Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

## Mechanochemical and Thermal Formation of 1H-Benzotriazole Coordination Polymers and Complexes of 3d-Transition Metals with Intriguing Dielectric Properties

Franziska A. Brede, Friedrich Mühlbach, Gerhard Sextl and Klaus Müller-Buschbaum

### Neat grinding conditions for the reaction of $MCl_2$ (M = Mn, Co, Zn) and BtzH

The reactions were carried out in a stainless steel vial (volume 25 ml) with stainless steel milling balls (2 x Ø = 12 mm, 3 x Ø = 10 mm) and a frequency of 25 Hz.

**Table S1.** Investigated neat grinding conditions.

| transition metal chloride | milling time (min) | diffraction number |
|---|---|---|
| $MnCl_2$. | 1 | S1-I |
| | 3 | S1-II |
| | 5 | S1-III |
| $CoCl_2$ | 1 | S2-I |
| | 3 | S2-II |
| | 5 | S2-III |
| $ZnCl_2$ | 3 | S3-I |
| | 5 | S3-II |
| | 8 | S3-III |

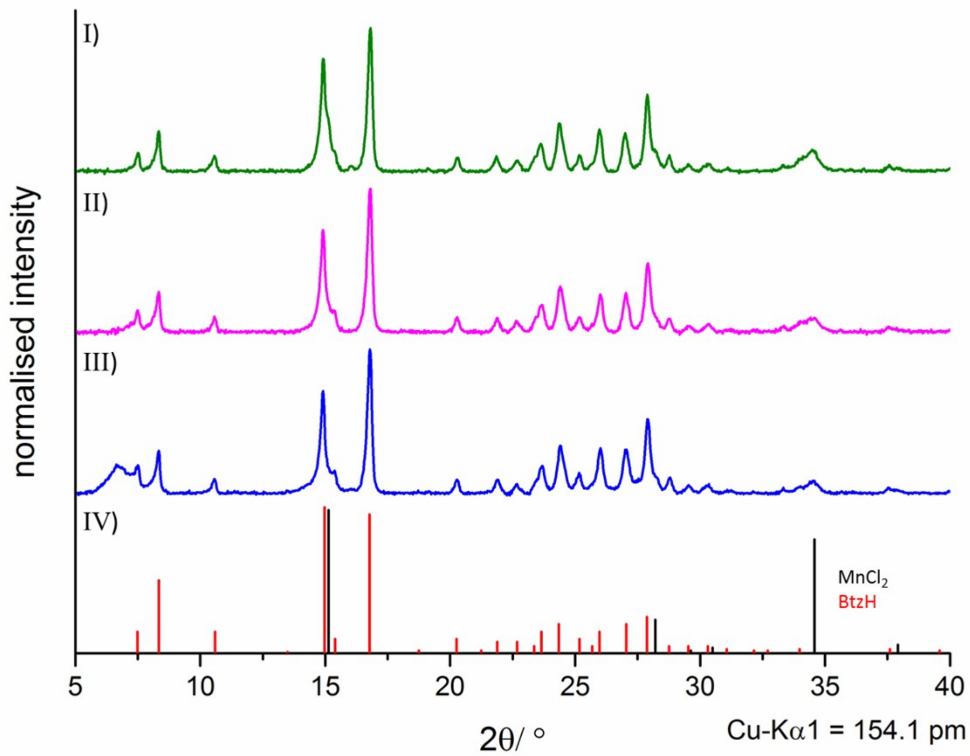


**Fig. S1** PXRD investigation of the mechanochemical treatment of $MnCl_2$ with BtzH without LAG.

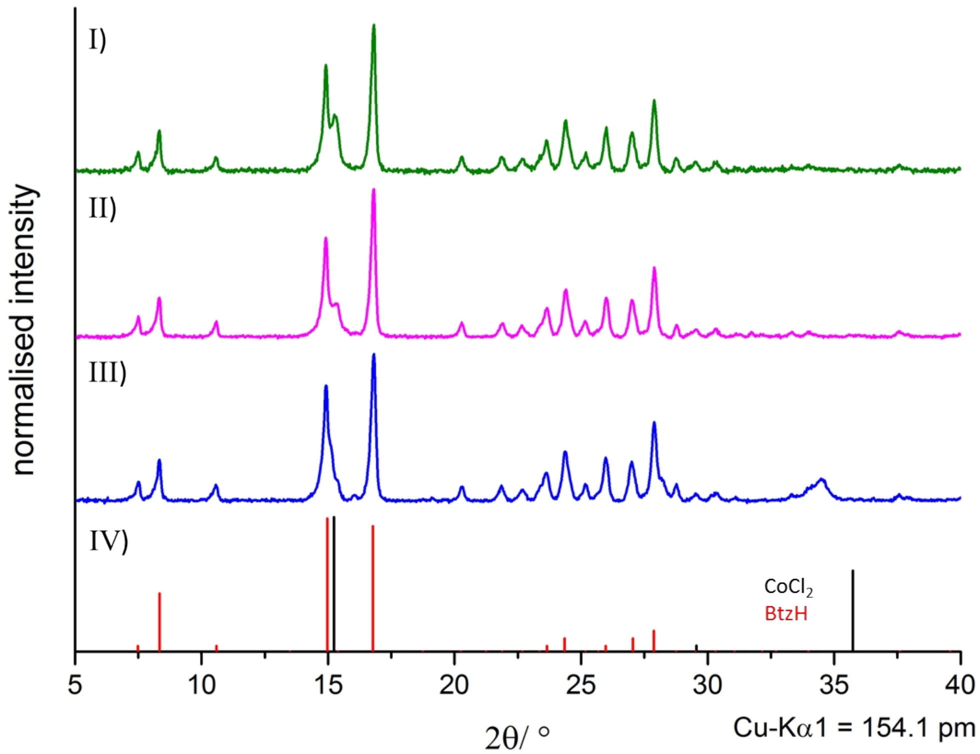


**Fig. S2** PXRD investigation of the mechanochemical treatment of $CoCl_2$ with BtzH without LAG.

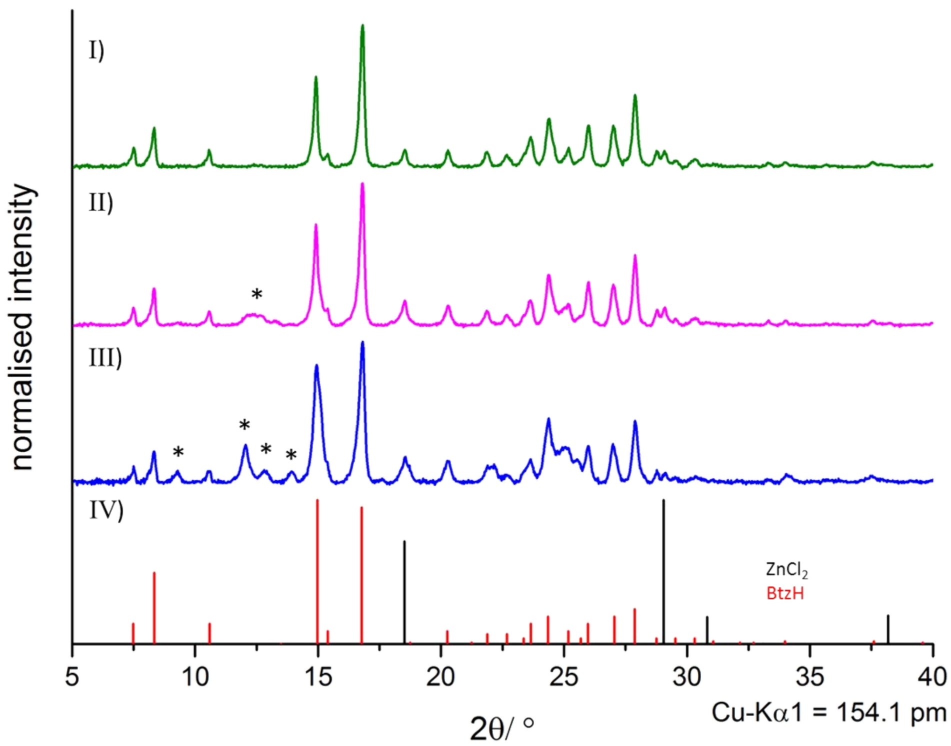


**Fig. S3** PXRD investigation of the mechanochemical treatment of $ZnCl_2$ with BtzH without LAG. Marked with asterisks: unknown reflections.

## LAG- conditions for the reaction of $MCl_2$ (M = Mn, Co, Zn) and BtzH

**Table S2.** Tested LAG-conditions.

| transition metal chloride | solvent | milling time (min) | milling balls (ø) | diffraction number |
|---|---|---|---|---|
| $MnCl_2$. | acetonitrile | 1 | 5x5 mm, 2x10 mm | S4-II |
| | | 30 | 5x5 mm, 2x10 mm | S4-III |
| | toluene | 1 | 15 x 3mm | S4-V |
| | | 30 | 5x5 mm, 2x10 mm | S4-VI |
| $CoCl_2$ | acetonitrile | 1 | 5x5 mm, 2x10 mm | S5-I |
| | | 1 | 15 x 3 mm | S5-II |
| | | 30 | 15x5 mm, 2x10 mm | S5-III |
| | toluene | 1 | 15 x 3 mm | S5-IV |
| | | 20 | 5x5 mm, 2x10 mm | S5-V |
| | | 20 | 3x10 mm | S5-VI |
| | | 30 | 15 x 3 mm | S5-VII |
| $ZnCl_2$ | acetonitrile | 1 | 15 x 3 mm | S6-I |
| | | 30 | 5x5 mm, 2x10 mm | S6-II |
| | toluene | 1 | 15 x 3 mm | S6-III |
| | | 30 | 5x5 mm, 2x10 mm | S6-IV |

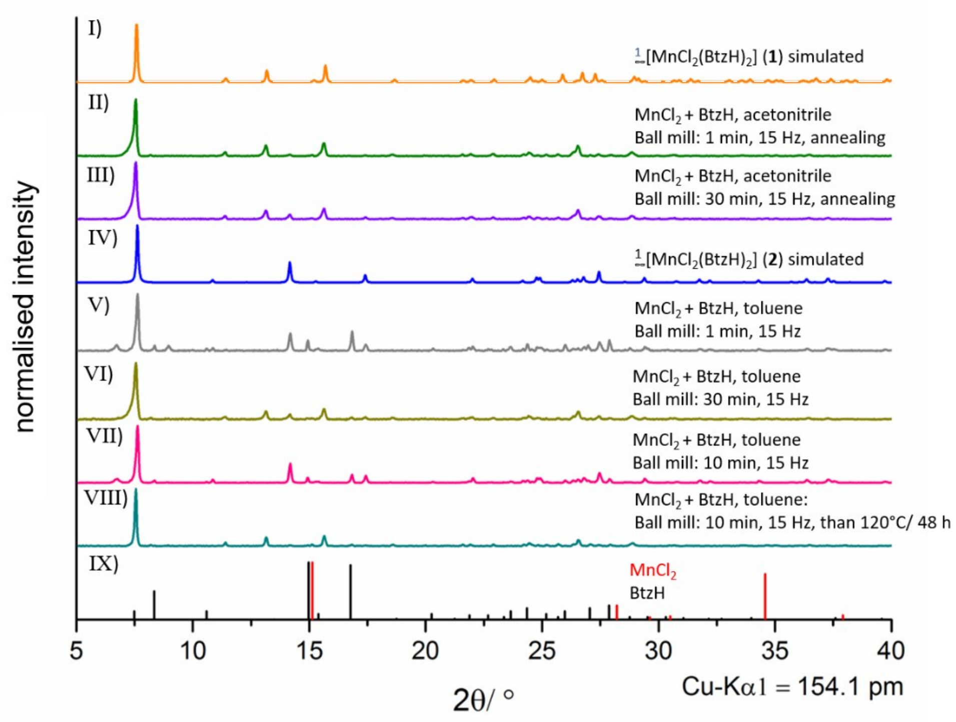


**Fig. S4** PXRD investigation of the mechanochemical LAG treatment of $MnCl_2$ and BtzH with the two solvents toluene and acetonitrile.

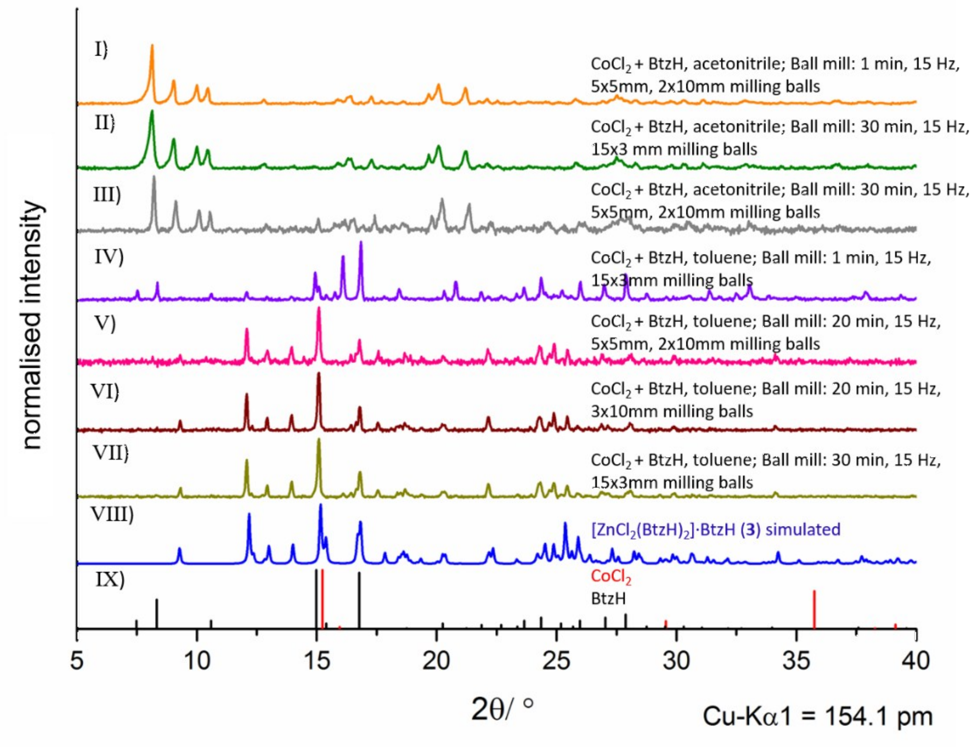


**Fig. S5** PXRD investigation of the mechanochemical LAG treatment of $CoCl_2$ and BtzH with the two solvents toluene and acetonitrile.

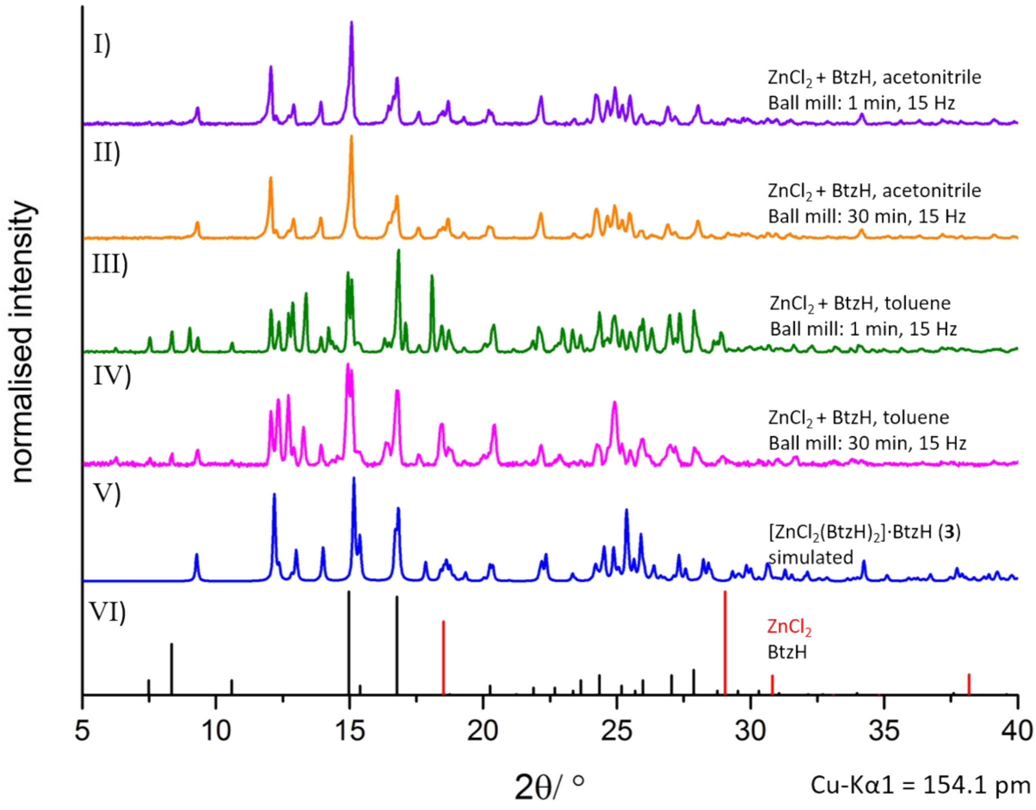


**Fig. S6** PXRD investigation of the mechanochemical LAG treatment of $ZnCl_2$ and BtzH with the two solvents toluene and acetonitrile.

**Phase transition from the monoclinic coordination polymer α-$_\infty$[$MnCl_2(BtzH)_2$] (2) into the orthorhombic form β-$_\infty$[$MnCl_2(BtzH)_2$] (1)**

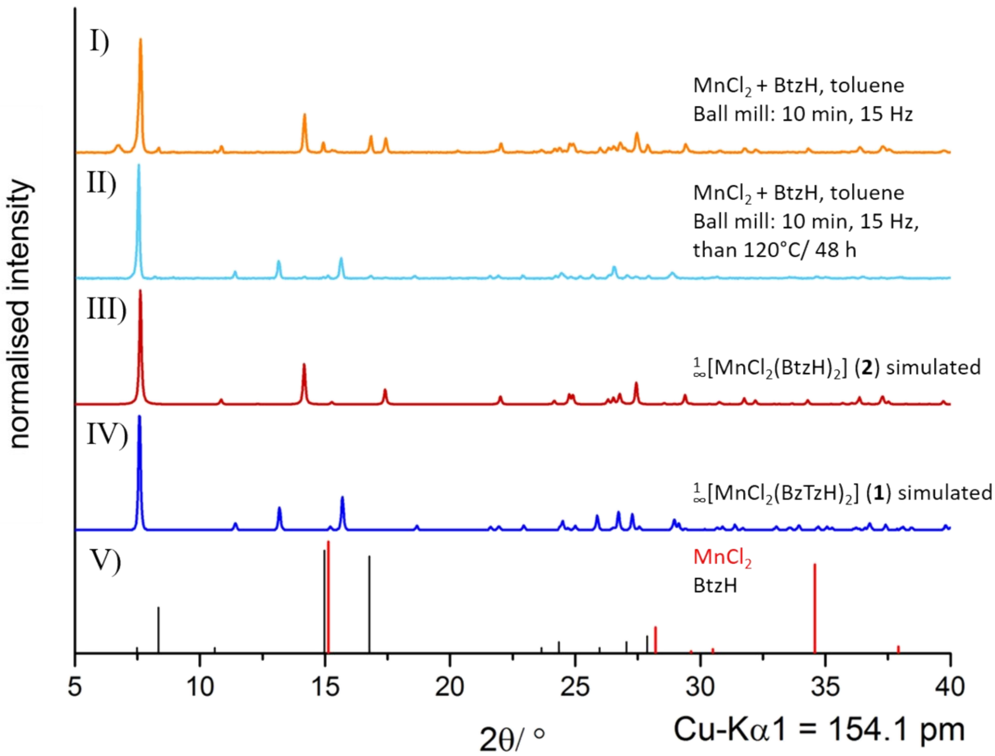


**Fig. S7** PXRD investigation of the phase transition from the monoclinic coordination polymer α-$_\infty$[$MnCl_2(BtzH)_2$] (**2**) (powder pattern I) in the orthorhombic form β-$_\infty$[$MnCl_2(BtzH)_2$] (**1**) (powder pattern II) by input of thermal energy.

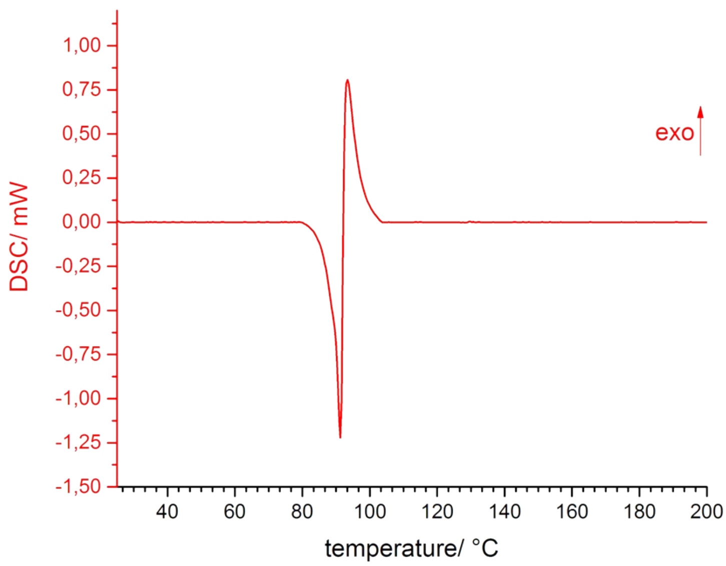


**Fig. S8** DSC measurement of polymer α-$_\infty$[$MnCl_2(BtzH)_2$] (**2**). The phase transition into the higher symmetrical form β-$_\infty$[$MnCl_2(BtzH)_2$] (**1**) takes place at a temperature of 80 °C.

## PXRD investigations

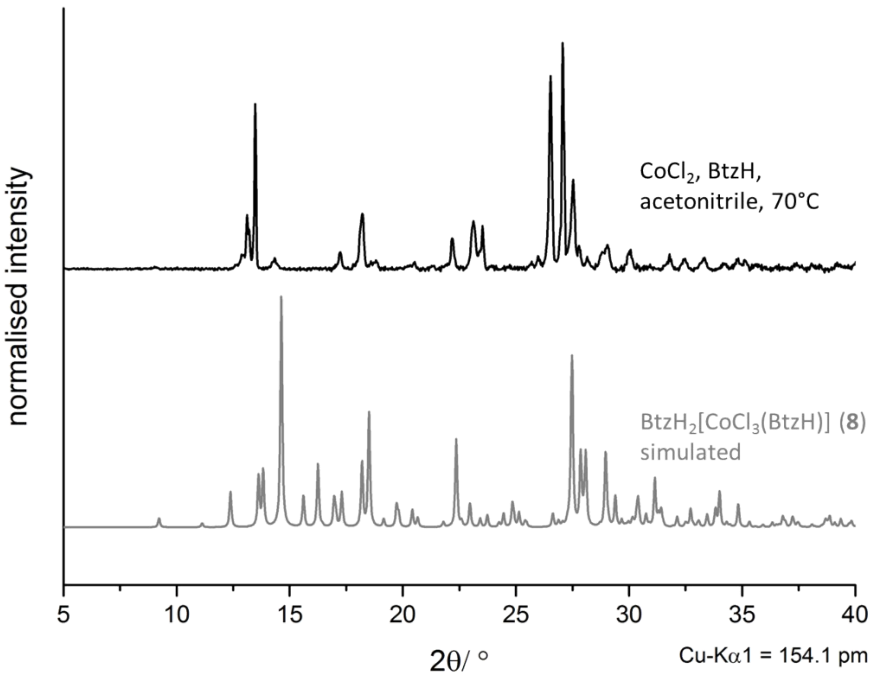


**Fig. S9** Comparison of the simulated powder pattern of BtzH$_2$[CoCl$_3$BtzH] (**8**) with the dried mixture from which single crystals of **8** could be obtained.

**Table S3.** Crystallographic data and results from Rietveld refinement of powder X-ray diffraction experiments of $[CoCl_2(BtzH)_2]\cdot BtzH$ (**4**).

| | **Co(4)** |
|---|---|
| Formula | $CoCl_2N_9C_{18}H_{15}$ |
| $F_w$/ gmol$^{-1}$ | 487.22 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| | a = 713.58(2) |
| Cell paramter/ pm | b = 3593.72(13) |
| | c = 725.95(3) |
| Angles/ ° | $\beta$ = 102.825(3) |
| Cell volume/ $10^6$ pm$^3$ | 1815.19(11) |
| $\rho_{calcd}$/gcm$^{-3}$ | 1.78(1) |
| μ / cm$^{-1}$ | 90.29(1) |
| Z | 4 |
| Radiation | Cu-$K_\alpha$ (λ = 154.1 pm) |
| Diffractometer | Bruker D8 Discover |
| Geometry | Transmission |
| Range/ ° | $5 \leq 2\theta \leq 60$ |
| Reflections | 612 |
| Data points | 5435 |
| Refined parameters | 616 |
| (Background) | (11) |
| $R_p$ | 0.018 |
| $wR_p$ | 0.079 |
| $R_{Bragg}$ | 0.954 |
| $\chi^2$ | 2.66 |
| *Wght. Durbin Watson* | 0.532 |

## Thermal investigations

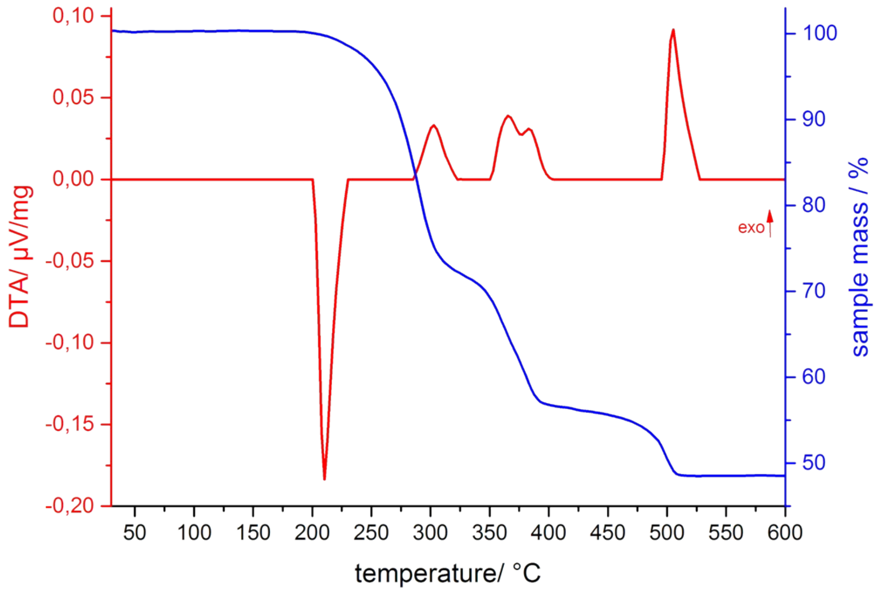


**Fig. S10** Simultaneous DTA/TG of $_\infty[MnCl_2(BtzH)_2]$ (**1**). Heating rate: 10 °C/min; gas flow: 40 ml/min of a 1/1 mixture of Ar and $N_2$.

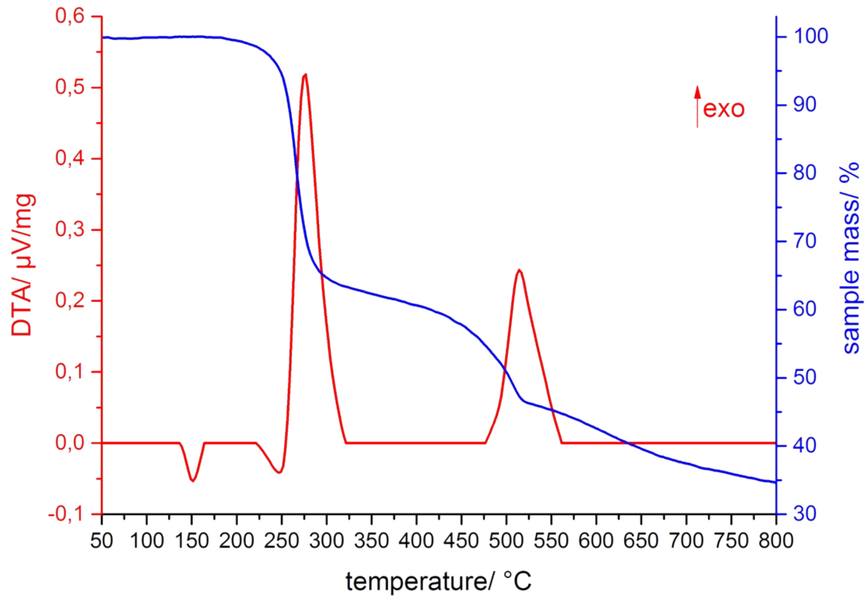


**Fig. S11** Simultaneous DTA/TG of $[ZnCl_2(BtzH)_2]\cdot BtzH$ (**3**). Heating rate: 10 °C/min; gas flow: 40 ml/min of a 1/1 mixture of Ar and $N_2$.

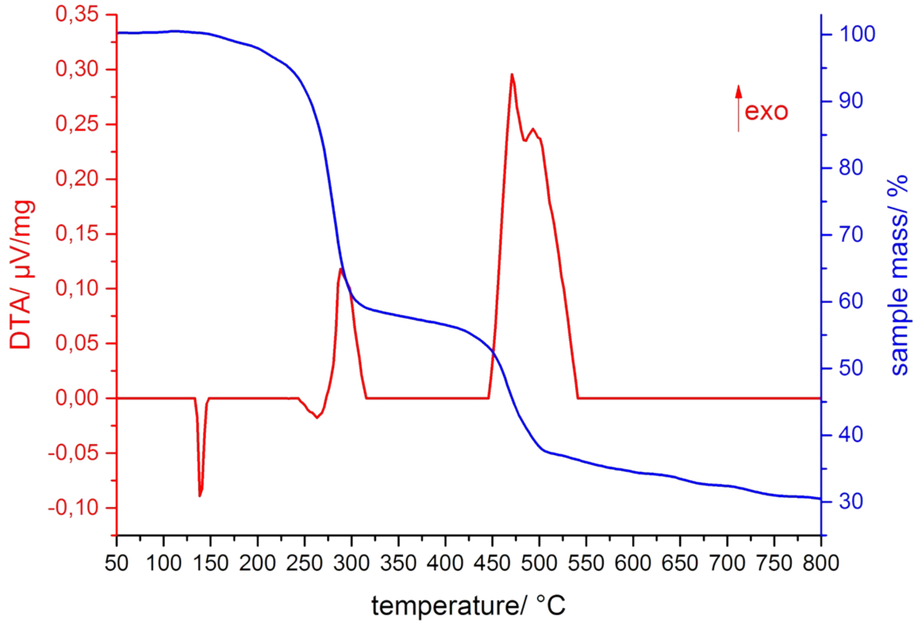


**Fig. S12** Simultaneous DTA/TG of $[CoCl_2(BtzH)_2]$·BtzH (**4**). Heating rate: 10 °C/min; gas flow: 40 ml/min of a 1/1 mixture of Ar and $N_2$.

## Dielectric properties

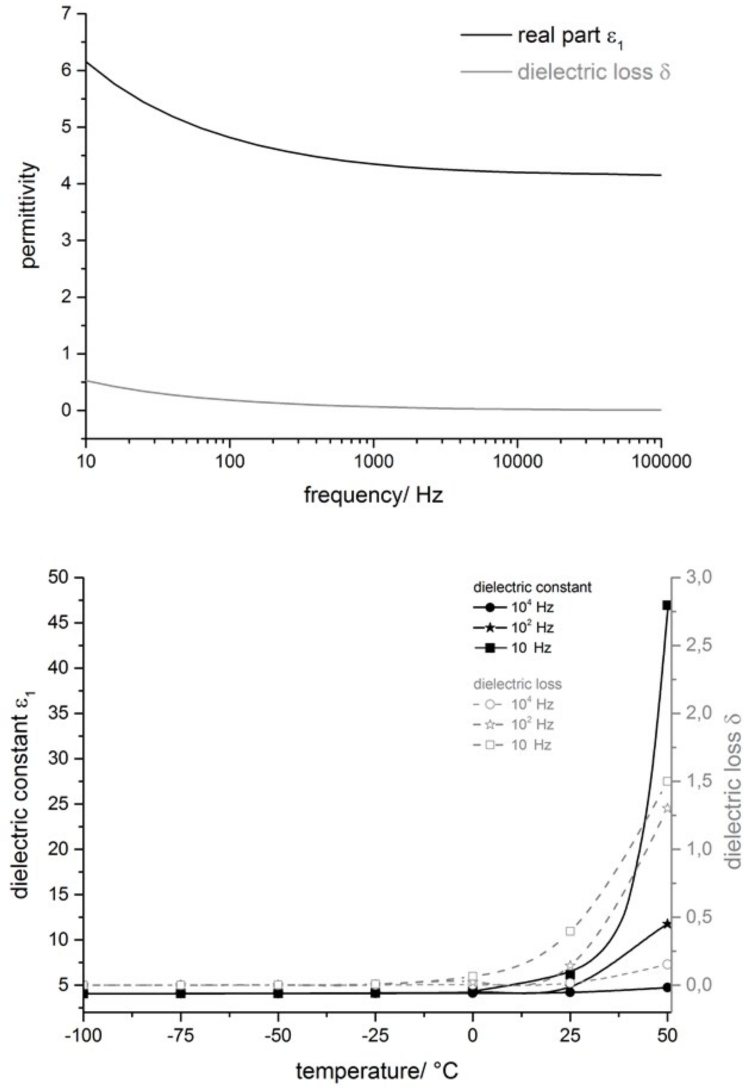


**Fig. S13** Frequency-dependent and temperature-dependent dielectric constants and dielectric losses of $[CoCl_2(BtzH)_2]{\cdot}BtzH$ (**4**).