Supplementary Information

Guest-Tunable Dielectric Sensing Using a Single Crystal of HKUST-1

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Table of contents

1.1 Experimental methods

The solvothermal technique was employed to synthesize 'big' single crystals of HKUST-1, with a lateral dimension of *ca*. 250-300 μm. Both copper (II) nitrate trihydrate $Cu(NO_3)_2 \cdot 3H_2O$ (0.49 g) and trimesic acid H_3BTC(0.24 g) were dissolved separately in 3 mL of H_2O and C_2H_5OH, respectively in 20 mL vial. Afterwards, 3 mL of DMF solvent was added into the metal solution accompanied by the linker solution and 12 mL of glacial acetic acid. The sealed vial was heated to 55 °C and held at this temperature for the next 72 hrs followed by a very slow cooling rate to room temperature. The crystals were washed with C_2H_5OH for at least 6 times by removing the supernatant before drying them in the ambient condition. The structure of the HKUST-1 was confirmed using the Miniflex Rigaku bench-top X-ray diffractometer by placing a single crystal of HKUST-1 on the sample holder, where the <100> lattice direction of the crystal was oriented normal to the base of the holder. The XRD spectra (Figure S4) were measured from the Bragg diffraction angle (2θ) of 2° to 32° at the scan rate of 0.5°/min and step size of 0.01°.

Molecular iodine (I_2) was encapsulated into the framework by transferring a few HKUST-1 crystals into a small glass vial and keeping them inside an enclosed vessel containing solid iodine (I_2) for 24 hrs. The presence of iodine in the form I_2 was confirmed by the Raman spectra (Figure S6) recorded *via* a Bruker Senterra Raman microscope with a 50× objective. The 532 nm excitation laser was operated at 50 mW power in the spectral range of 40-4000 cm^{-1}.

The HIOKI-3536 LCR meter was used to carry out the electrical measurements (dielectric and AC conductivity) in the frequency range of 100 Hz-2 MHz. The faces normal to <100> lattice direction of crystals were silver coated (RS PRO silver conductive paint) and positioned between the two probe electrodes (Ø 210 μm) after calibrating the whole system (open and short compensation) to account for the crystal thickness. The dielectric and conductivity were determined by using the following equations:

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \qquad \text{.........................(1)}$$

$$\varepsilon'' = \varepsilon' \tan \delta \qquad \text{........... ....(2)}$$

$$\sigma = \frac{d}{ZA} \qquad \text{......... ....(3)}$$

where ε' and ε'' are the real and imaginary parts of the dielectric constant, C is the capacitance, Z is the impedance, σ is the conductivity, $\tan \delta$ is the loss tangent, d is the crystal thickness, and A is the surface area of the silver-coated crystal facet.

1.2 Experimental setup and analysis of dielectric and conductivity data from LCR meter

The electrical properties of the HKUST-1 crystal on the <100> lattice direction was measured using the Hioki-IM3536 LCR meter in the frequency range of 4 Hz to 2 MHz at room temperature. To do this, an enclosed chamber made from polycarbonate was designed to expose one single crystal to a specific guest environment (Figure S1). The crystals were silver-coated on the opposite {100}-oriented planes because measurements were based on a parallel-plate capacitor principle. Two spring-loaded electrodes were aligned using a multi-axis stage.

Before guest exposure, the setup was calibrated (open and short LCR compensation) and the crystal was evacuated with inert gas nitrogen (N_2). Thereafter, the polar guest solvents were poured into the bubbler and carried to the crystal by the nitrogen flow (12 L/h). A constant gas influx was maintained throughout the experiment.

Each individual inclusion and expulsion cycle of guests was carried out after ensuring the stability in the LCR output data under a constant nitrogen flow (12 L/h). The relative concentration of guests in the chamber was maintained by controlling the overall inert gas pressure. The humidity was measured using a thermo-hygrometer with a sensitivity range of 2%-98% RH.

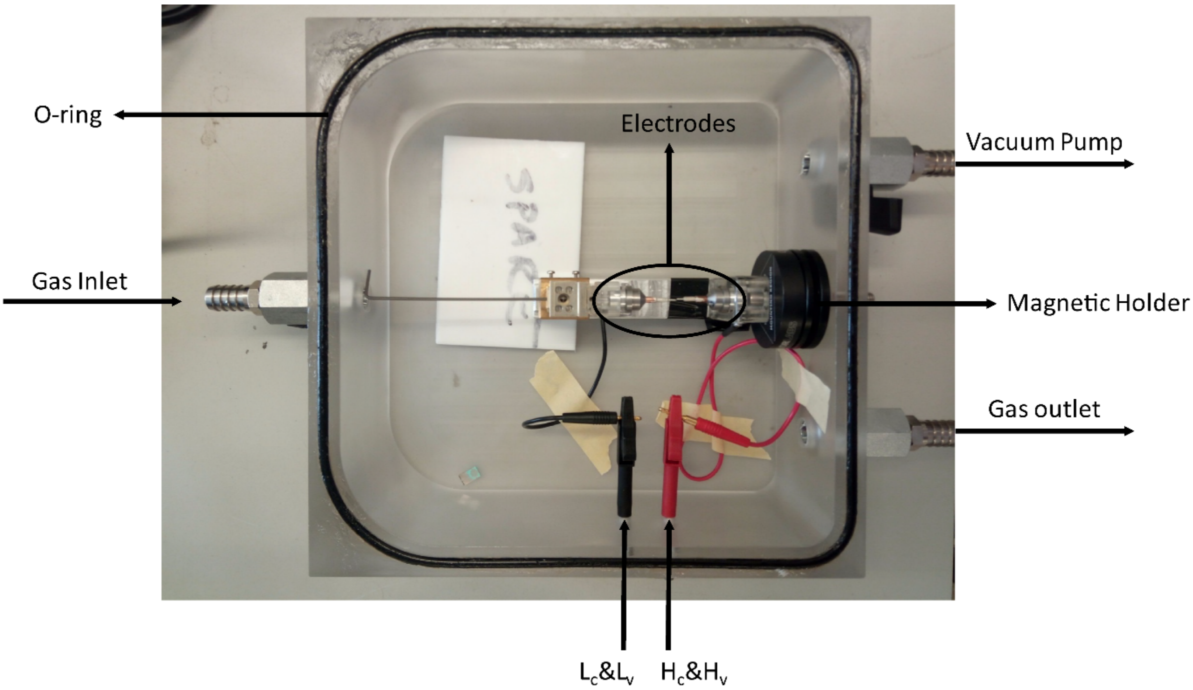


Figure S1: Experimental setup designed to conduct the single-crystal dielectric measurements on HKUST-1 MOF. The top lid is not shown for clarify. The connections to the electrodes are: L = low, H = high, C = current, V = voltage

1.3 HKUST-1 crystal coating and mounting between the probe electrodes

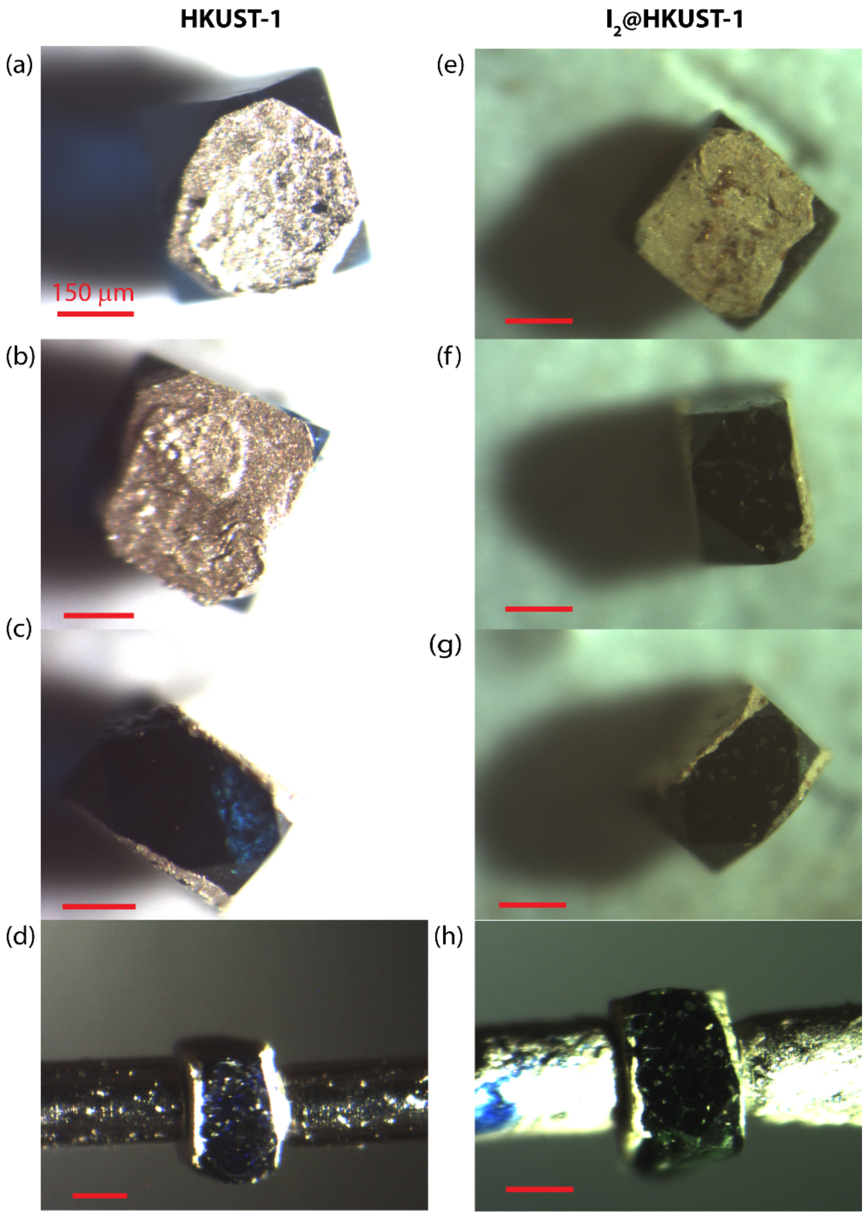


Figure S2: Silver-coated single crystals viewed from top and sides (a)-(c) HKUST-1 crystal and (e)-(g) I_2@HKUST-1 crystal. (d) and (h) show the mounting of the crystal between the spring-loaded electrodes. Scale bar is 150 μm.

1.4 Optical images of HKUST-1 crystal during guest inclusion and expulsion cycles

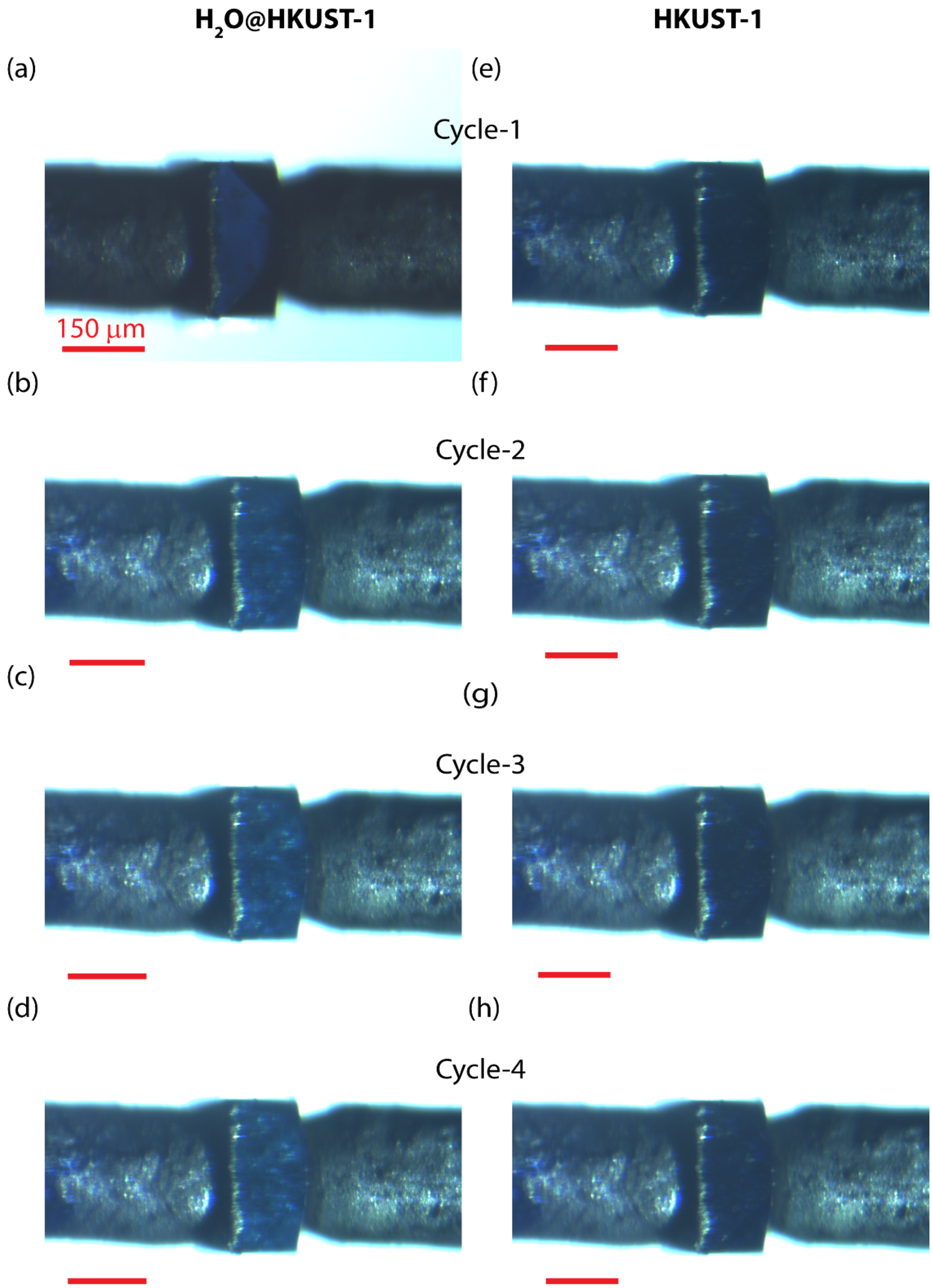


Figure S3: Fine-scale crack generation visible inside the single crystals mounted between two spring-loaded electrodes, under (a)-(d) guest inclusion and (e)-(h) guest expulsion cycles. The cracks stabilized after the second guest expulsion cycle. Scale bar is 150 μm.

1.5 Effect of I_2 on FWHM of the XRD spectra

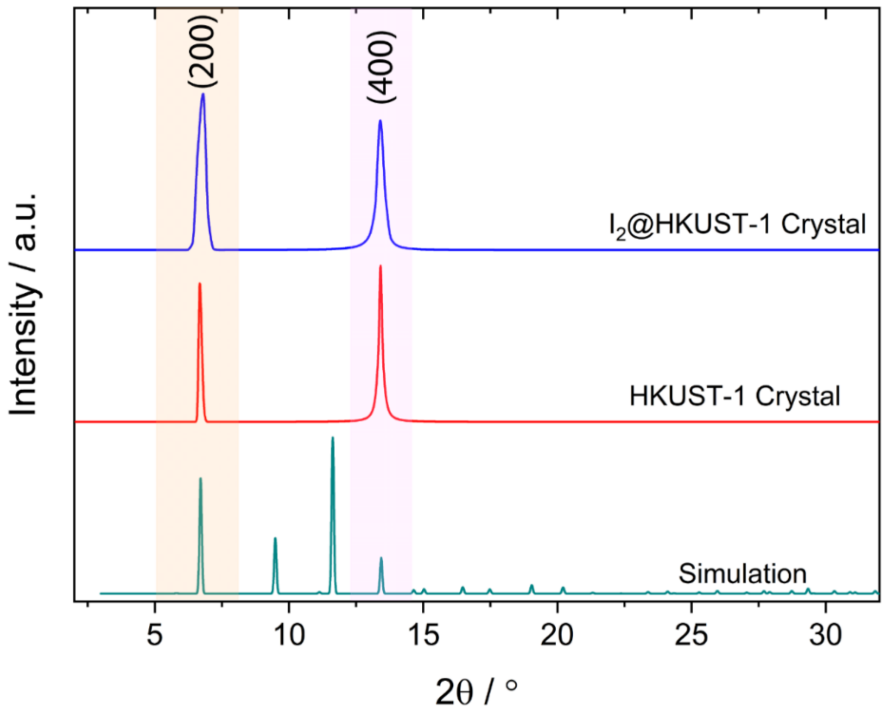


Figure S4: X-ray diffraction patterns of pristine and I_2 encapsulated HKUST-1 single crystals, showing broadening of the {100}-oriented Bragg peaks upon I_2 sorption. The simulated XRD pattern is for a powder sample hence all peaks are visible.

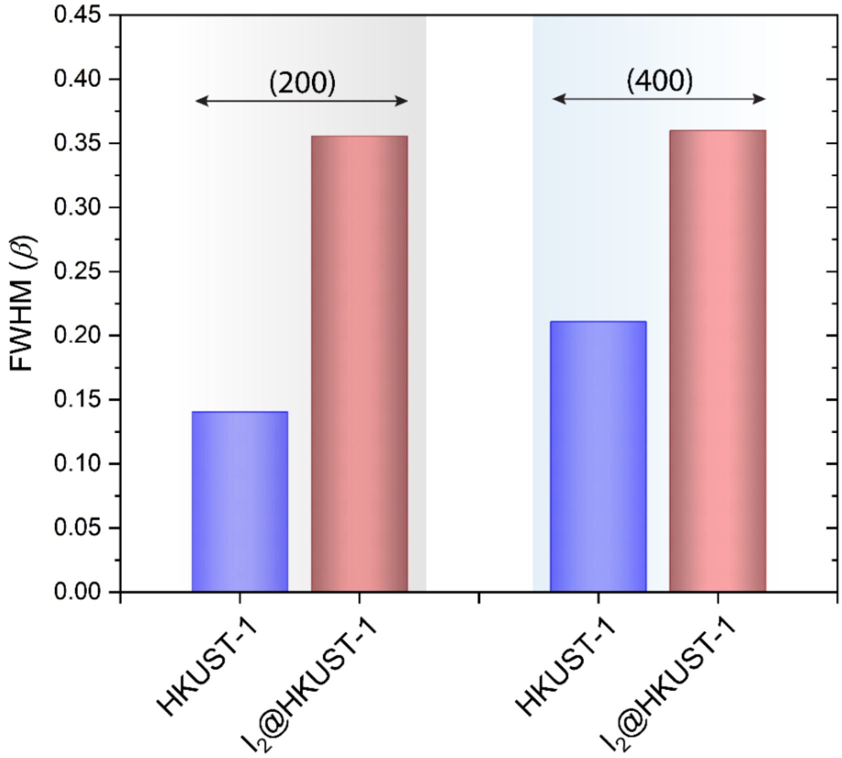


Figure S5: Comparative FWHM plot of the (200) and (400) planes of the HKUST-1 single crystal with and without the encapsulated I_2 molecules.

1.6 Raman spectroscopy

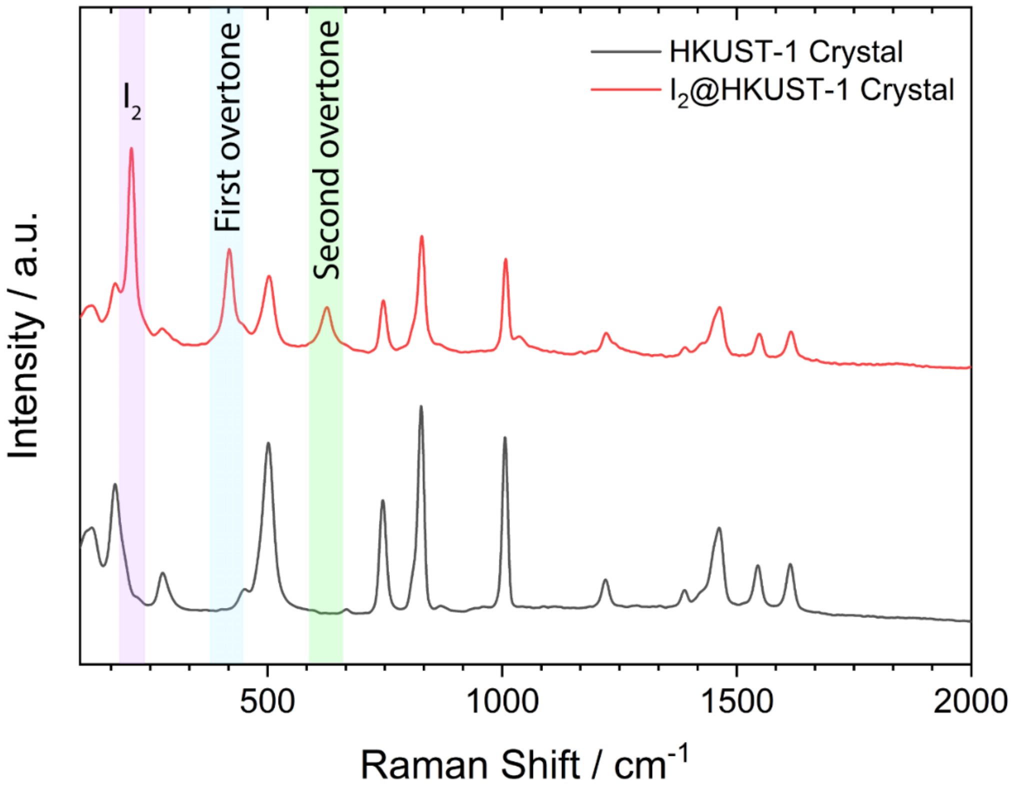


Figure S6: Raman spectra of the pristine and I_2-encapsulated HKUST-1 single crystals.

1.7 Effect of guest encapsulation on dielectric properties of the HKUST-1 single crystal

1.7.1 Imaginary part of dielectric constant (ε'')

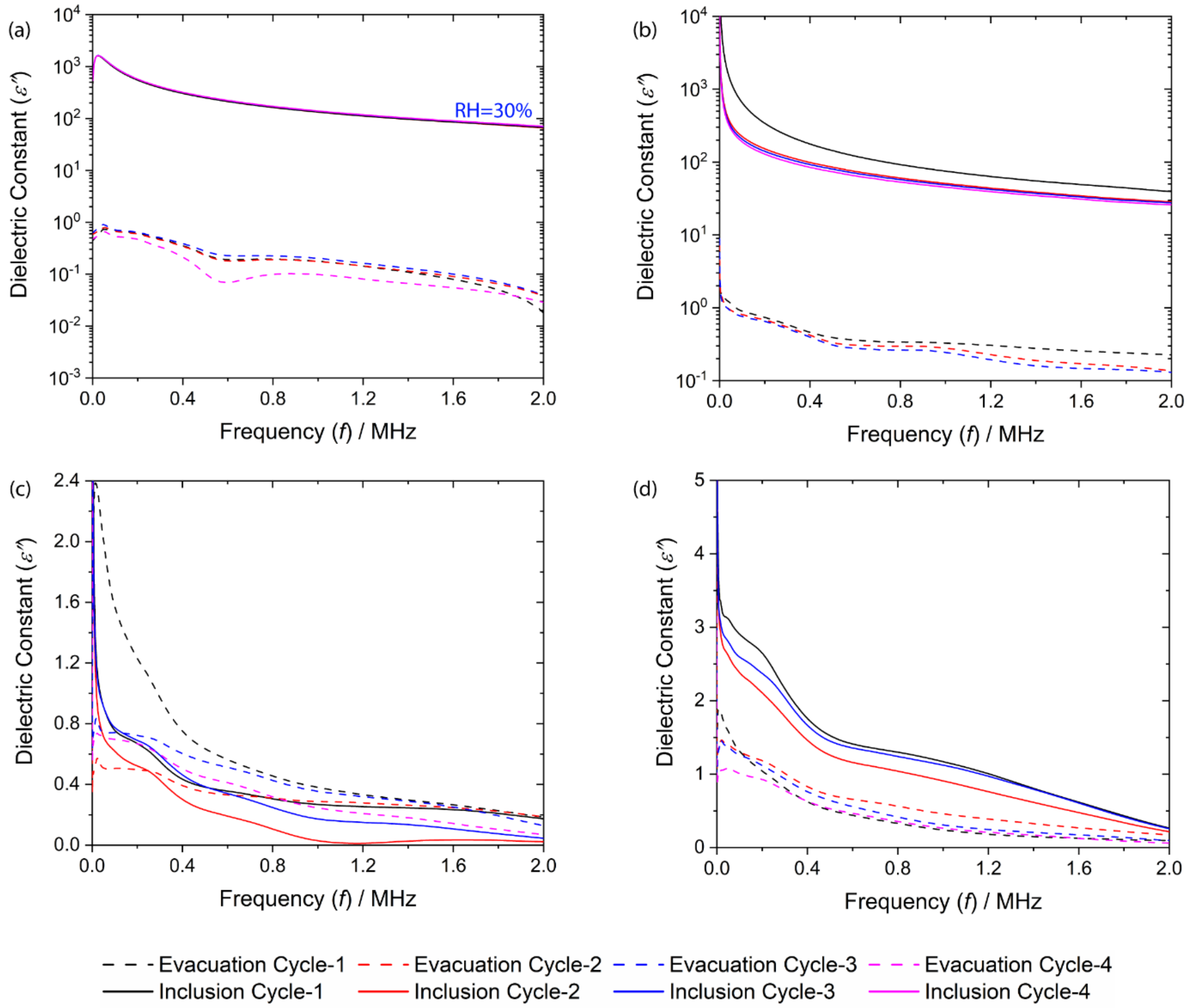


Figure S7: Imaginary part of the dielectric constant (ε'') as a function of frequency in the <100> lattice direction of HKUST-1 crystal for cyclic guest encapsulation: (a) H_2O, (b) I_2 and H_2O, (c) CH_3OH, and (d) C_2H_5OH, respectively.

1.7.2 Loss tangent (*tan δ*)

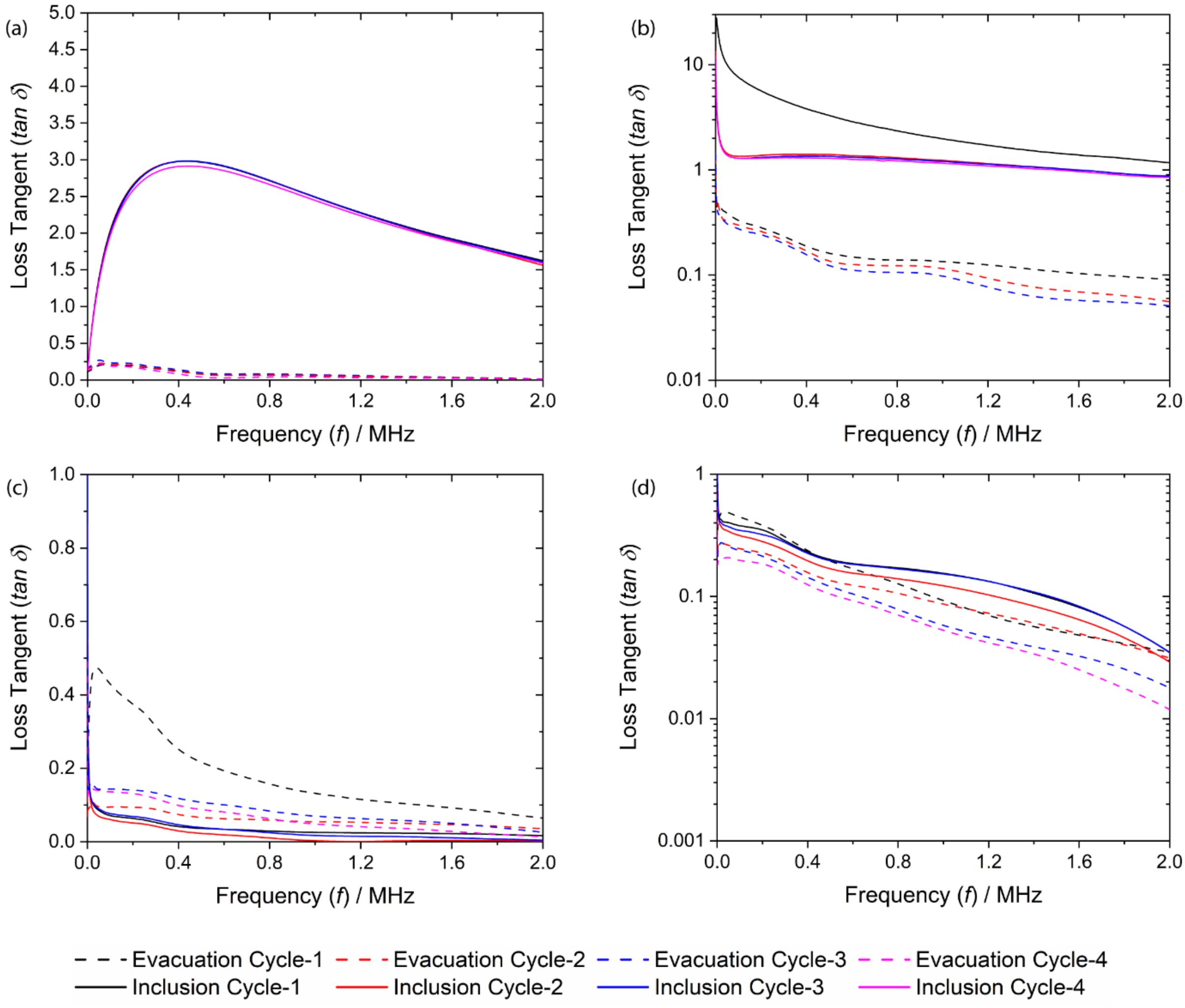


Figure S8: Dielectric loss tangent (*tan δ*) as a function of frequency in the <100> lattice direction of HKUST-1 crystal in the presence of different guest environments: (a) H_2O, (b) I_2 and H_2O, (c) CH_3OH, and (d) C_2H_5OH, respectively.

1.7.3 AC conductivity (σ)

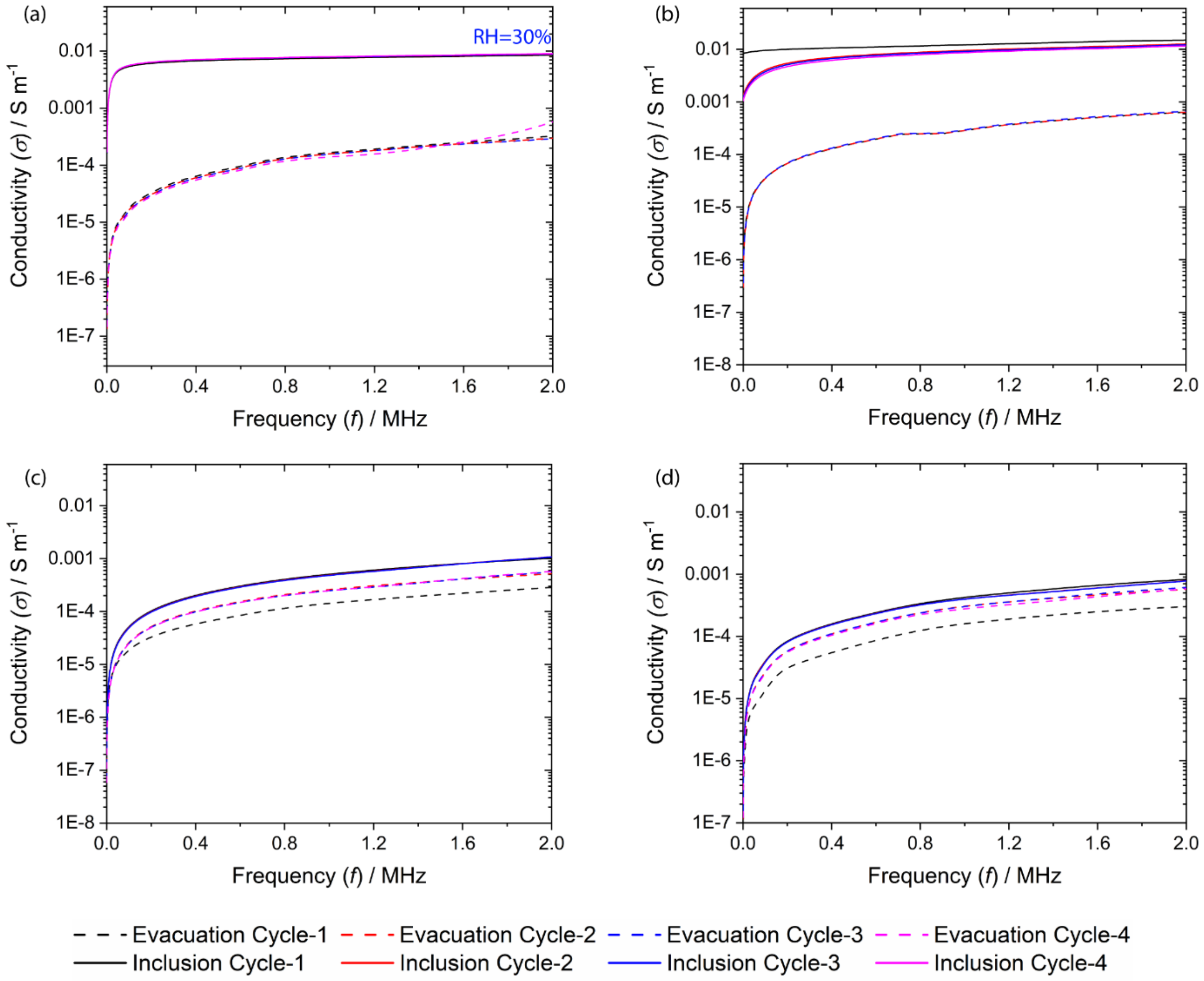


Figure S9: The frequency-dependent AC conductivity data on the <100> lattice direction of HKUST-1 framework in the presence of (a) H_2O, (b) I_2 and H_2O, (c) CH_3OH, and (d) C_2H_5OH, respectively.

1.8 Effect of different humidity levels on electrical properties of HKUST-1 single crystal

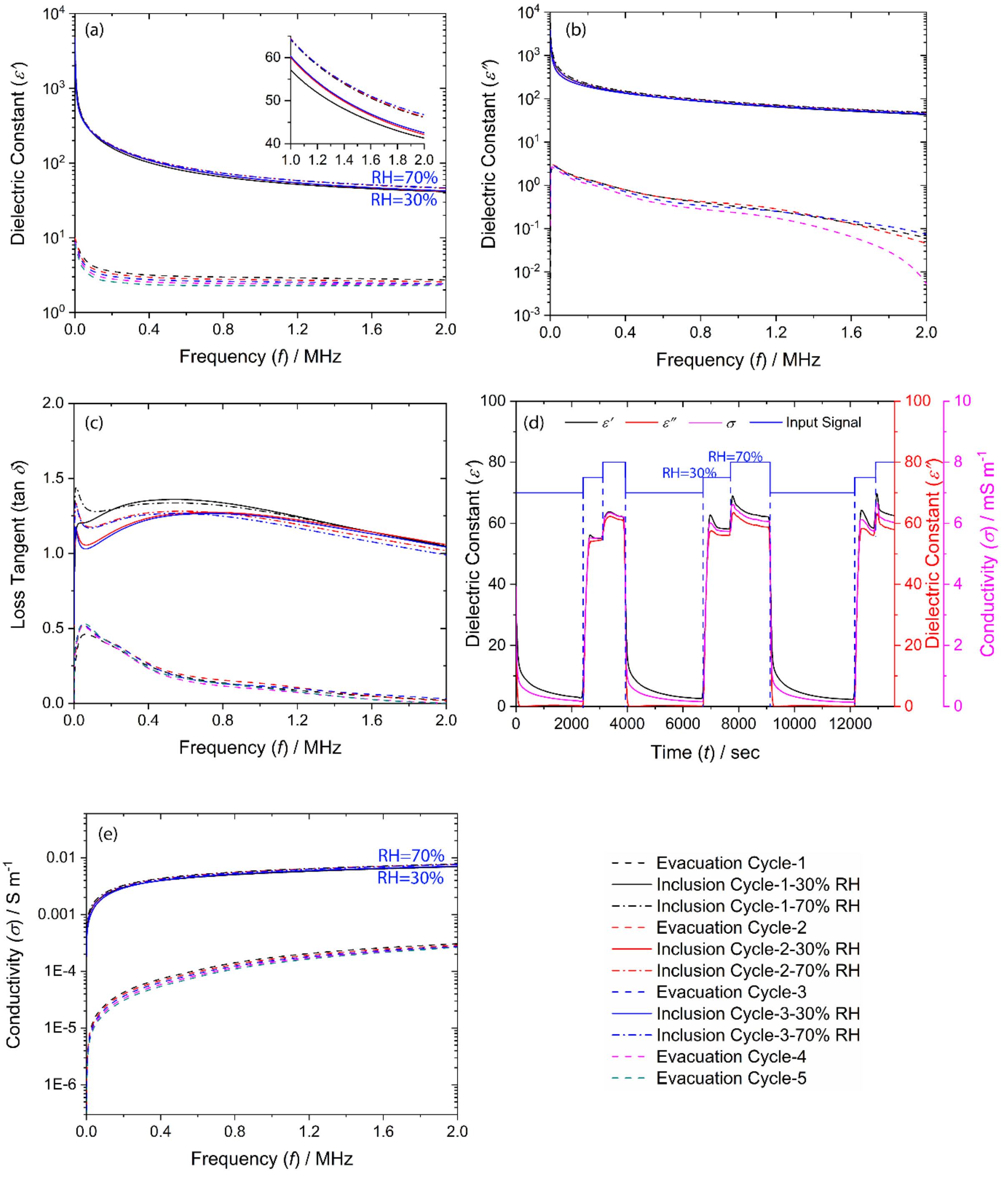


Figure S10: Electrical properties of HKUST-1 crystal at 30% and 70% RH conditions. (a)-(b) Real and imaginary parts of the dielectric constant, (c) loss tangent, (d) cyclic measurements during guest inclusion and expulsion, and (e) frequency-dependent AC conductivity.

1.9 Comparative time-dependent cyclic response of the real part of dielectric constant

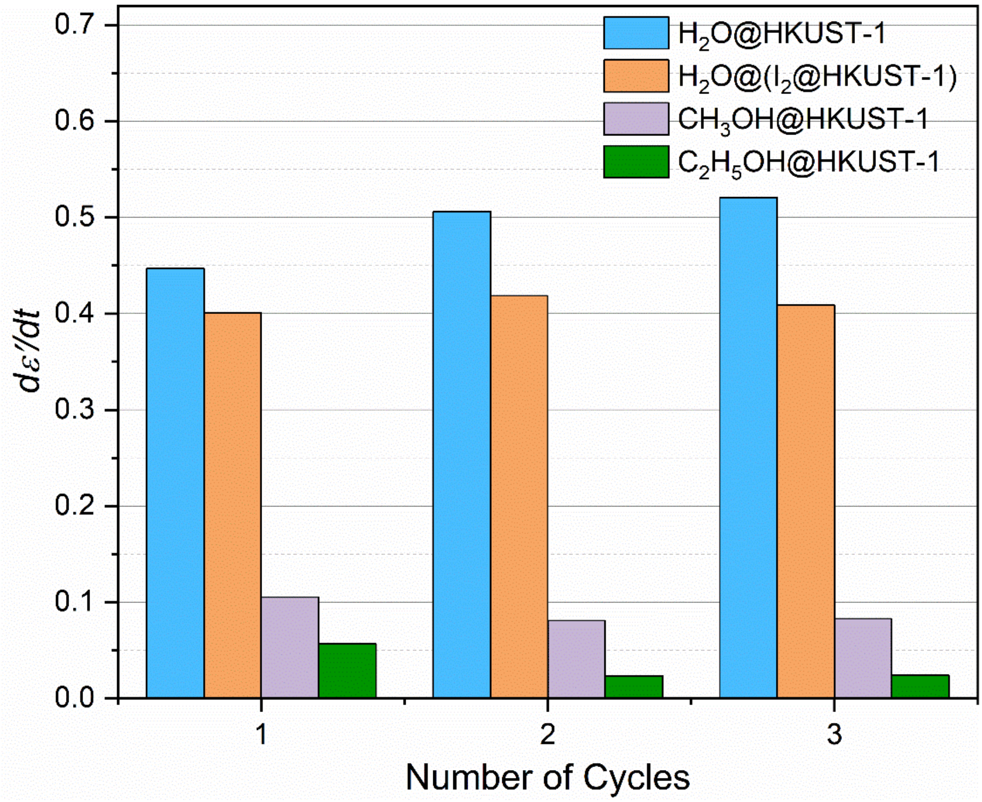


Figure S11: Comparative inclusion rates of the different guest molecules for the first three cycles.

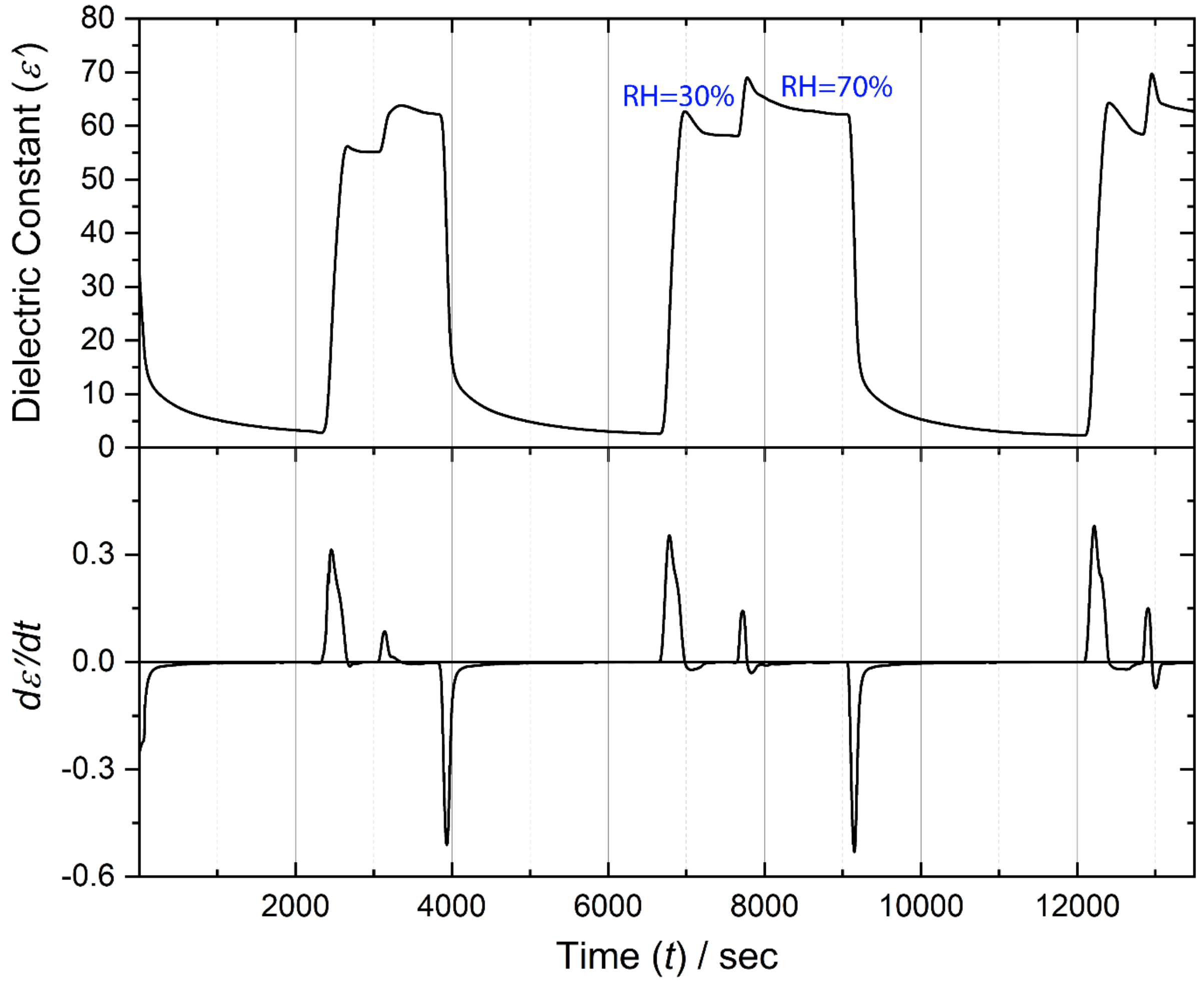
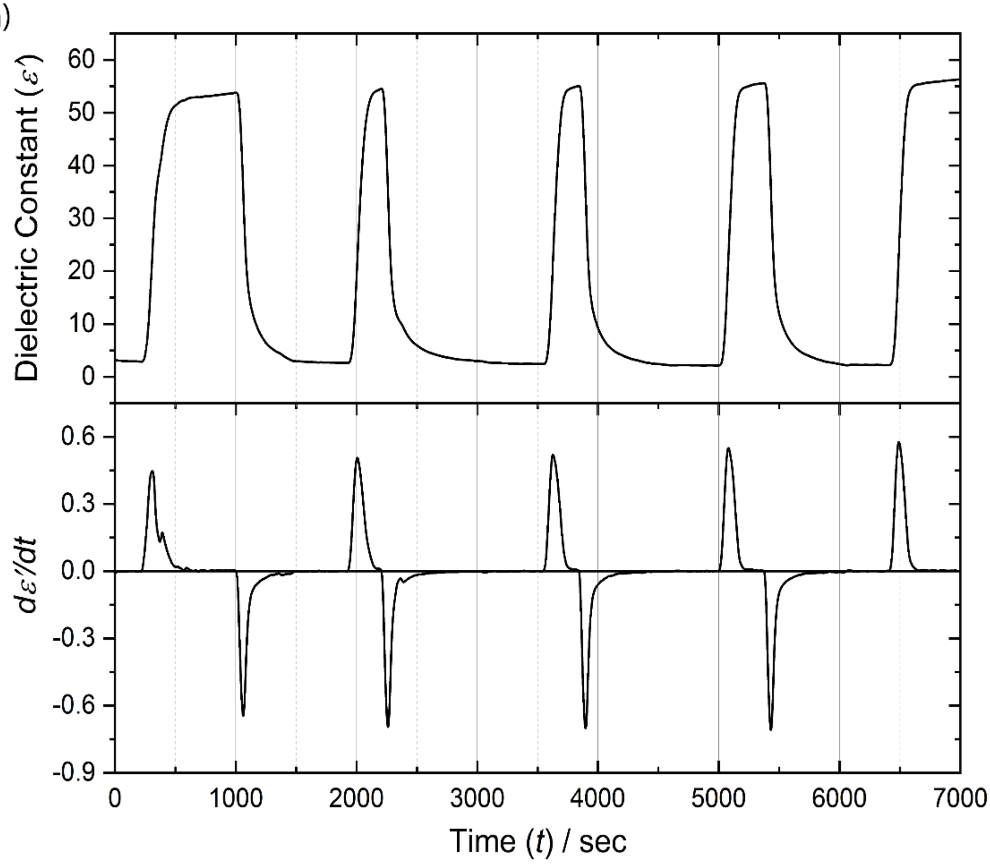


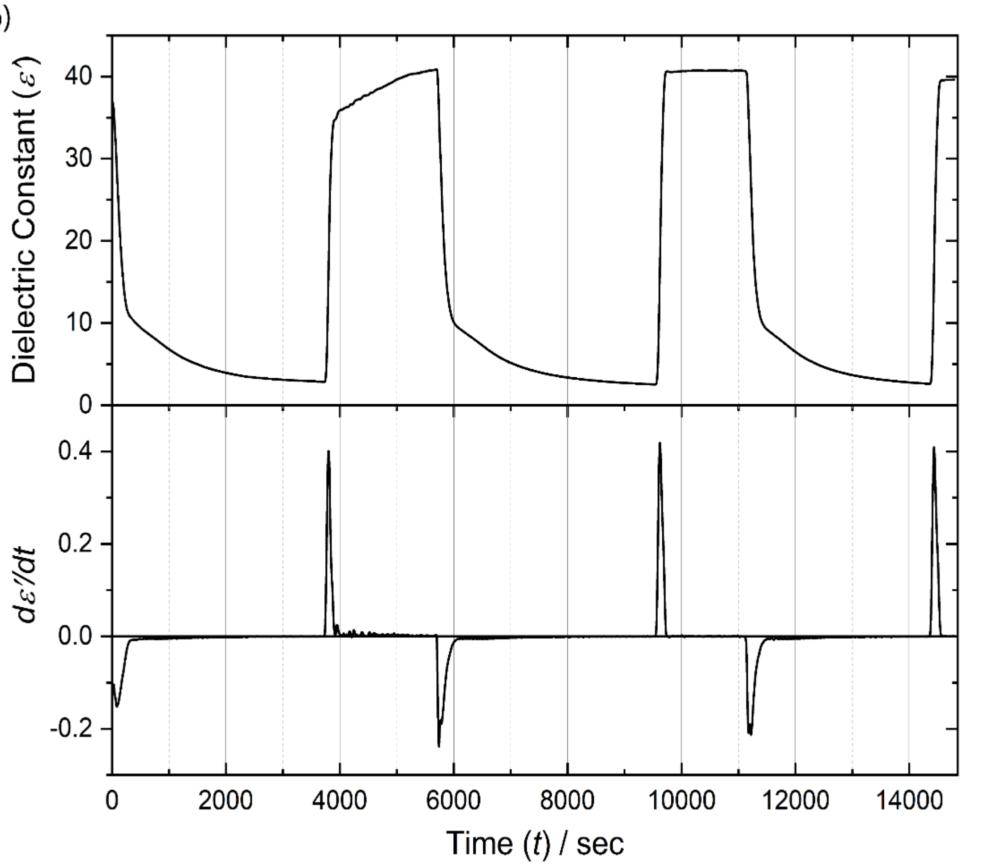
Figure S12: First-order derivative of the real part of dielectric constant with respect to time, showing transient inclusion-expulsion cycles of H_2O as a guest in 30% and 70% RH condition. The rise times (t_r) for H_2O inclusion are 160 sec (for 30% RH) and 77.2 sec (when RH increased from 30% to 70% RH) and the fall time (t_f) is 395 sec (from 70% RH to 0).

(a)



Dielectric Constant (ε')
$d\varepsilon'/dt$
60
50
40
30
20
10
0
0.6
0.3
0.0
-0.3
-0.6
-0.9
0
1000
2000
3000
4000
5000
6000
7000
Time (t) / sec

(b)



Dielectric Constant (ε')
$d\varepsilon'/dt$
40
30
20
10
0
0.4
0.2
0.0
-0.2
0
2000
4000
6000
8000
10000
12000
14000
Time (t) / sec

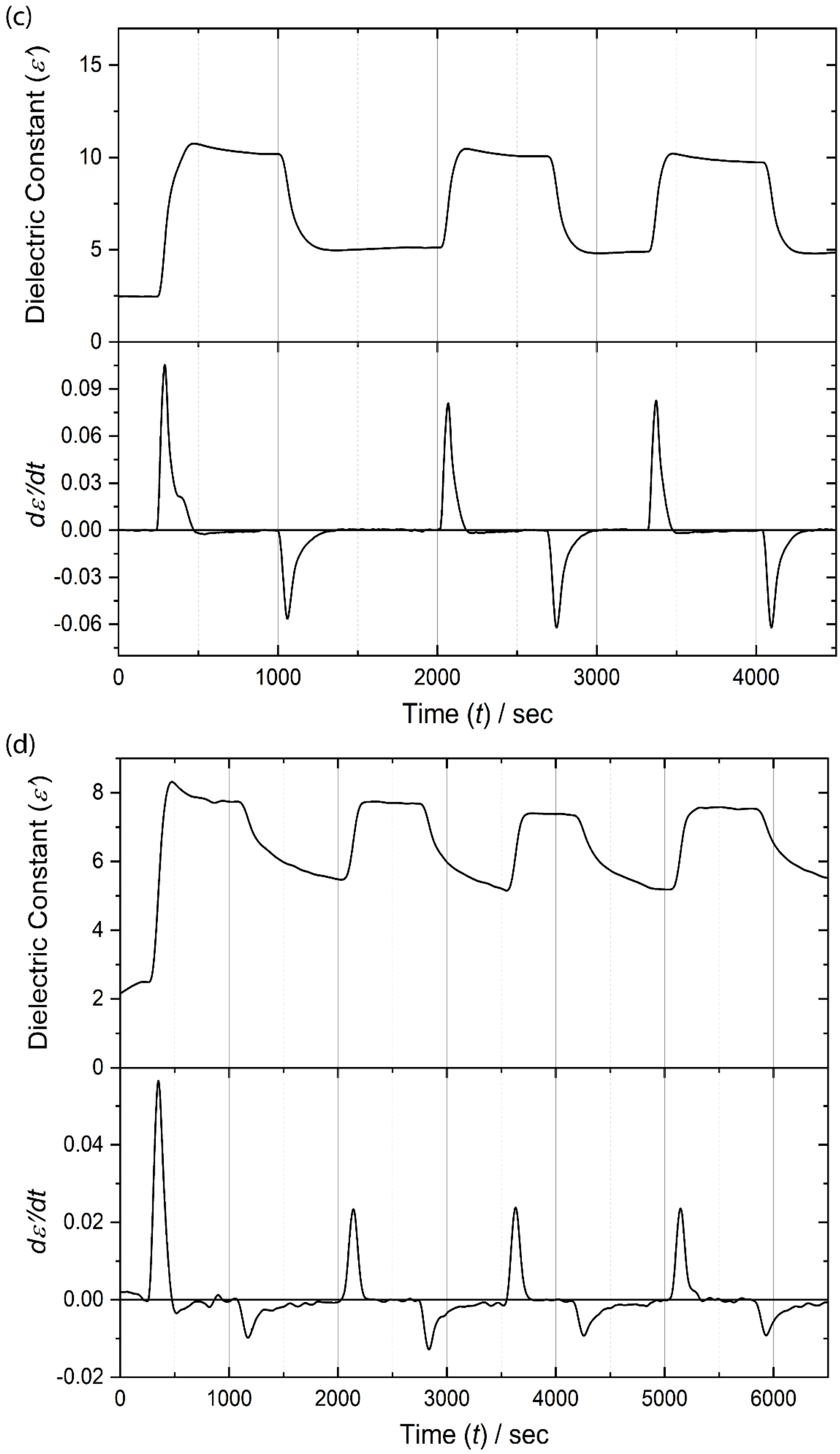


Figure S13: First-order derivative of the real part of dielectric constant with respect to time, showing transient inclusion-expulsion cycles of polar and non-polar guest species: (a) H_2O, (b) I_2 and H_2O, (c) CH_3OH, and (d) C_2H_5OH.