Anti-sieve effect in guest inclusion by thiacalix[4]arene giving a surge in thermal stability of its clathrates prepared by solid-phase guest exchange

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Electronic Supplementary Information

TG/DSC/MS data for

- initial dried host **1**;
- **1**·0.27C_2HCl_3, **1**·1.03C_5H_5N, and intermediate **1**·0.32C_5H_5N clathrates;
- products of thiacalix[4]arene (**1**) saturation with headspace of liquid H_2O and CH_3OH;
- guest exchange products formed by equilibration of **1**·C_5H_5N clathrate with headspace of liquid 1,2-$C_2H_4Cl_2$, CH_2Cl_2, and C_6H_6;
- X-ray diffraction data for host **1**, its clathrates **1**·C_5H_5N and **1**·0.32C_5H_5N, guest exchange product for methanol **1**·0.65MeOH, and clathrate **1**·⅔H_2O calculated from single crystal X-ray data;
- Experimental and calculated powder diffractograms after indexing and refinement of unit-cell data.

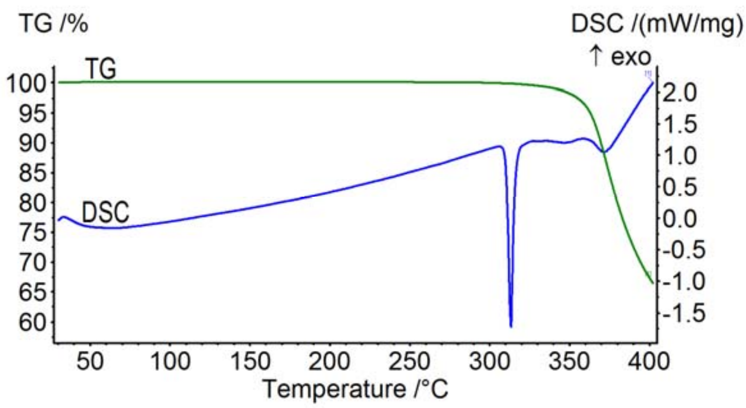

Fig. S1. Data of TG/DSC/MS analysis of initial dried host **1**.

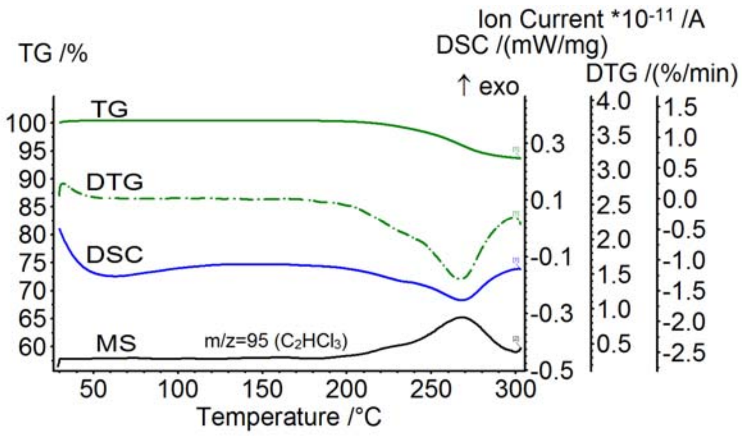

Fig. S2. Data of TG/DSC/MS analysis of **1**·0.27C_2HCl_3 clathrate.

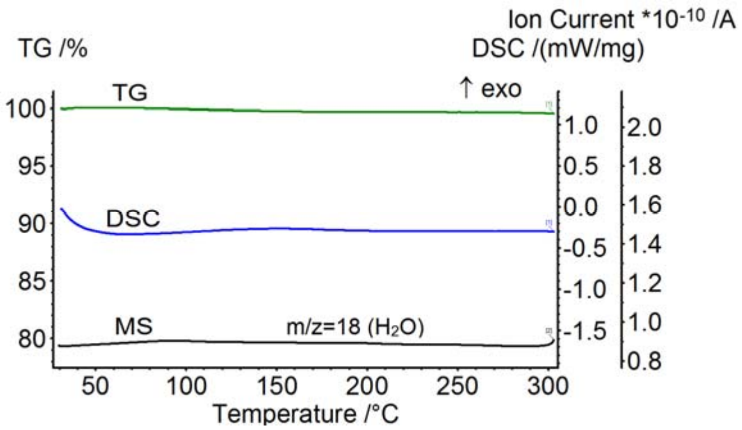

Fig. S3. Data of TG/DSC/MS analysis of the product of **1** saturation with headspace of liquid water.

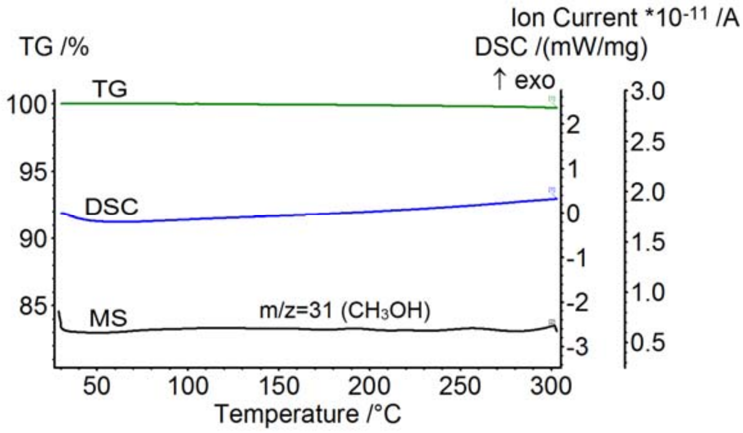

Fig. S4. Data of TG/DSC/MS analysis of the product of **1** saturation with headspace of liquid methanol.

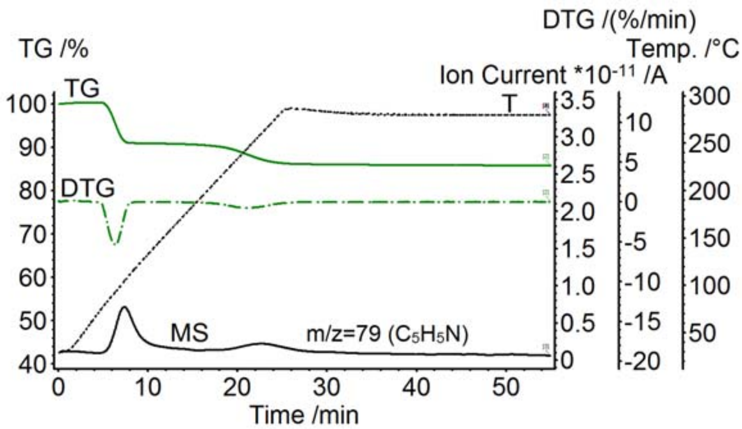

Fig. S5. Data of TG/MS analysis of $\mathbf{1}\cdot1.03C_5H_5N$ clathrate. Clathrate parameters: Δm=14.04, S=1.03, T_{on}: 86, 215.

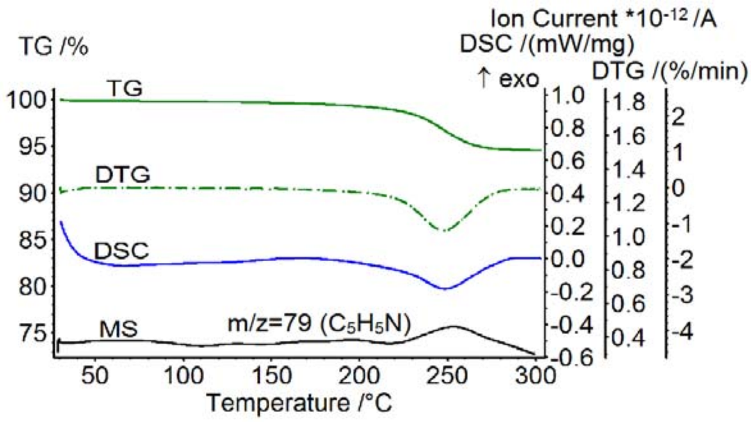

Fig. S6. Data of TG/DSC/MS analysis of intermediate clathrate $\mathbf{1}\cdot0.32C_5H_5N$.

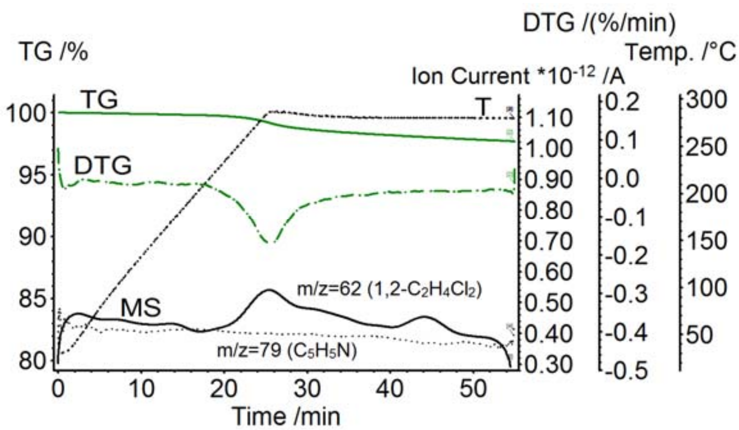

Fig. S7. Data of TG/MS analysis of the guest exchange product formed by equilibration of $\mathbf{1}\cdot C_5H_5N$ clathrate with headspace of liquid 1,2-$C_2H_4Cl_2$.

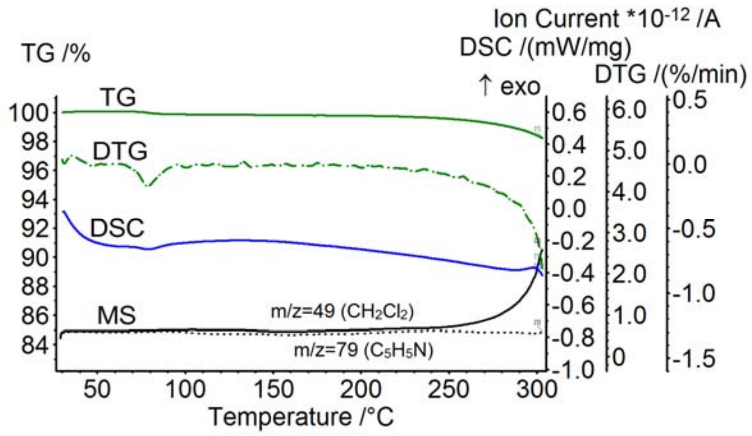

Fig. S8. Data of TG/DSC/MS analysis of the guest exchange product formed by equilibration of **1**·C_5H_5N clathrate with headspace of liquid CH_2Cl_2.

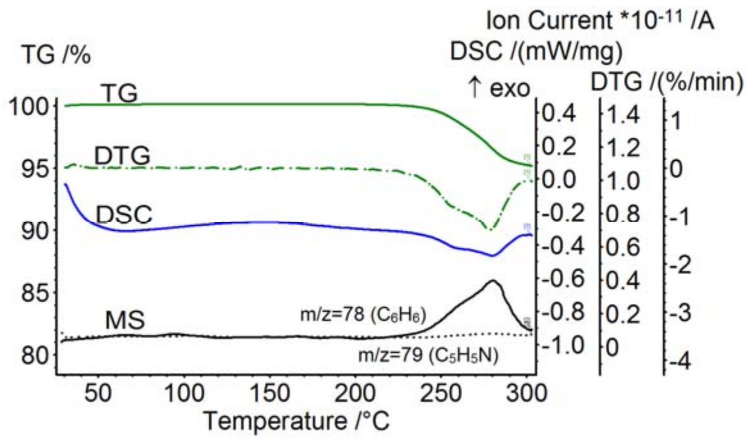

Fig. S9. Data of TG/DSC/MS analysis of the guest exchange product formed by equilibration of **1**·C_5H_5N clathrate with headspace of liquid C_6H_6.

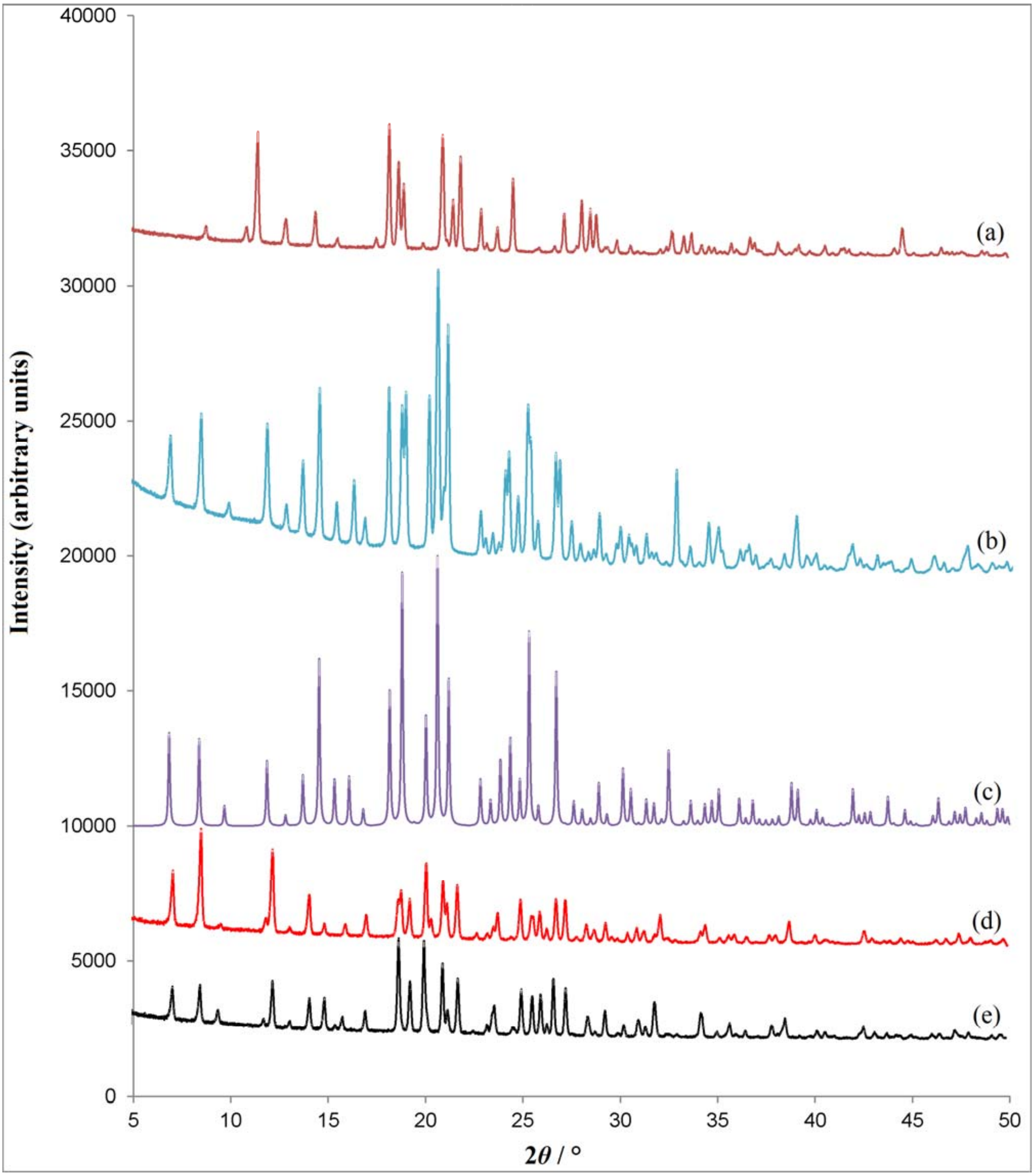

Fig. S10. X-ray powder diffractograms for samples of: (a) **1**·C_5H_5N; (b) intermediate **1**·0.32C_5H_5N; (c) **1**·⅔H_2O as calculated from single crystal X-ray data [1]; (d) the dried host **1**; (e) the guest exchange product **1**·0.65 MeOH. Intensities in diffractogram (b) were divided by 3.

Experimental and calculated X-Ray powder diffractograms after indexing and refinement of unit-cell data are presented in Figures S10-S12. Indexing [2] and full pattern decomposition were performed using TOPAS V.3 [3] software. Profile parameters, background and lattice parameters were refined by the least squares process [4].

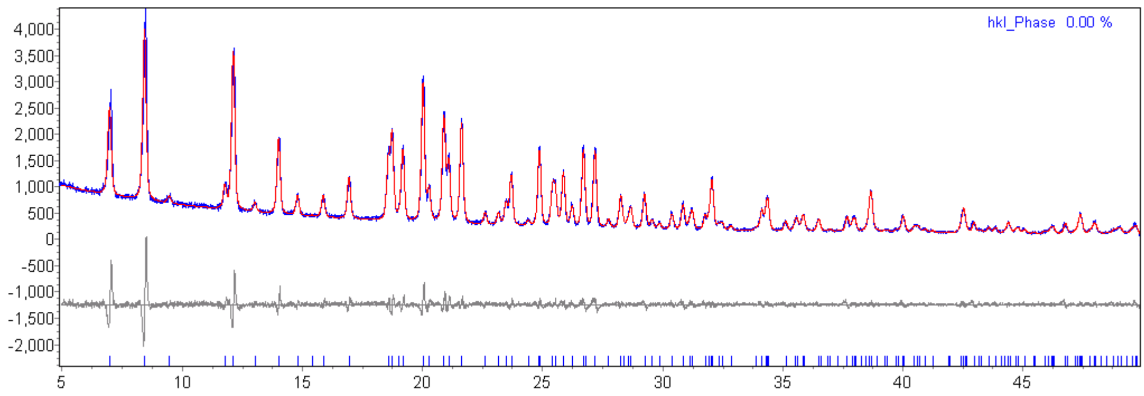

Fig. S11. Experimental XRPD pattern (blue), best fit (red) and differential curve (black) for dried host **1** (R_{wp} = 8.55). Blue vertical bars represent Bragg positions for the calculated unit cell and *$P6_3$* space group.

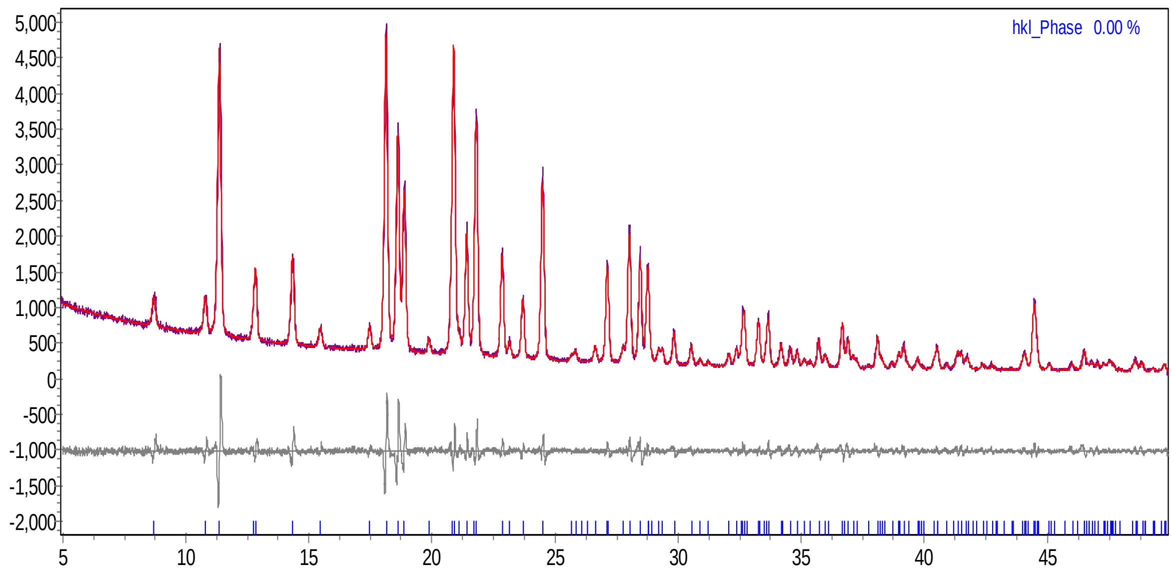

Fig. S12. Experimental XRPD pattern (blue), best fit (red) and differential curve (black) for clathrate **1**·1.00C_5H_5N (R_{wp} = 8.58). Blue vertical bars represent Bragg positions for the calculated unit cell and *$Pmn2_1$* space group.

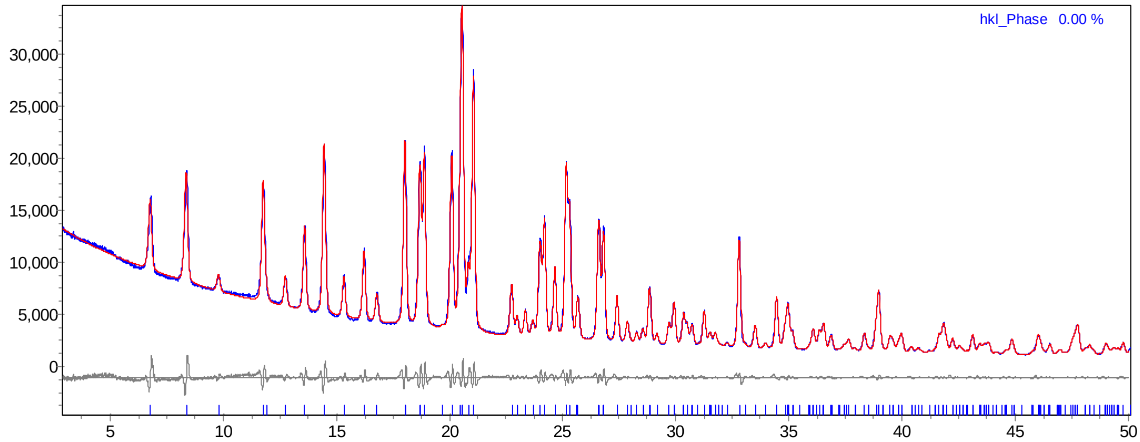

Fig. S13. Experimental XRPD pattern (blue), best fit (red) and differential curve (black) for clathrate **1**·0.32C_5H_5N (R_{wp} = 3.64). Blue vertical bars represent Bragg positions for the calculated unit cell and *P6₃* space group.

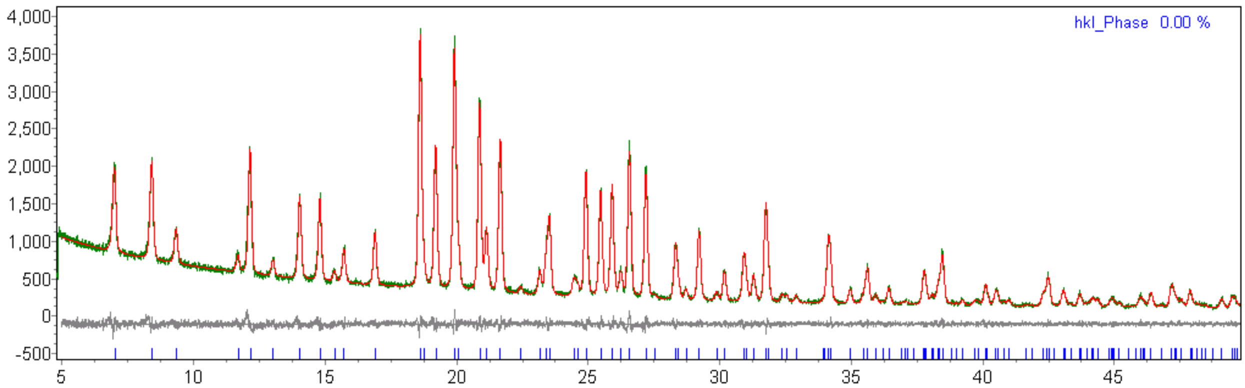

Fig. S14. Experimental XRPD pattern (blue), best fit (red) and differential curve (black) for the guest exchange product **1**·0.65MeOH (R_{wp} = 5.20). Blue vertical bars represent Bragg positions for the calculated unit cell and *P6₃* space group.

References

1. H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. de Cian, and J. Fischer, *Tetrahedron Lett.*, 1998, **39**, 2311–2314.

2. A. A. Coelho, *J. Appl. Crystallogr.*, 2003, **36**, 86–95.

3. TOPAS V3: General profile and structure analysis software for powder diffraction data. Technical Reference, Bruker AXS, Karlsruhe, Germany, 2005, 117 p.

4. R. W. Cheary and A. A. Coelho, *J. Appl. Crystallogr.*, 1992, **25**, 109-121.