Electronic Supplementary Material (ESI) for CrystEngComm.

Methods.

SC-XRD; A suitable crystal was selected and mounted on a suitable support on an XtaLAB Synergy R, HyPix diffractometer. The crystal was kept at a steady temperature during data collection. The structure was solved with the ShelXT 2018/2 structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The model was refined with version 2018/3 of ShelXL 2018/3 using Least Squares minimisation. Further details of the crystallographic analysis are summarised in the CIF file deposited at the CCDC.

Crystals	CCDC number
1-$CHCl_3$	2258378
1-$CHBr_3$	2281393
1-CH_2Cl_2	2279856
1-CH_2Br_2	2281391

FTIR spectroscopy; FT-IR spectra (Nicolet Avatar 370 DTGS, Thermo Fisher) with a resolution of 4 cm^{-1} were collected using KBr disks.

TG; Thermogravimetric (TG) measurements were performed using a Rigaku Thermo Plus TG8120 instrument under an N_2 flow.

DSC; DSC measurements were performed using a Mettler Toledo DSC 1 STAR system.

Powder XRD; Measurements were performed using a Rigaku Mini Flex 600 at 2θ of 2°–20°.

Dielectric permittivity measurements; dielectric permittivity measurements were performed by ac two-probe measurements using pellets. Silver or gold paste was used for electrodes and electrical contacts were made using gold wires. Temperature-dependent dielectric permittivity was measured using an Agilent E4980A Precision LCR meter in an air atmosphere. The typical applied ac voltage was 1 V, and the frequency range was 100 Hz–1 MHz.

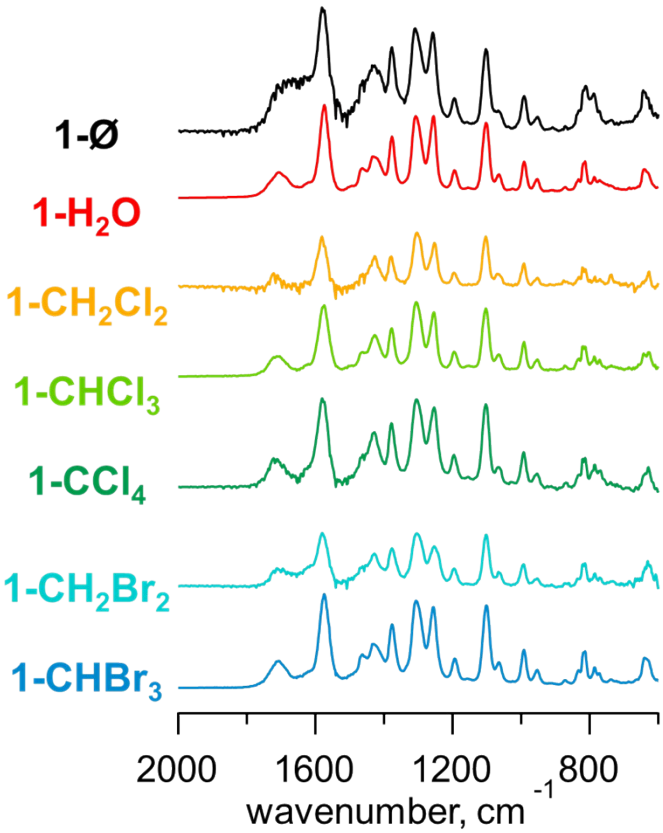
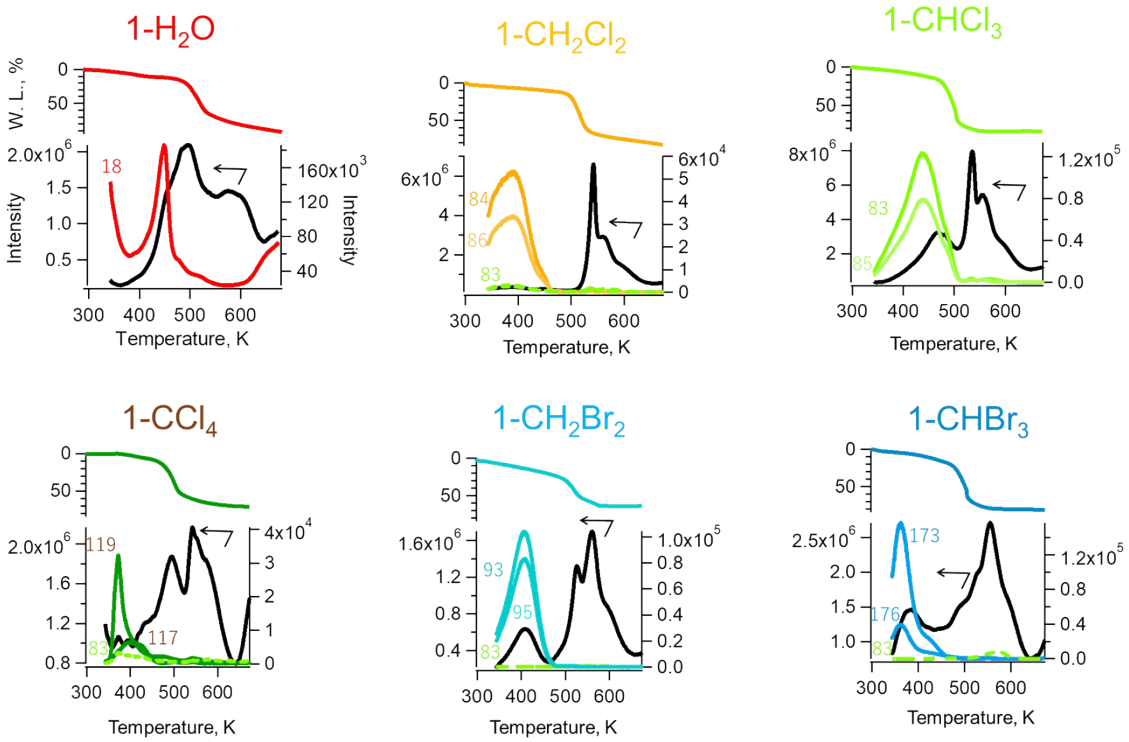


Figure S1. FT-IR spectra



Compound	*m/z*	
H_2O	18(100)	
CH_2Cl_2	84(100)	86(39.2)
$CHCl_3$	83(100)	85(65.6)
CCl_4	117(100)	119(96.0)
CH_2Br_2	93(72.4)	95(62.4)
$CHBr_3$	173(100)	176(78.8)

Figure S2. TG and real-time GC-MS measurements on the gases generated while the sample was heated and table of *m/z* of guest molecules.

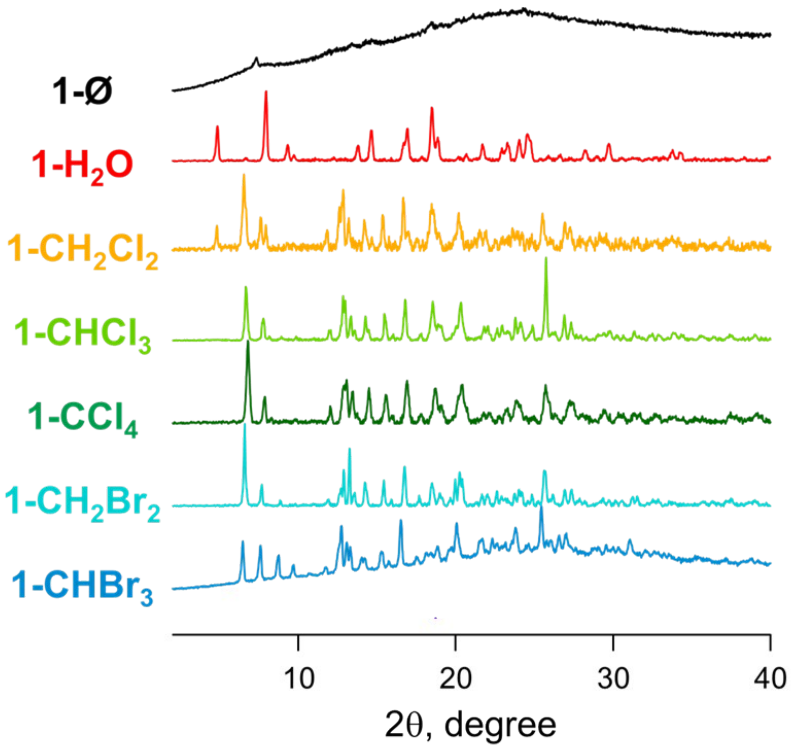


Figure S3. Powder XRD patterns of compounds.

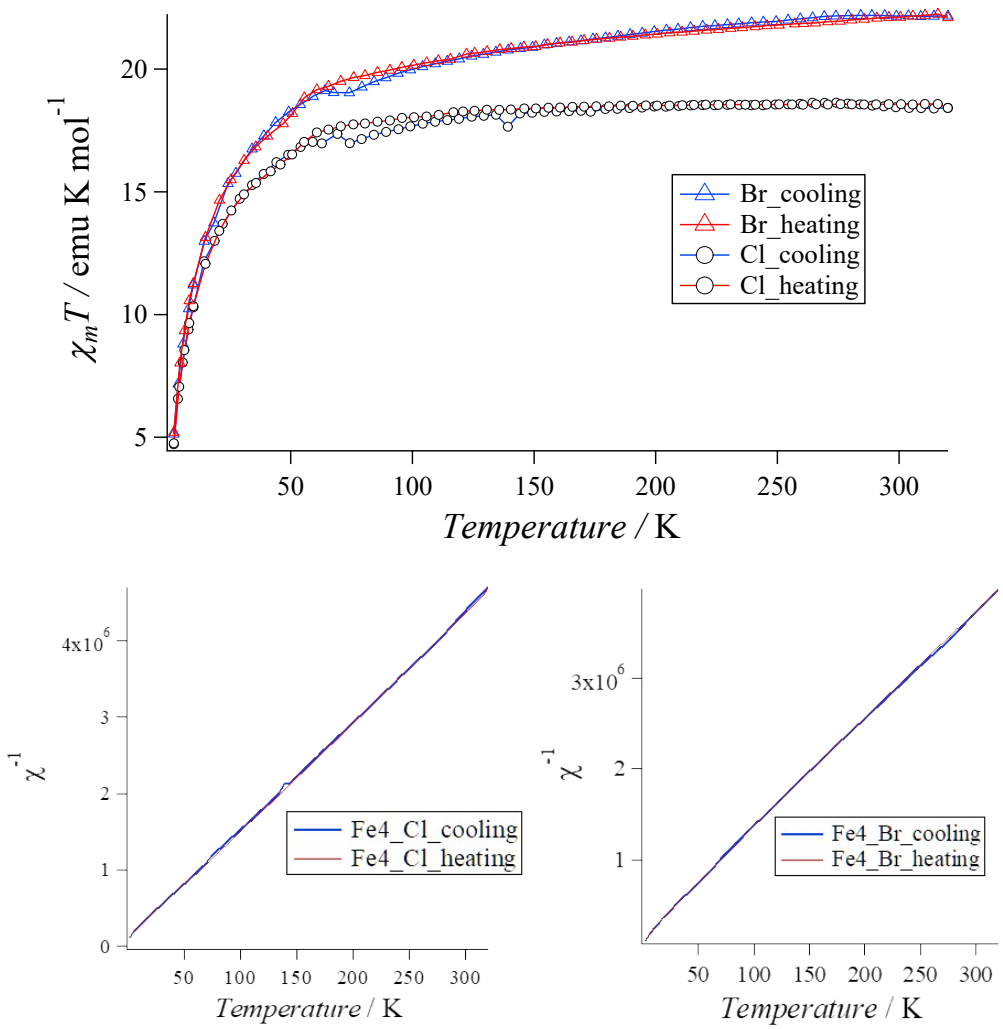


Figure S4. Temperature dependent magnetic susceptibility measurement at 2-310 K of **1-CH_2X_2** (X=Cl, Br). Magnetic measurements were performed using a Quantum Design MPMS-5S. The temperature dependence of the molar magnetic susceptibility was measured between 2 and 350 K in an external field of 5,000 Oe. Samples were fixed in polyvinylidene chloride foils for measurements at 5 K/min.

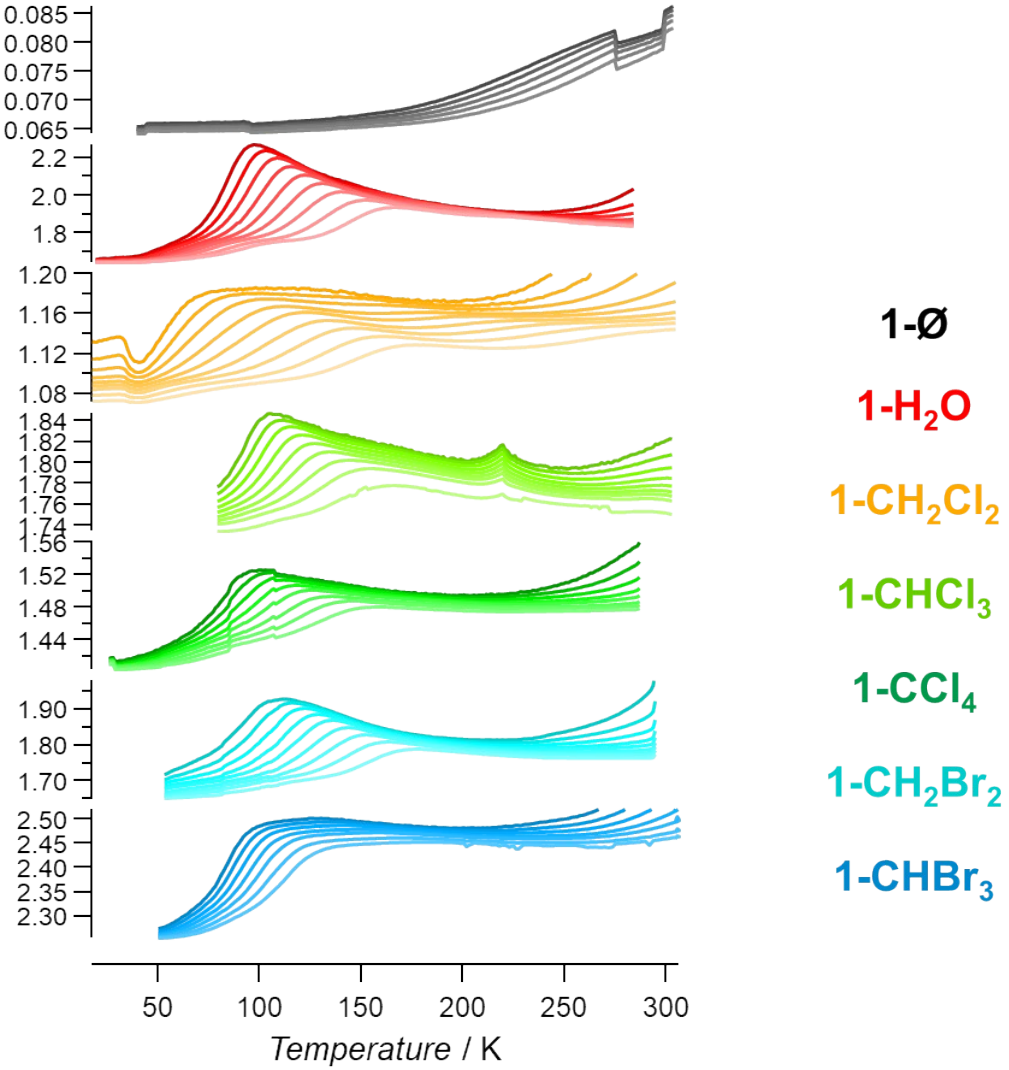


Figure S5. Temperature dependence of real parts of complex permittivity.

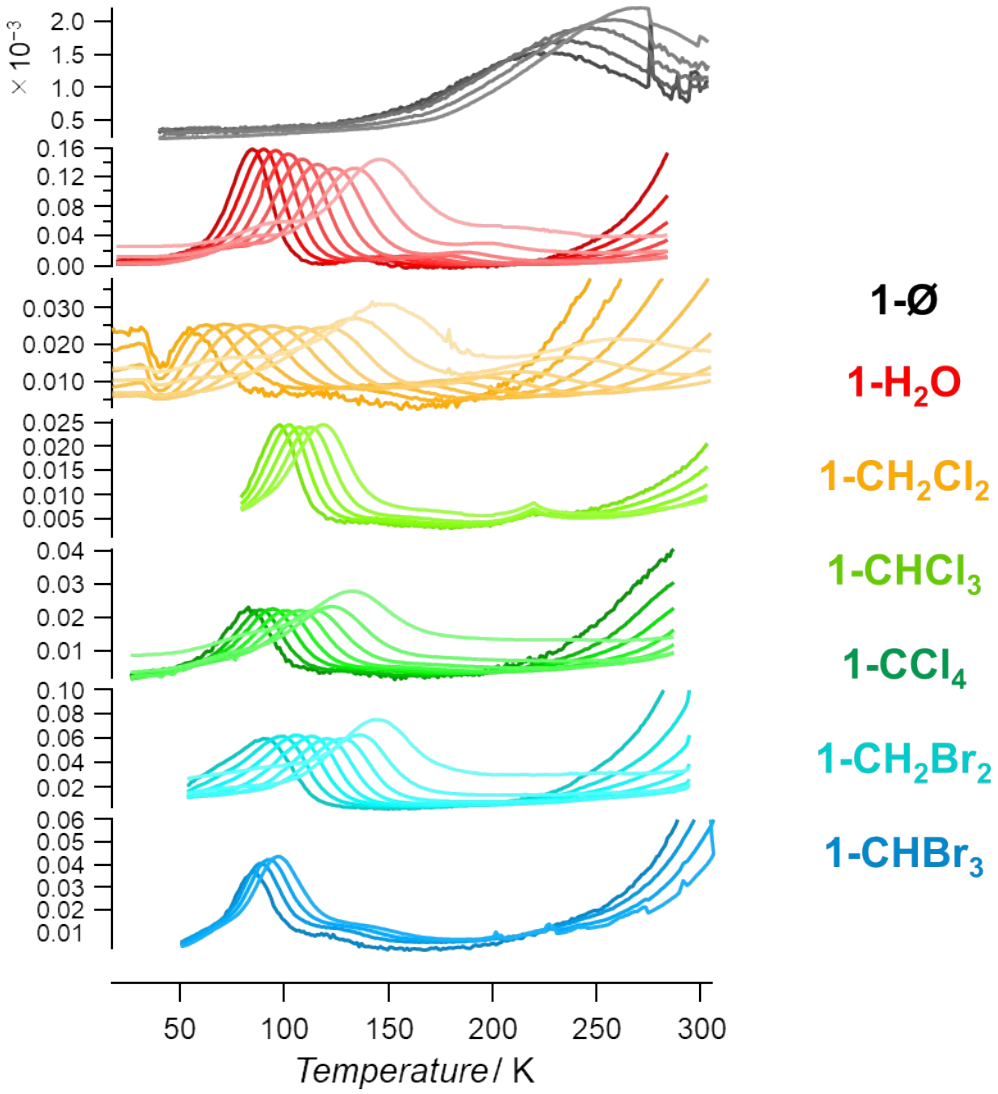


Figure S6. Temperature dependence of imaginary parts of complex permittivity.

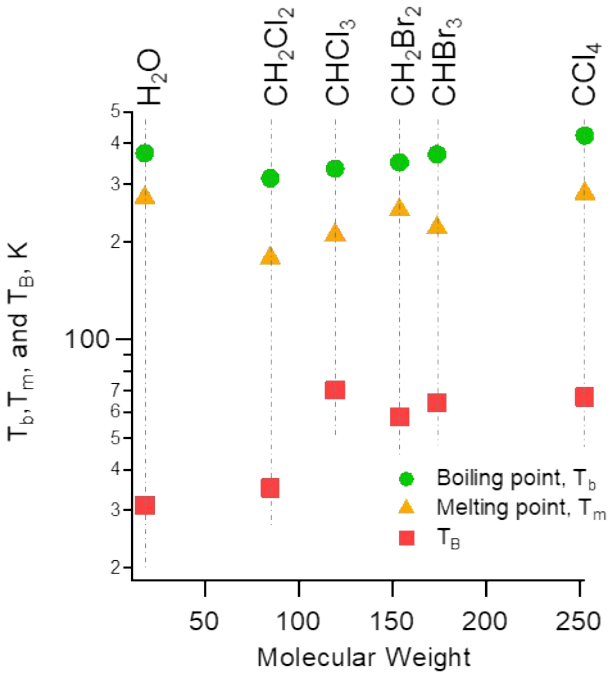


Figure S7. Plot of boiling point (T_b), melting point (T_m), and temperature at 0.01 Hz in Arrhenius analysis (T_B) with molecular weight of the guest.