Electronic Supplementary Information

Materials with high proton conductivity above 200 °c based on nanoporous metal–organic framework and non-aqueous ionic media

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Instruments and methods.

Chemical C, H, N, S analysis data were obtained on Eurovector 600 analyzer. Powder X-ray diffraction (PXRD) data were obtained on Shimadzu XRD 7000S diffractometer (Cu Kα radiation, λ = 1.54178 Å): 2θ step = 0.03, counting time = 1.0−2.5 s, 2θ scan range = 3−25°. For all studied compounds the powder X-ray diffraction patterns are present in Fig. S1−S3. Fourier-transform infrared (FT-IR) spectra in the range 300–4000 cm^{-1} were recorded on Vertex 80 spectrometer as KBr pellets. The spectra are present in Fig. S4, S5. Thermogravimetric analyses (TGA) were obtained on NETZSCH TG 209 F1 instrument. The sample quantity ranged from 2 to 10 mg. All samples were heated under a He atmosphere from room temperature up to 250 °C at 2 $deg \cdot min^{-1}$ heating rate. The TDG data are reported in Fig. S6. Scanning electron microscopy images were taken on Hitachi S-3400N microscope at accelerating voltage 20 kV and the working distances up to 5 μm. The samples were examined with a low vacuum without applying a conductive coating. The images are displayed on Fig. S7. The N_2 (99.999% purity gas was used) adsorption-desorption isotherm measurements at 77K within the range of relative pressures P/P_0 from 10^{-6} to 0.995 were carried out on Quantochrome "Autosorb iQ". The MIL@salt compounds were activated in dynamic vacuum using standard "outgas" option of the equipment. Differential scanning calorimetry (DSC) measurements were carried out on DSC 204 F1 Phoenix (Netzsch). All samples were weighted with the following examination upon 3-4 cycles heating/cooling in the range 25−250°C with isothermal aging at 150°C during half an hour. After that the samples were weighted again. The DSC measurements were performed using a heat flow method at the constant heating/cooling rate of 6 °C /min in an unsealed aluminum crucible with

lid under Ar stream. Signals of base line of an empty crucible were subtracted from the experimental data. The sensitivity calibration of the sample carrier sensors and temperature scale graduation were carried out by melting of standard samples (Hg, Ga, $C_{10}H_8$, C_6H_5COOH, KNO_3, In, Sn, Bi) [D. P. Pishchur, V. A. Drebushchak, *J. Therm. Anal. Cal.* **2016**, *124*, 951]. Temperature and enthalpy ΔH values were averaged after the all heating/cooling repetitions. The DSC data for the composites are shown on Fig. S8.

The AC impedance measurements for pelleted samples (pellets with 5.8 mm in diameter, 1–2 mm thickness) were carried out by two-probe method using Pt-pressed electrodes with Impedance Meters (LCR-821 or Z-350M) in the frequency range above 1 Hz – 1 MHz. For the conductivity measurements of bulk (benz)imidazolium triflate salts the corresponding pellets and the attached electrodes were additionally supported by silicone glue to prevent the pellet collapse above the melting point. The measurements were carried out with the heating or cooling rate 1–2 deg·min^{-1} in the temperature range from 25 °C to 230 °C in air flow (humidity = 0.32 mol.% or RH ≈ 15% at room temp.). Typical impedance plots (*e.g.* Fig. S9) feature a part of a semicircle at higher frequencies and a tail at low frequencies, which deals with the mobile ions being blocked by the electrode – electrolyte interfaces. The higher-frequency minimum/intercept along the *x*-axis of the impedance plots was used to calculate the bulk resistance of the samples.

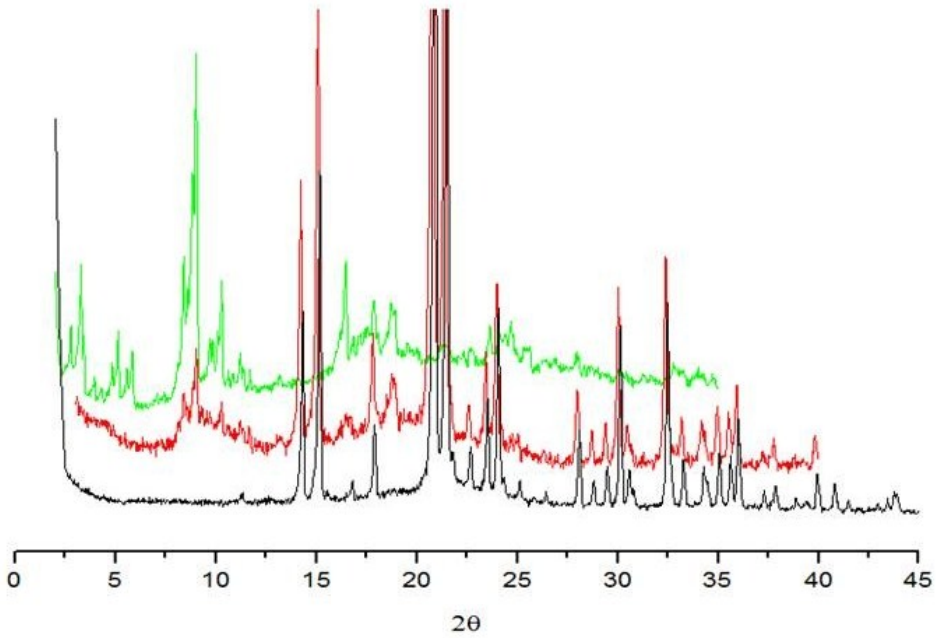


Fig. S1. PXRD patterns of MIL-101 (green), imidazolium triflate **1** (black) and MIL·10(**1**) composite (red).

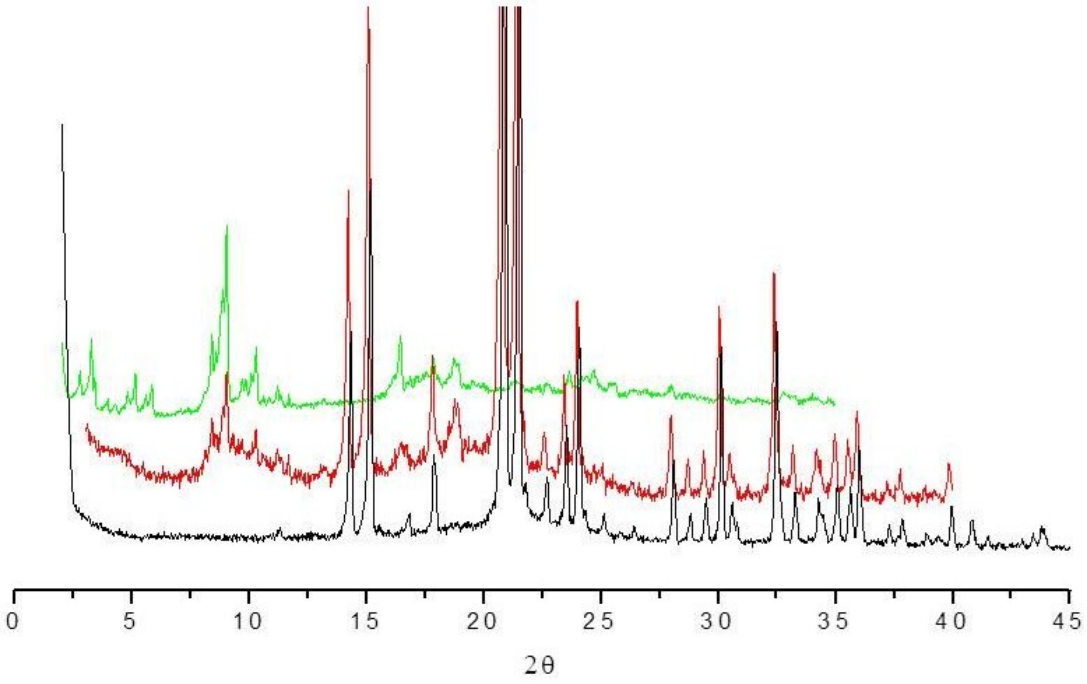


Fig. S2. PXRD patterns of MIL-101 (green), imidazolium triflate **1** (black) and MIL·20(**1**) composite (red).

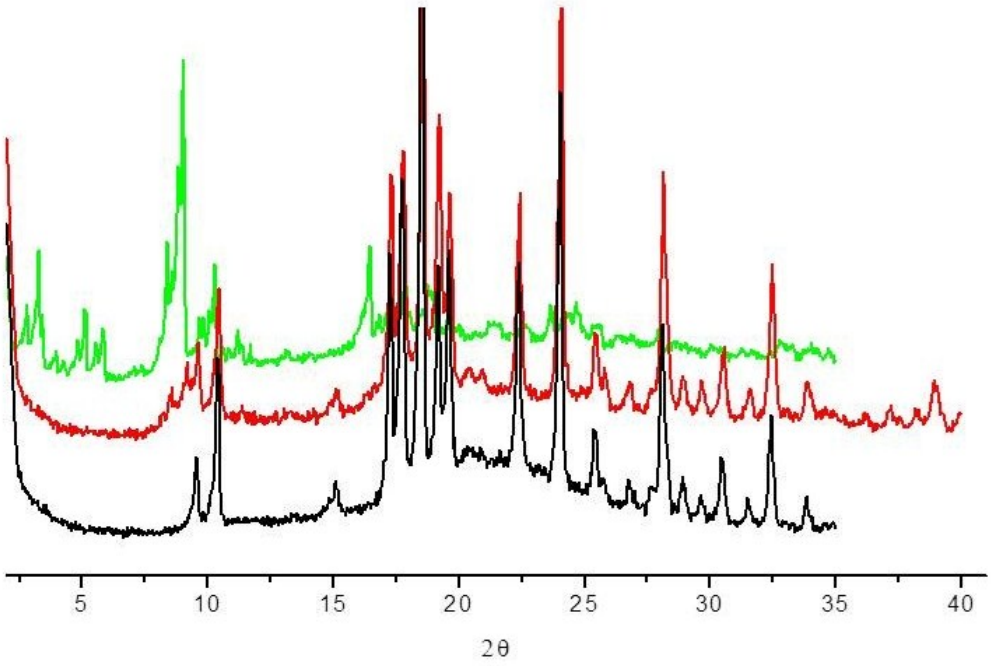


Fig. S3. PXRD patterns of MIL-101 (green), benzimidazolium triflate **2** (black) and MIL·20(**2**) composite (red).

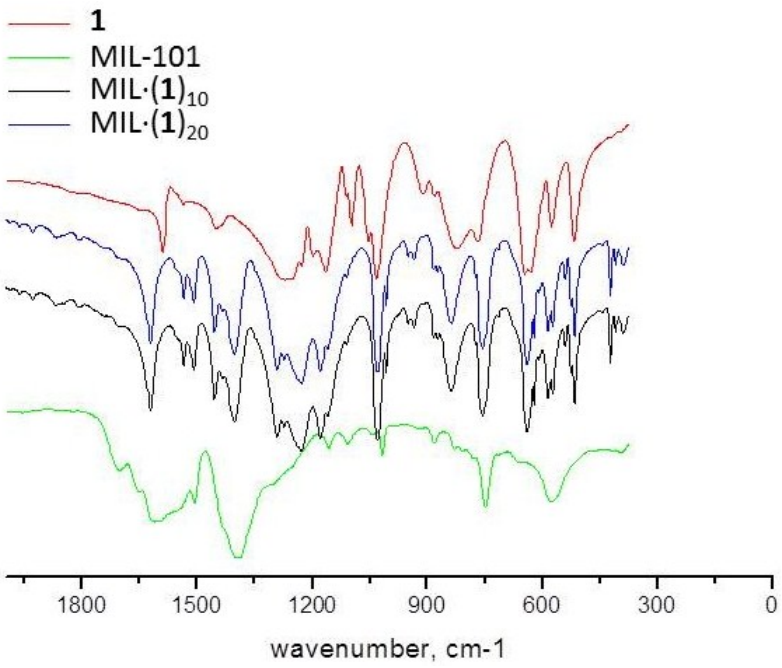


Fig. S4. FT-IR spectra of MIL-101 (green), imidazolium triflate **1** (red), MIL·10(**1**) (black) and MIL·20(**1**) composites (blue).

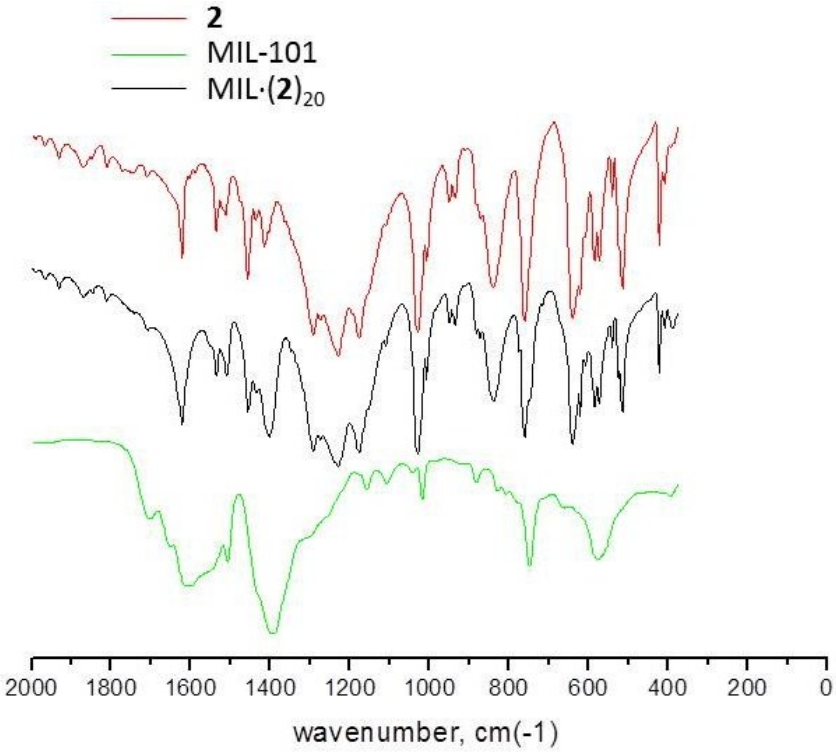
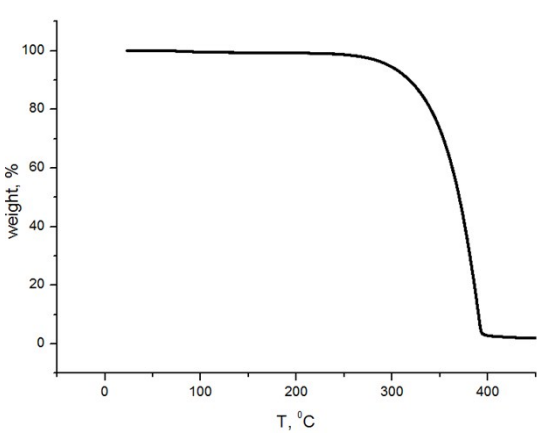
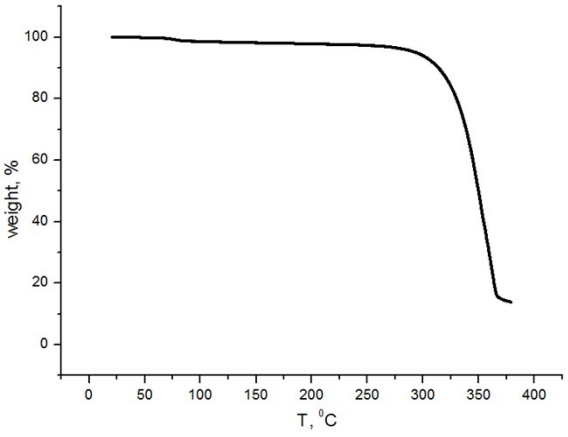


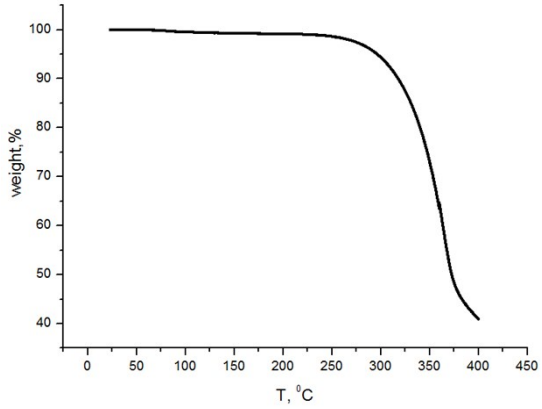
Fig. S5. FT-IR spectra of MIL-101 (green), benzimidazolium triflate **2** (red) and MIL·20(**2**) composite (black).



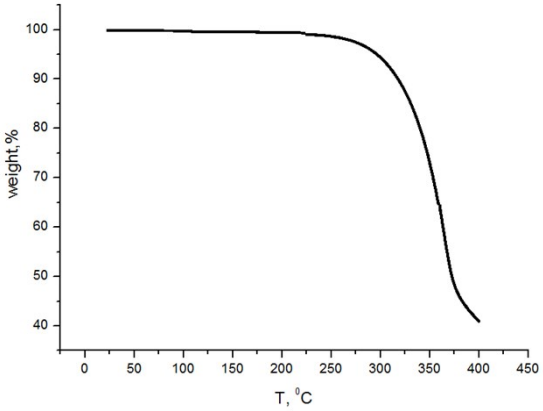
1



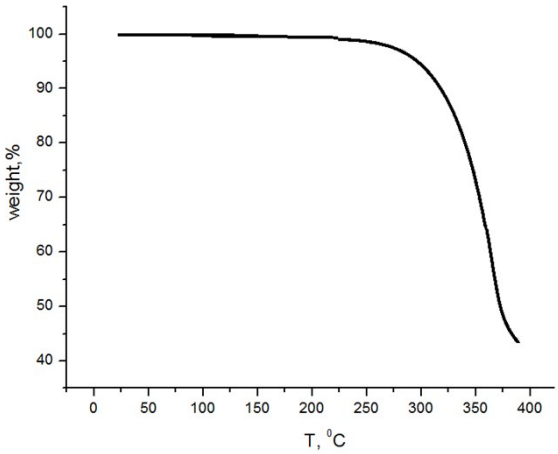
2



MIL·10(**1**)

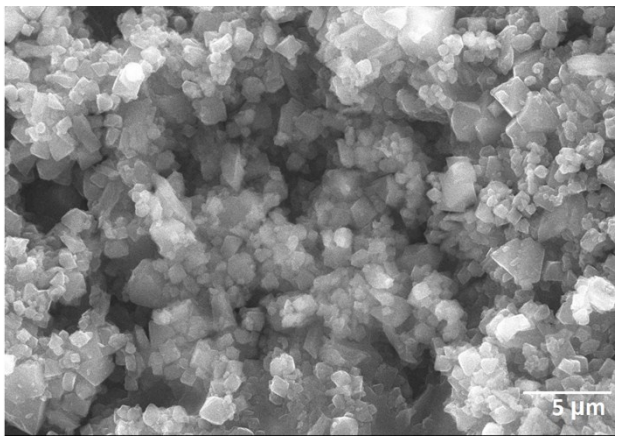


MIL·20(**1**)

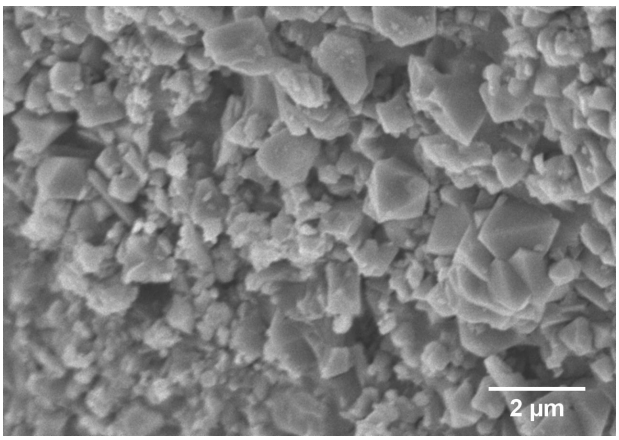


MIL·20(**2**)

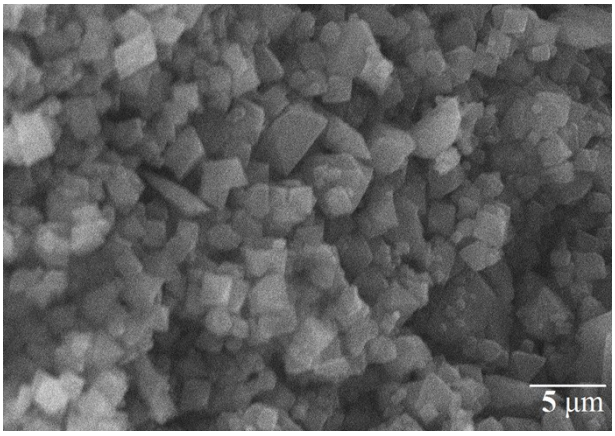
Fig. S6. TGA data of the (benz)imidazolium triflate salts and the MIL@salt nanocomposites.



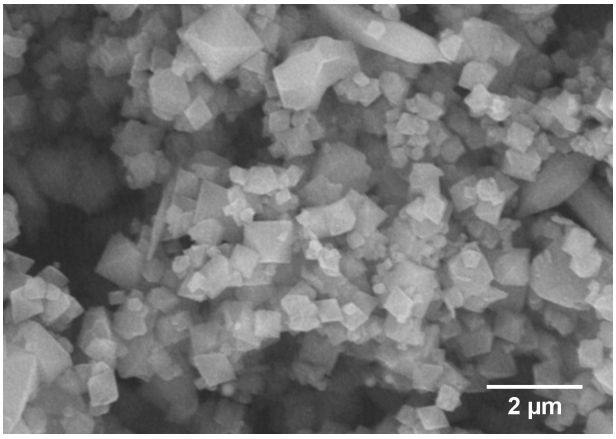
MIL·10(**1**)



MIL·20(**1**)



MIL·10(**2**)



MIL-101

Fig. S7. SEM images of MIL@salt nanocomposites and MIL-101 (bottom right).

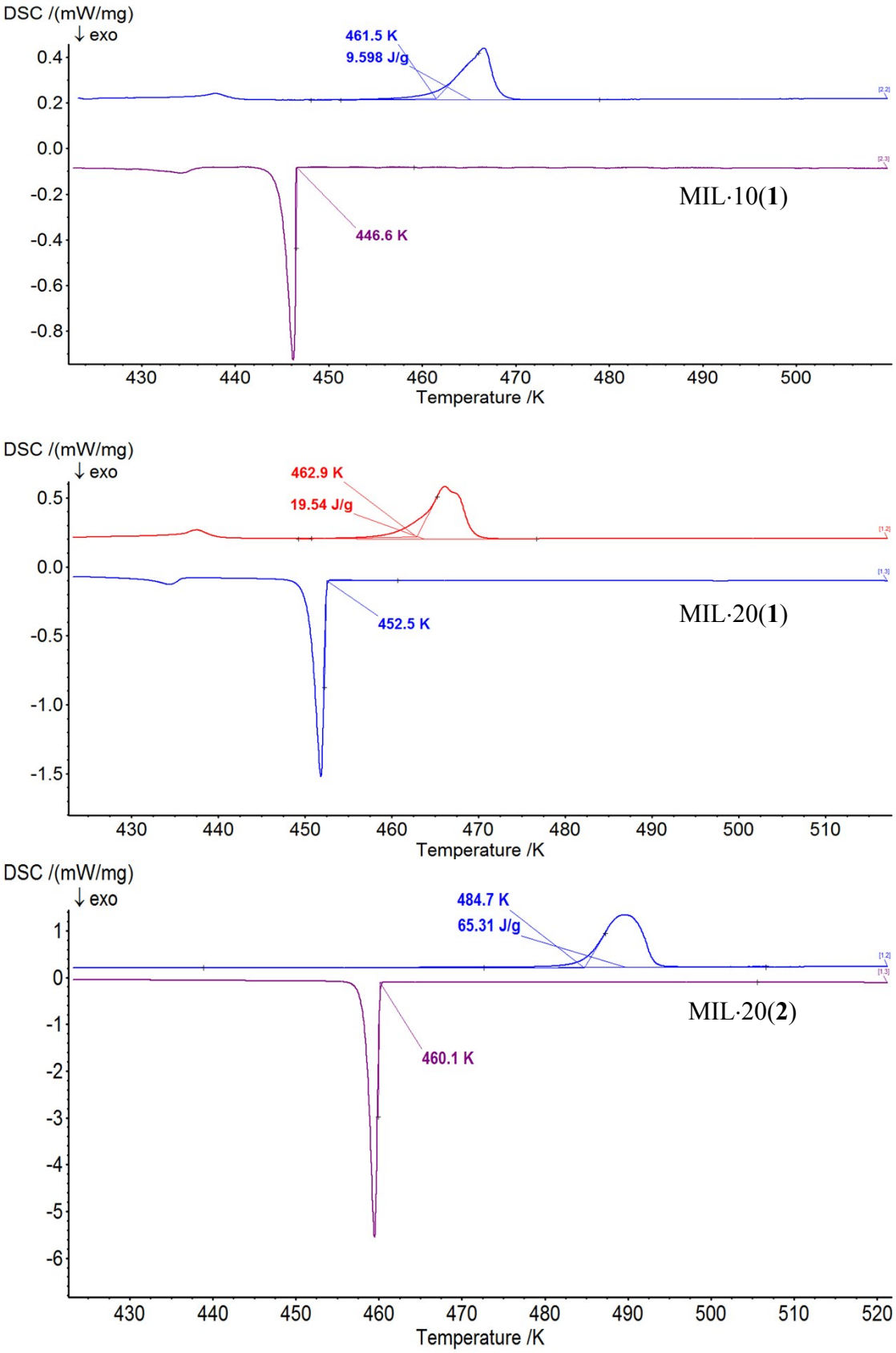


Fig. S8. DSC data of the nanocomposites MIL·10(**1**) (top), MIL·20(**1**) (middle), MIL·20(**2**) (bottom).

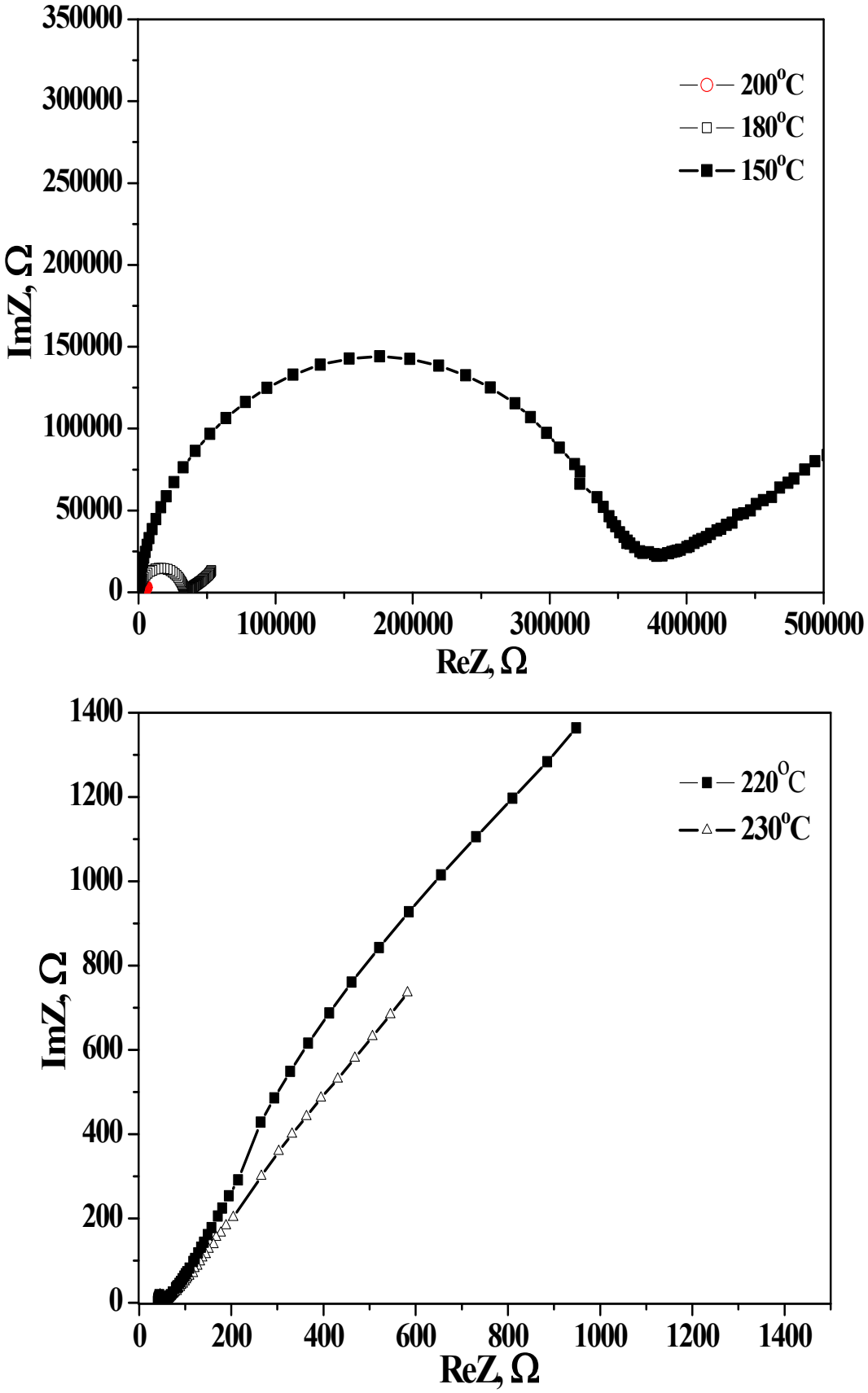


Fig. S9. Impedance spectra of the nanocomposite MIL·20(**1**) at different temperatures.