 156 | - | -4 |
| 5 | 158 | 147 | 210 | -3 |
| 6 | 166 | 155 | 211 | -3 |
| 8 | 158 | 148 | 213 | -3 |
| 10 | 159 | 149 | 217 | -3 |
| 12 | 154 | 143 | 220 | -2 |
| 14 | 151 | 141 | 223 | -2 |
| 16 | 139 | 129 | 228 | -2 |
| 18 | 127 | 118 | 232 | -2 |
| 20 | 111 | 101 | 230 | -2 |
| 22 | 121 | 111 | 230 | -1 |
| 24 | - | 0 | 230 | - |
| 28 | - | 0 | 231 | - |
| 30 | - | 0 | 230 | - |
| 50 | - | 0 | 231 | - |
| 100 | 118 | 91 | 235 | - |

**Table 2S.** End points of the first decomposition step ($T_{end}^{(1)}$), temperatures of DTG-peaks ($T_{max}^{(1)}$, $T_{max}^{(2)}$) and the second exothermic peak enthalpy ($\Delta H_{col}^{(2)}$) of decomposition of clathrates prepared by saturation of *tert*-butylcalix[6]arene with vapors of individual and mixed chloroform and tetrachloromethane.

| $\varphi$ ($CHCl_3$), vol.% | $T_{end}^{(1)}$,°C | $T_{max}^{(1)}$,°C | $T_{max}^{(2)}$, °C | $\Delta H_{col}^{(2)}$, kJ mol$^{-1}$ |
|---|---|---|---|---|
| 0 | 168 | 157 | 200 | -2 |
| 2 | 168 | 158 | 201 | -3 |
| 4 | 167 | 158 | 215 | -2 |
| 6 | 166 | 157 | 217 | -2 |
| 8 | 153 | 144 | 222 | -2 |
| 12 | 153 | 143 | 224 | - |
| 15 | 143 | 130 | 225 | - |
| 20 | 132 | 105 | 237 | - |
| 56 | - | 81 | 235 | - |
| 70 | - | 90 | 233 | - |
| 100 | - | 202 | 230 | - |

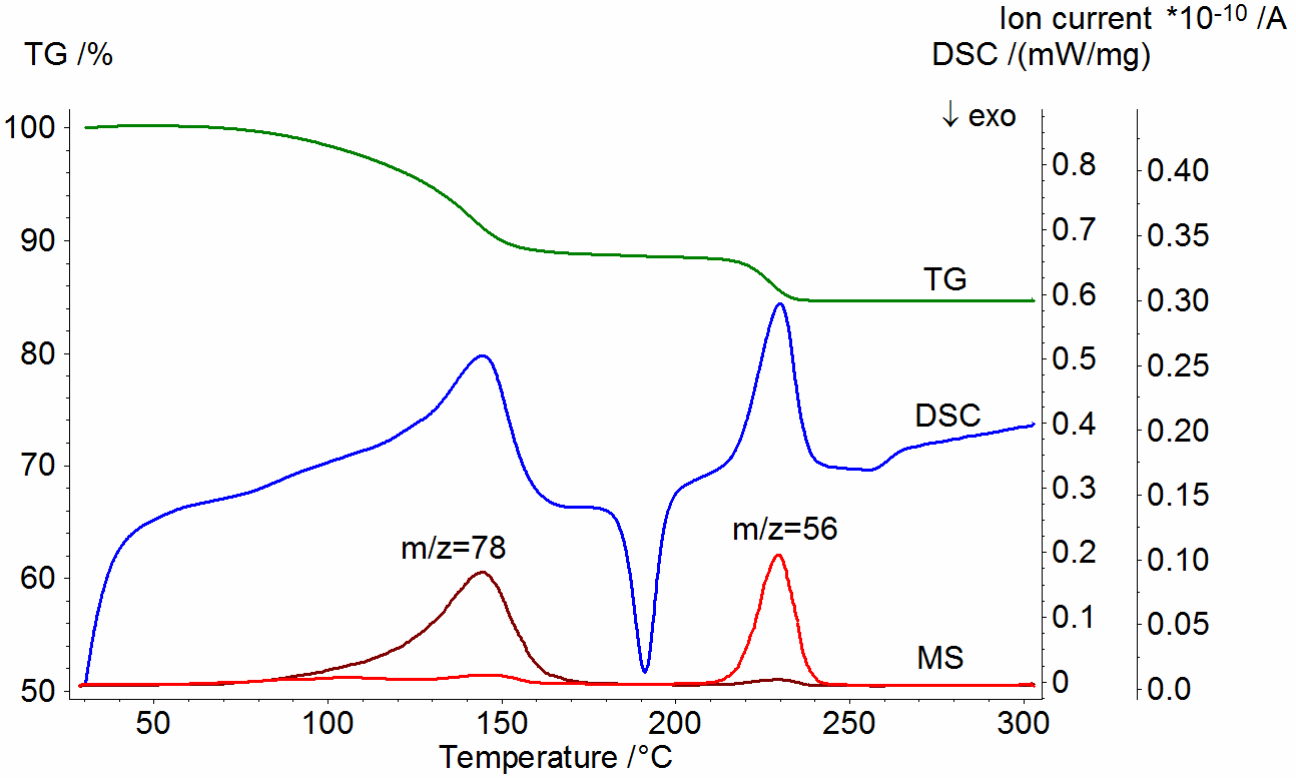


**Fig. S16** The data of TG/DSC/MS analysis for mechanical mixture of host **1** clathrates with $C_6H_6$ and *c*-$C_6H_{12}$. Ion thermograms of $C_6H_6$ (m/z=78) and *c*-$C_6H_{12}$ (m/z=56) are shown. Heating rate 10 K min$^{-1}$.

The mechanical mixture contains 54% (w/w) of **1**•2.86 $C_6H_6$ and 46% (w/w) of **1**•1.18 *c*-$C_6H_{12}$. This mixture gives nearly the same guest ratio in solid host phase as the product of host **1** saturation by headspace of cyclohexane solution (16 vol.%) in benzene at 25°C.