Electronic supplementary information

Metastable porous phase of *tert*-butylcalix[6]arene with large tunable free volume for non-threshold enclathration of volatiles

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Supplemental XRPD and TG-DSC data for different forms of *tert*-butylcalix[6]arene and its clathrates, vapor sorption isotherms of guests on α and β_0 forms of *tert*-butylcalix[6]arene.

All powder X-ray diffraction data (**XRPD**) were collected on Bruker *D*8 Advance diffractometer equipped with Vantec linear PSD, using Cu Kα radiation (40 kV, 40 mA). No monochromation was employed. Room-temperature data were collected in the Bragg–Brentano mode with a flat-plate sample. The sample was lightly grounded and loaded into a standard sample holder, which was kept spinning (30 rpm) throughout the data collection. Patterns were recorded in the 2Θ range between 5 and 40°, in 0.007° steps, with a step time of 2 s. Five powder patterns were collected and summed for each sample.

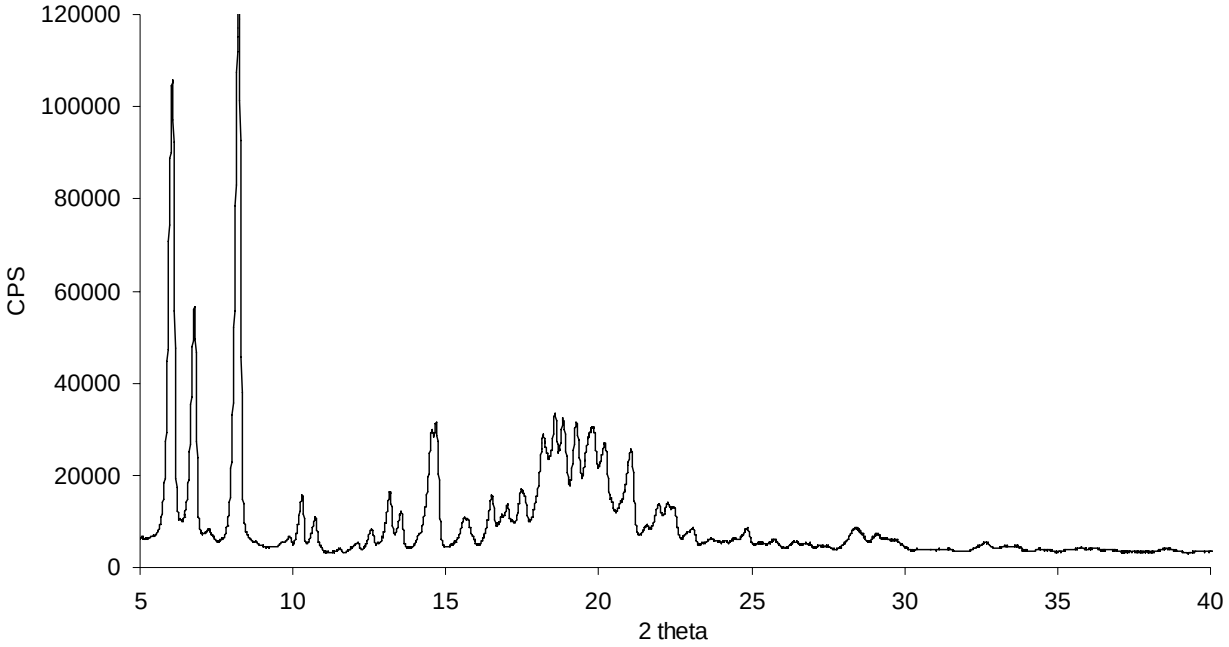

Fig. S1 XRPD diffractogram of *tert*-butylcalix[6]arene clathrate with benzene (β-phase) prepared by saturation of host powder with guest vapor at 298 K.

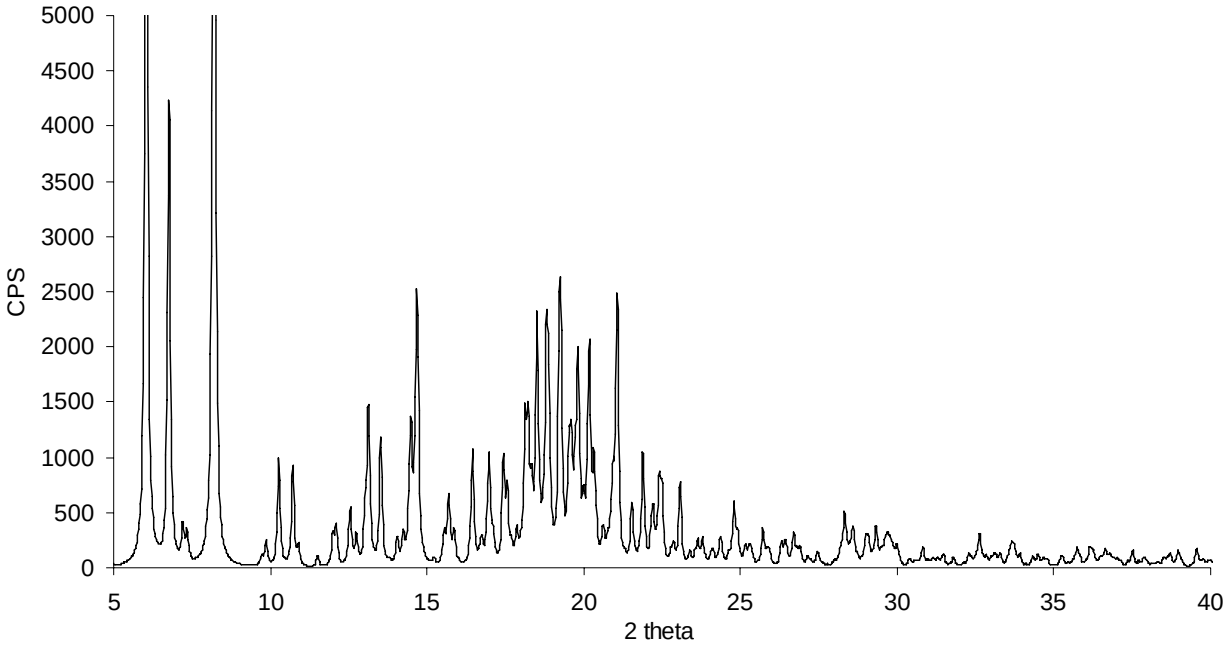

Fig. S2 XRPD diffractogram of *tert*-butylcalix[6]arene clathrate with benzene (β-phase) calculated from single crystal X-ray data [M. Halit, D. Oehler, M. Perrin, A. Thozet, R. Perrin, J. Vicens, M. Bourakhouadar, *J. Inclusion Phenom. Macrocyclic Chem,* 1988, **6**, 613-623].

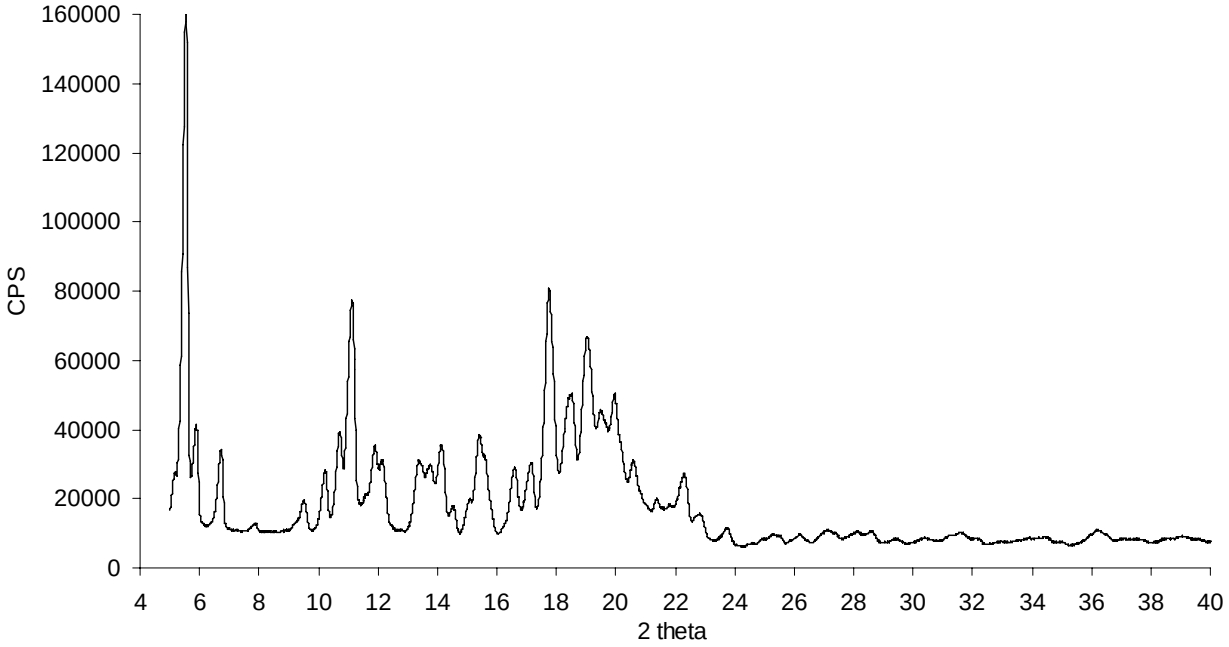

Fig. S3 XRPD diffractogram of *tert*-butylcalix[6]arene (α-phase).

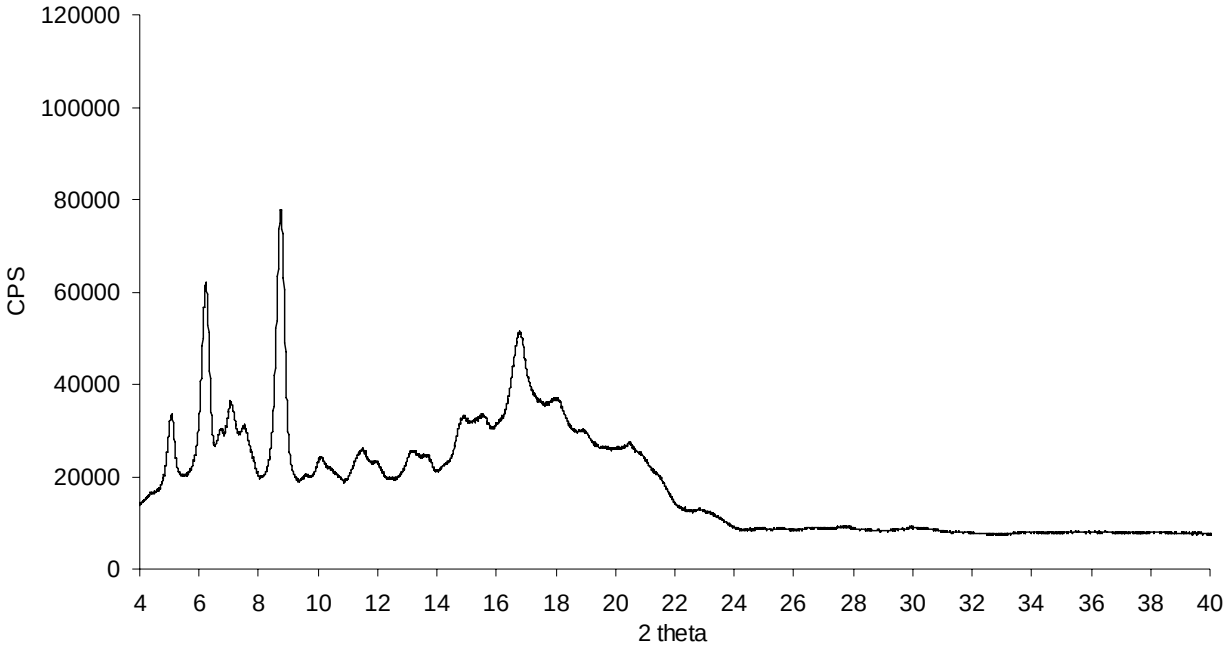

Fig. S4 XRPD diffractogram of *tert*-butylcalix[6]arene (β_0-phase).

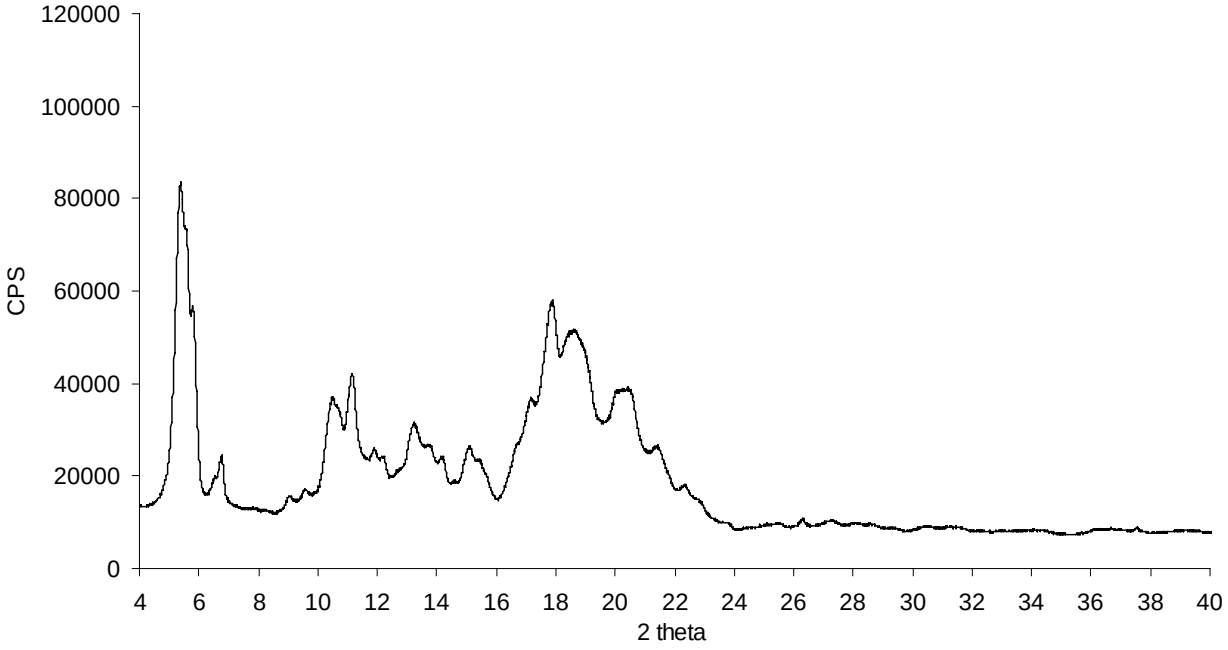

Fig. S5 XRPD diffractogram of *tert*-butylcalix[6]arene (α'-phase).

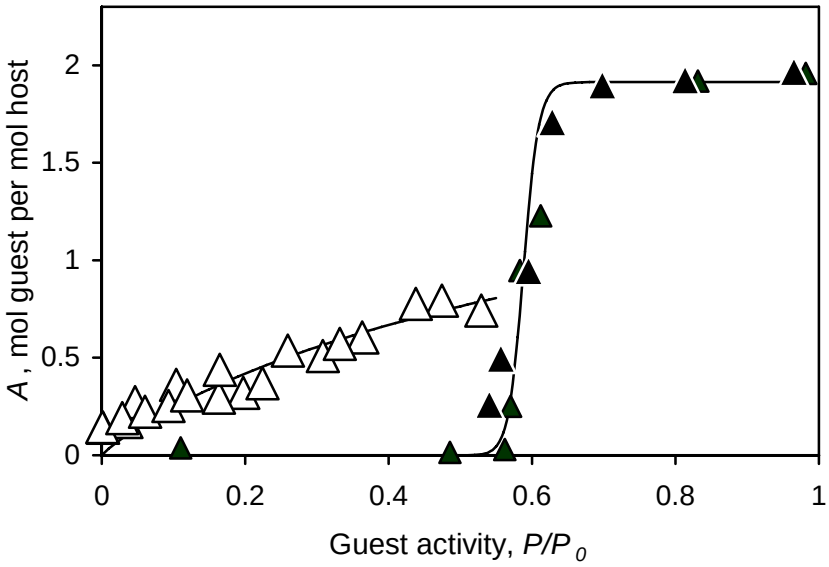

Fig. S6 Isotherms of dichloromethane vapor sorption at 298 K by powder of (△) α-phase of *tert*-butylcalix[6]arene (**1**), and (▲) β_0-phase of **1** prepared by heating of **1**•3.49CCl_4 clathrate under vacuum (0.1 kPa) at 150°C for 8 h.

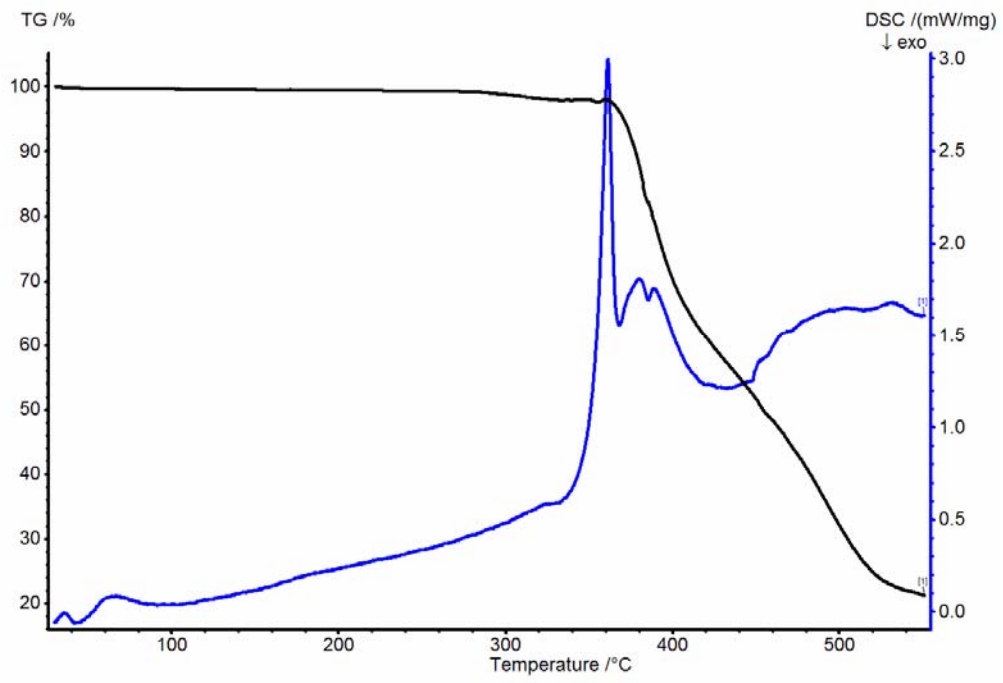

Fig. S7 The data of simultaneous TG/DSC analysis of pure *tert*-butylcalix[6]arene (α-phase). Heating rate 10 K min^{-1}

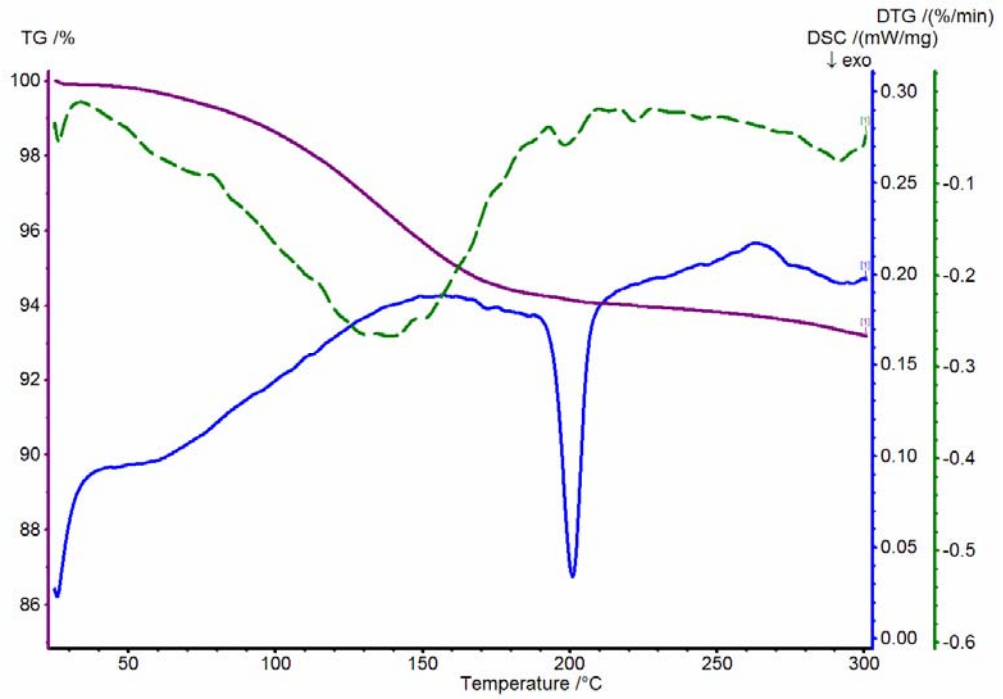

Fig. S8 The data of simultaneous TG/DSC analysis of *tert*-butylcalix[6]arene clathrate with Me_2CO. Heating rate 4 K min^{-1}

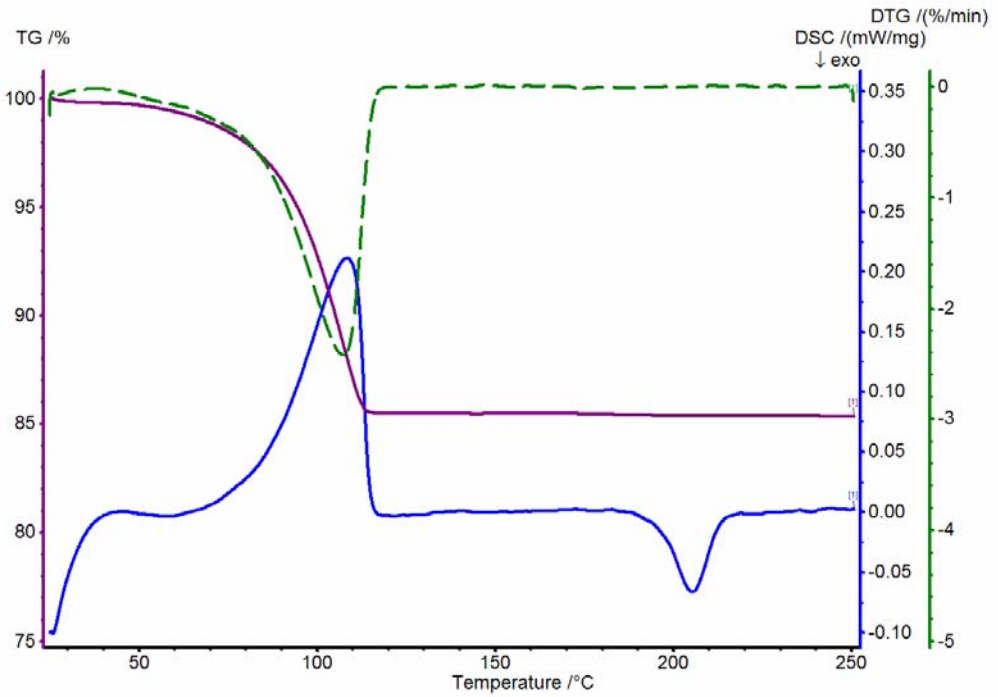

Fig. S9 The data of simultaneous TG/DSC analysis of *tert*-butylcalix[6]arene clathrate with CH_2Cl_2. Heating rate 4 K min^{-1}

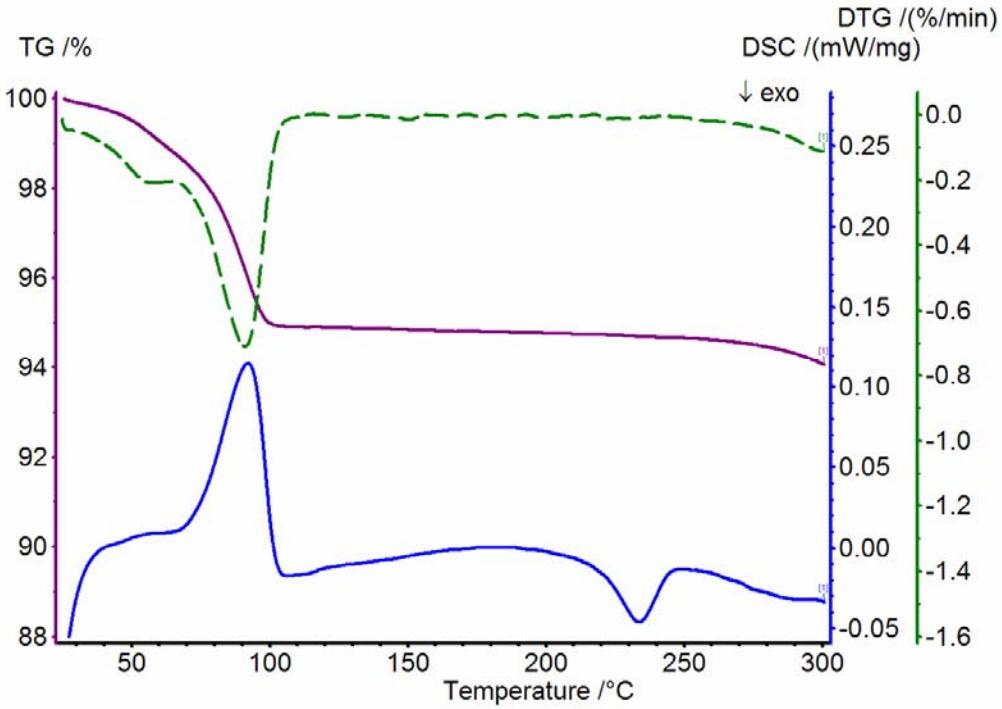

Fig. S10 The data of simultaneous TG/DSC analysis of *tert*-butylcalix[6]arene clathrate with CH_3CN. Heating rate 4 K min^{-1}

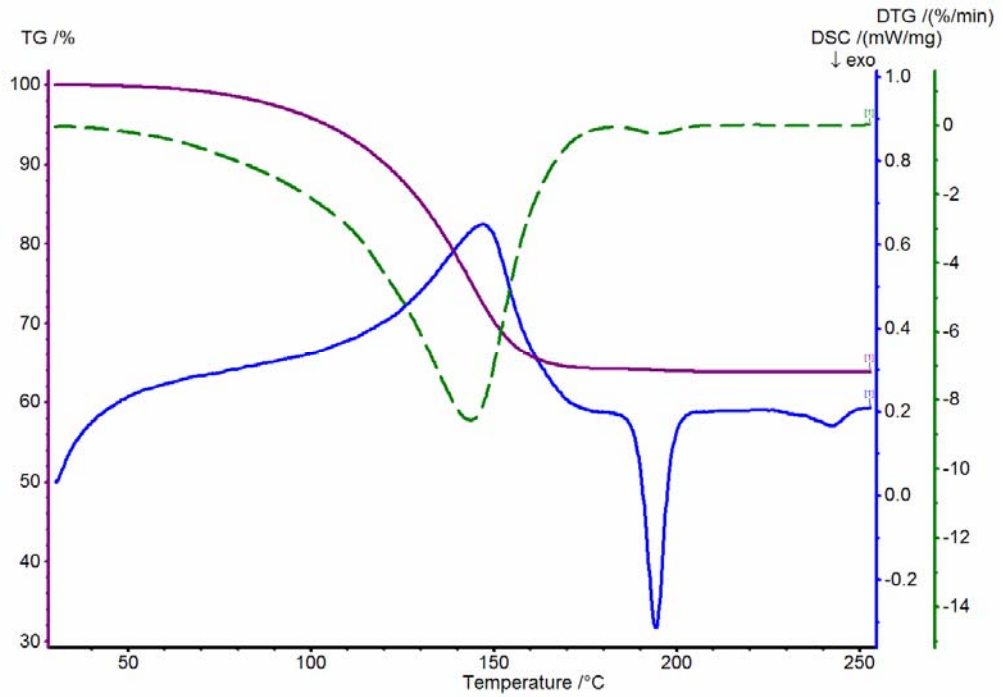

Fig. S11 The data of simultaneous TG/DSC analysis of *tert*-butylcalix[6]arene clathrate with CCl_4. Heating rate 10 K min^{-1}

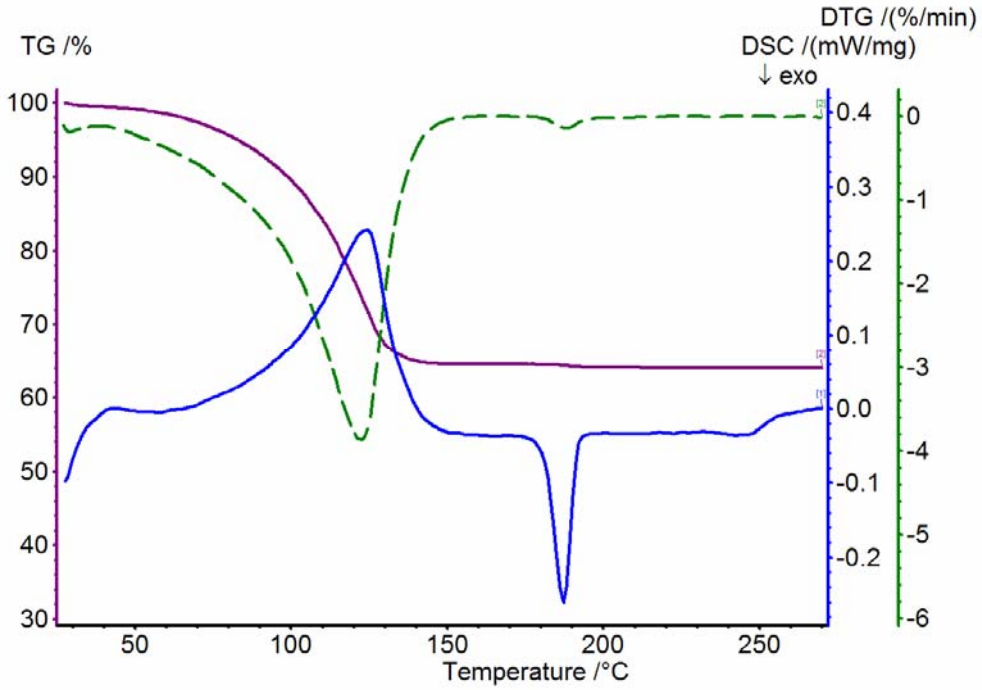

Fig. S12 The data of simultaneous TG/DSC analysis of *tert*-butylcalix[6]arene clathrate with CCl_4. Heating rate 4 K min^{-1}