# " Structural, Magnetic and Dielectric Properties of Two Novel Mixed-Valence Iron(II)-Iron(III) Metal Formate Frameworks "

by M. Maczka *et al*

Table S1. Experimental details for $[C_2H_5NH_3][Fe^{II}Fe^{III}(HCOO)_6]$, **2**, and $[(C_2H_5)_2NH_2][Fe^{II}Fe^{III}(HCOO)_6]$, **3**.

| | **3** | **2** |
|---|---|---|
| *Crystal data* | | |
| Chemical formula | $C_{10}H_{18}Fe_2NO_{12}$ | $C_8H_{14}Fe_2NO_{12}$ |
| $M_r$ | 455.95 | 427.90 |
| Crystal system, space group | Trigonal, *P*-31*c* | Trigonal, *P*-31*c* |
| Temperature (K) | 260 | 298 |
| *a*, *c* (Å) | 8.4483 (2), 13.7058 (4) | 8.2294(2), 14.1221(5) |
| *V* (Å$^3$) | 847.18 (5) | 828.26 (5) |
| *Z* | 2 | 2 |
| Radiation type | Mo *K*α | Mo *K*α |
| μ (mm$^{-1}$) | 1.77 | 1.81 |
| Crystal size (mm) | 0.10 × 0.05 × 0.04 | 0.10 × 0.08 × 0.07 |
| *Data collection* | | |
| $T_{min}$, $T_{max}$ | 0.925, 1.000 | 0.874, 1.000 |
| No. of measured, independent and observed [*I* > | 10788, 542, | 8996, 527, |

| | | |
|---|---|---|
| $2\sigma(I)$] reflections | 482 | 459 |
| $R_{int}$ | 0.033 | 0.032 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.610 | 0.610 |
| *Refinement* | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.079, 1.08 | 0.038, 0.113, 1.09 |
| No. of reflections | 542 | 527 |
| No. of parameters | 43 | 39 |
| No. of restraints | 4 | 2 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.55, -0.35 | 1.00, -0.54 |

Table S2. IR frequencies (in $cm^{-1}$) of **2** and **3** together with the suggested assignments.[a]

| **3** | | **2** | | Assignment |
|---|---|---|---|---|
| 298 K | 4 K | 298 K | 4 K | |
| 3354sh | 3352sh | | | $\nu(NH_3)$ and $\nu(NH_2)$ |
| 3305w | 3302m | 3276sh | 3277sh | $\nu(NH_3)$ and $\nu(NH_2)$ |
| 3213sh | 3207sh | 3201w | 3216m, 2196sh | $\nu(NH_3)$ and $\nu(NH_2)$ |
| 3175m | 3171m | 3133vw | 3127w | $\nu(NH_3)$ and $\nu(NH_2)$ |
| 3106m | 3071m, 3037m | 3080w | 3077m | $\nu(NH_3)$ and $\nu(NH_2)$ |
| 3012w | 3007m | 3019vw | 3016w | $\nu(CH_3)$ and $\nu(CH_2)$ |
| 3001w | 2999m | 3000vw | 2996w | $\nu(CH_3)$ and $\nu(CH_2)$ |
| 2983w | 2979w | 2987vw | 2982w | $\nu(CH_3)$ and $\nu(CH_2)$ |
| 2971w | 2972w | 2969vw | 2977w | $\nu(CH_3)$ and $\nu(CH_2)$ |
| 2957w | 2959w | | | $\nu(CH_3)$ and $\nu(CH_2)$ |
| 2942w | 2938m | 2946w | | $\nu(CH_3)$ and $\nu(CH_2)$ |
| | | | 2929m | $\nu(NH_3)$ |
| 2910vw | 2919sh, 2904w | | | $\nu(CH_3)$ and $\nu(CH_2)$ |
| 2898vw | 2898w | | | $\nu(CH_3)$ and $\nu(CH_2)$ |
| 2875m | 2882m | 2881w | 2884m, 2877sh | $\nu_1(HCOO^-)$ |
| 2864sh | 2868m, 2857m | | | $\nu_1(HCOO^-)$ |
| 2826w | 2830w, 2818sh | | | overtone |
| | 2813w | | | |
| | | 1626sh | 1628sh | $\delta_{as}(NH_3)$ |
| 1586s | 1587s, 1570sh | 1585s | 1589s, 1574s | $\nu_4(HCOO^-)$ |
| | 1560sh | | | |
| | | 1485w | 1487w | $\delta_s(NH_3)$ |
| 1473vw | 1476w, 1464vw | 1463w | 1458w | $\delta(CH_3)$ and $\delta(CH_2)$ |

| | | | | |
|---|---|---|---|---|
| | 1459vw | | | |
| 1453w | 1450m | 1451w | 1447w | $\delta(CH_3)$ and $\delta(CH_2)$ |
| 1447w | 1441m | 1447w | 1444m | $\delta(CH_3)$ and $\delta(CH_2)$ |
| | 1425w | | | $\omega(NH_2)$ |
| | 1408vw | | | $\tau(NH_2)$ and $\delta_s(CH_3)$ |
| 1394m | 1395m | 1386s | 1395s, 1388s | $\nu_5(HCOO^-)$ |
| 1383m | 1387m | | | $\nu_5(HCOO^-)$ |
| 1378m | 1382m, 1380m | | | $\nu_5(HCOO^-)$ |
| | 1374m | | | $\nu_5(HCOO^-)$ |
| | 1366vw | | 1367sh | $\nu_2(HCOO^-)$ |
| 1346s | 1349s, 1343m | 1347s | 1348s | $\nu_2(HCOO^-)$ |
| | 1334s | | | |
| | | 1328sh | 1333sh | $\nu_2(HCOO^-)$ |
| 1261sh | 1269w | 1222w | 1227w | $\rho(CH_3)$ and $\rho(CH_2)$ |
| 1195w | 1202w | 1194w | 1196w | $\rho(CH_3)$ |
| 1158vw | 1167vw, 1160vw | | | overtones |
| | 1155vw | | | |
| 1072w | 1073w | | | $\rho(CH_3)$ |
| 1058w | 1061sh, 1057w | | | $\nu_6(HCOO^-)$ |
| 1055w | 1057m,1048sh | 1051w | 1057w | $\nu_6(HCOO^-)$ |
| | | | 1044w | $\nu_{as}(C\text{-}C)$ and $\nu_{as}(C\text{-}N)$ |
| 1032w | 1032vw | | | $\rho(CH_3)$ |
| 1024w | 1025w | | | $\rho(CH_3)$ |
| | | 992w | 998w | $\rho(NH_3)$ |
| | | 964w | 960w | $\rho(NH_3)$ |
| 907vw | 922w | | | $\nu_{as}(C\text{-}C)$ and $\nu_{as}(C\text{-}N)$ |

| | | | | |
|---|---|---|---|---|
| 896w | 906w | | | $\nu_{as}$(C-C) and $\nu_{as}$(C-N) |
| | | 870vw | 870vw | $\nu_{s}$(C-C) and $\nu_{s}$(C-N) |
| | 866w | | | $\rho(NH_2)$ |
| | 845vw | | | $\nu_{s}$(C-C) and $\nu_{s}$(C-N) |
| 810m | 817m, 808sh | 815m | 820m | $\nu_3(HCOO^-)$ |
| 790w | 788m | 785m | 781m | $\nu_3(HCOO^-)$ |
| 782w | 782m | | | $\nu_3(HCOO^-)$ |
| 761w | 762w | | | overtone |
| 665vw | 663vw, 639w | | | overtone |

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder

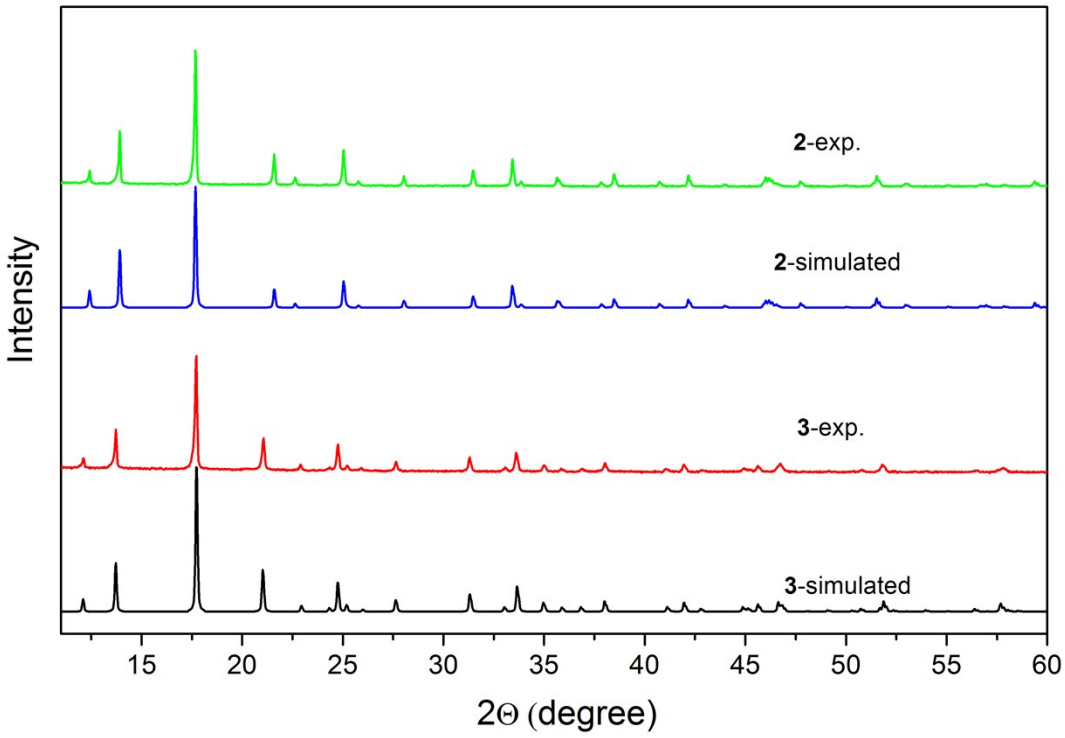


Figure S1. Powder XRD patterns for the as-prepared bulk samples of **2** and **3** with the calculated ones based on the single crystal structures at room temperatures.

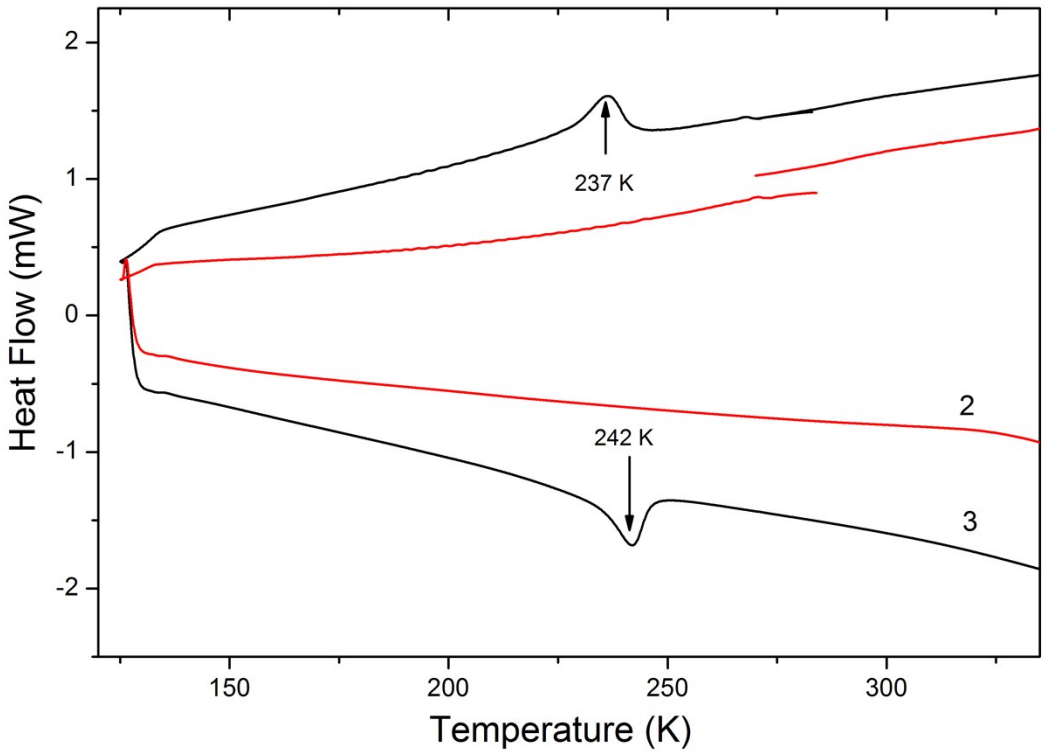


Figure S2. DSC traces for **2** and **3** in heating and cooling modes.

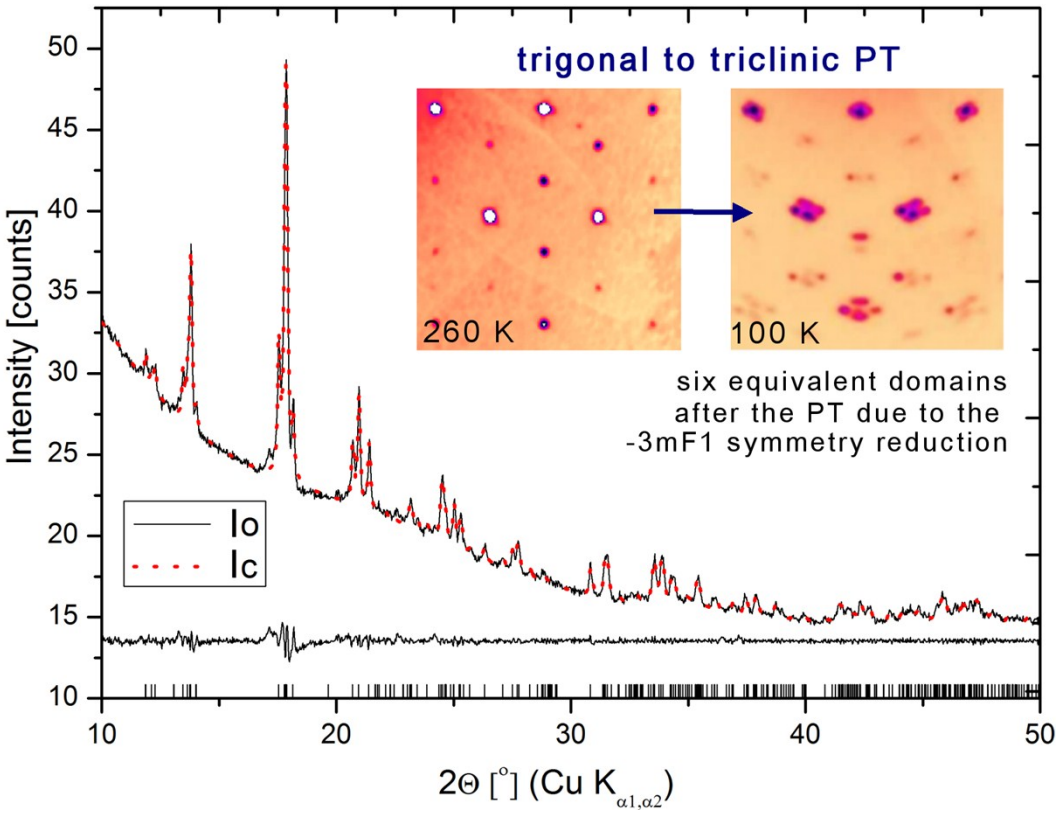


Figure S3. The results of the Le Bail fit of the XRD pattern in phase II of **3** using a triclinic unit cell with parameters a= 8.307(1)Å, b=8.585(1)Å, c=13.540(1)Å, α=89.5(1), β=89.3(1), γ=119.7(1), T=205 K. The residuals between the fits and the positions of the Bragg peaks are given in the bottom. In the inset the reciprocal space reconstruction of hk0 layer in phase I and II are presented. The phase transition (PT) to the triclinic phase induces lattice twinning to six equivalent domains. $I_o$,$I_c$: observed and calculated intensity.

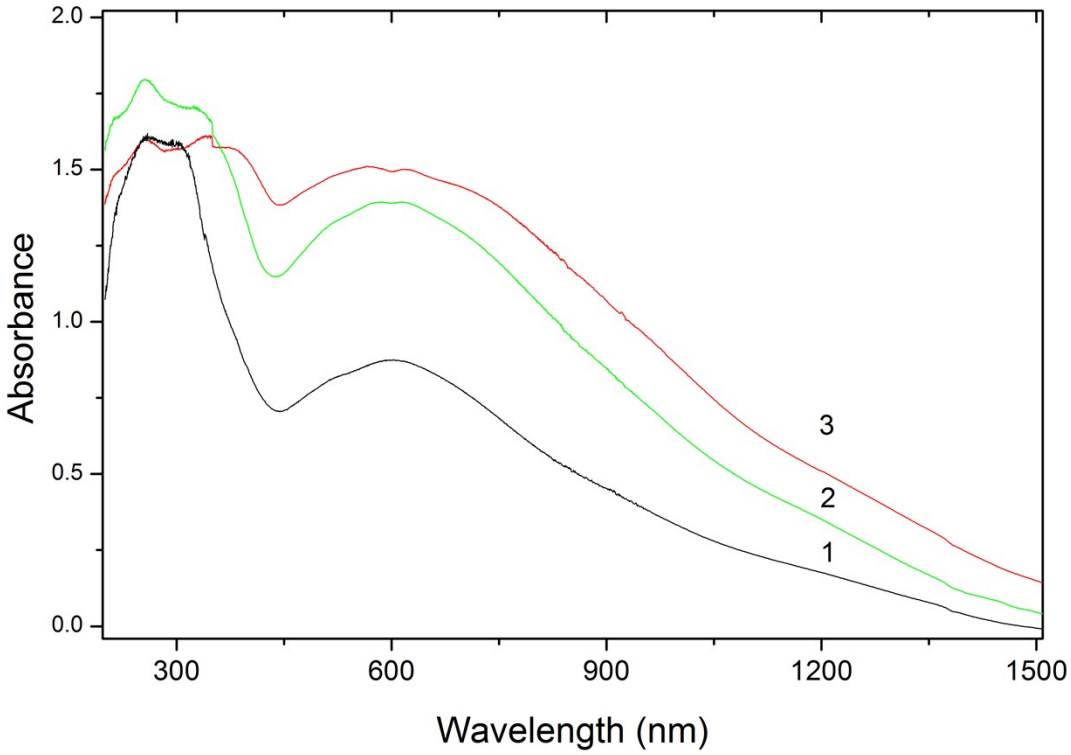


Figure S4. Diffuse reflectance spectra of **2** and **3**. For the comparison sake, spectrum of **1** is also shown.

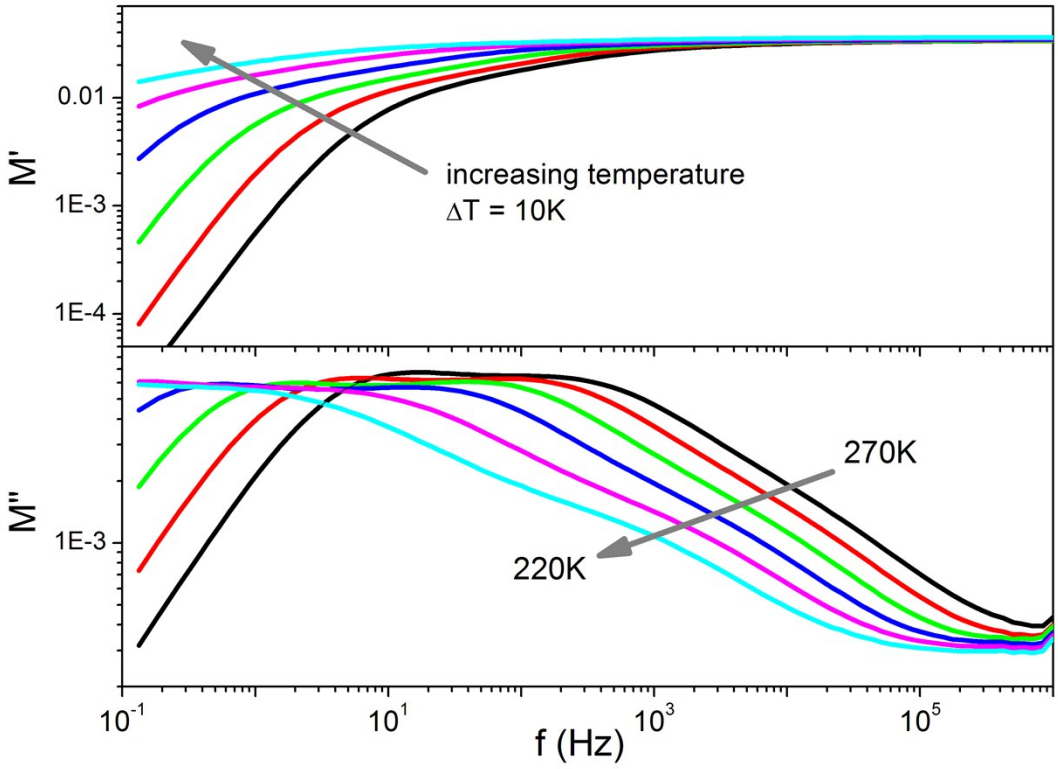


Figure S5. The frequency dependence of the real M' and imaginary M" parts of the electric modulus for **3**.

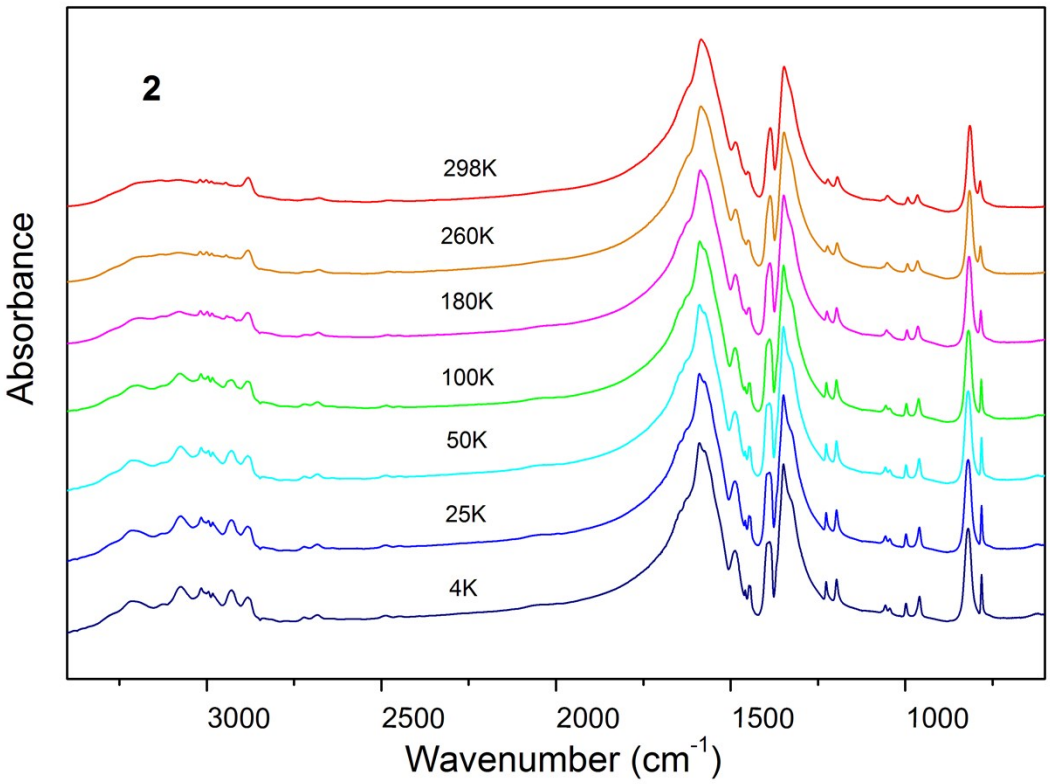


Figure S6. IR spectra of **2** recorded at various temperatures.

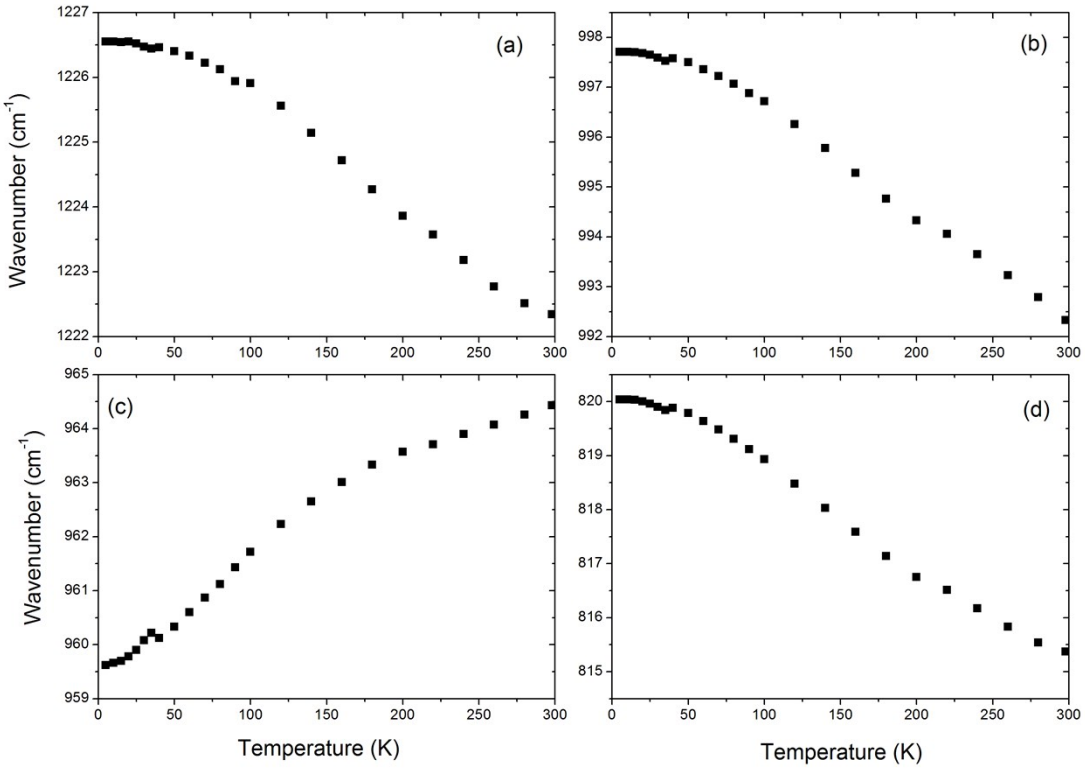


Figure S7. Temperature evolution of a few selected IR wavenumbers of **2** corresponding to (a) $\rho(CH_3)$ and $\rho(CH_2)$; (b) $\rho(NH_3)$; (c) $\rho(NH_3)$ and (d) $\nu_3(HCOO^-)$ modes.

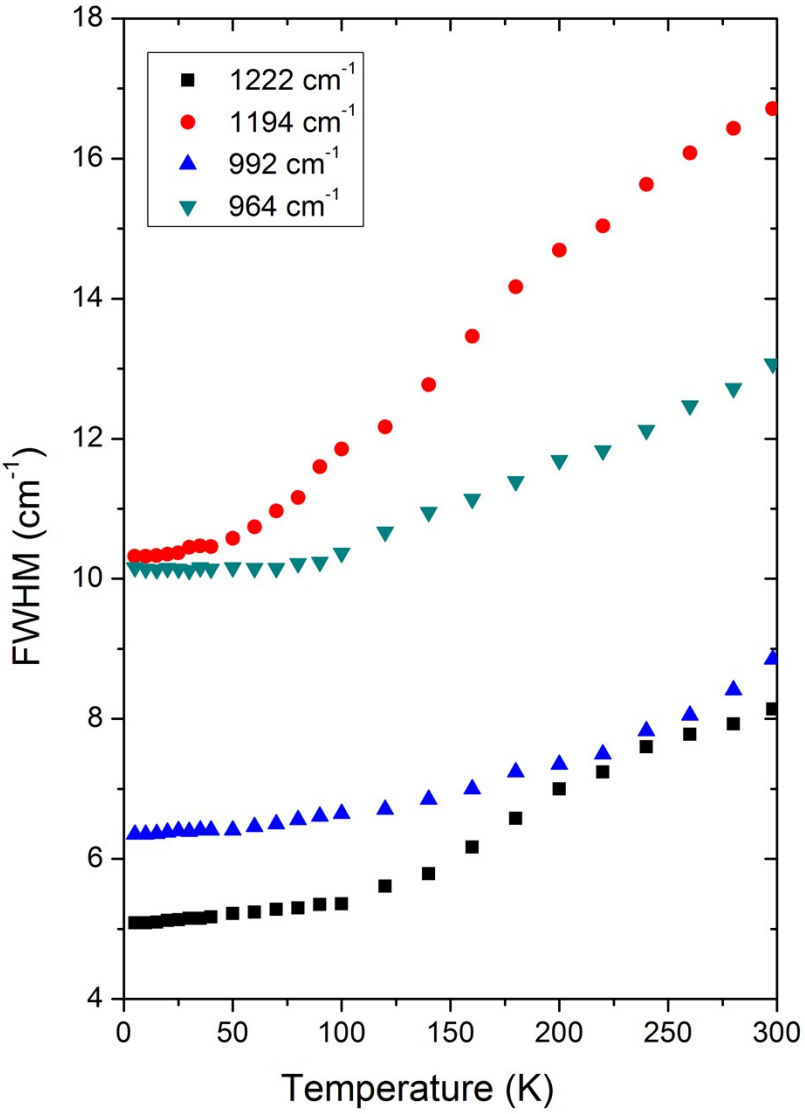


Figure S8. FWHM as a feunction of temperature for a few selected IR modes of **2**.

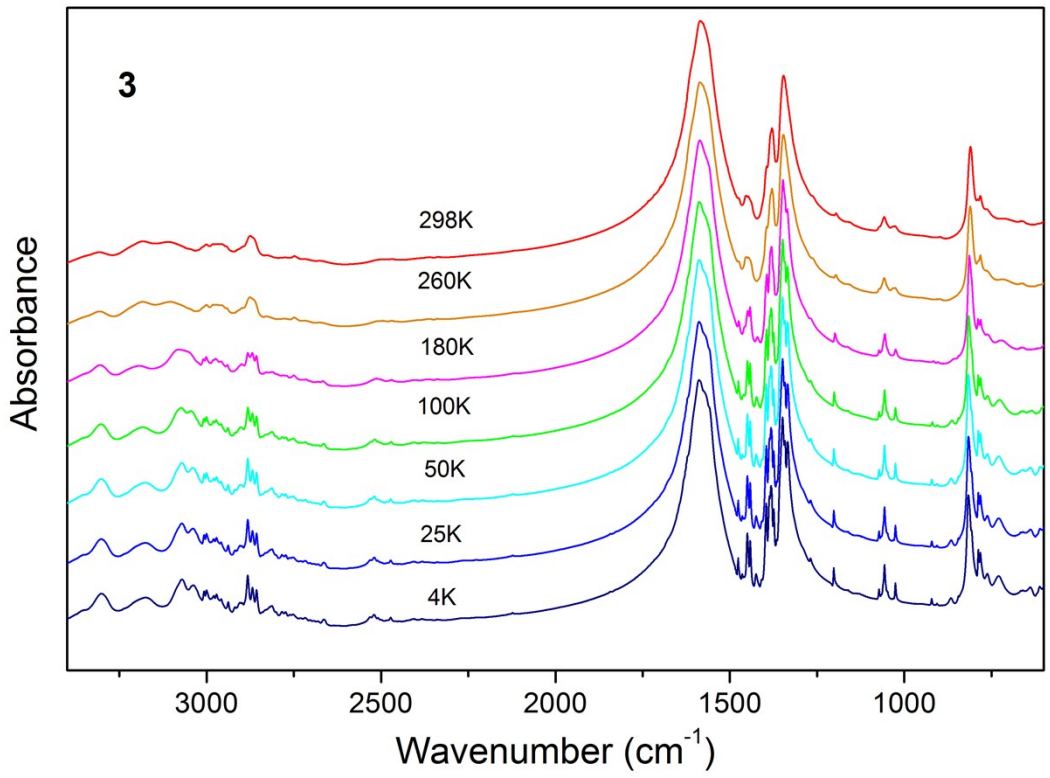


Figure S9. IR spectra of **3** recorded at various temperatures.

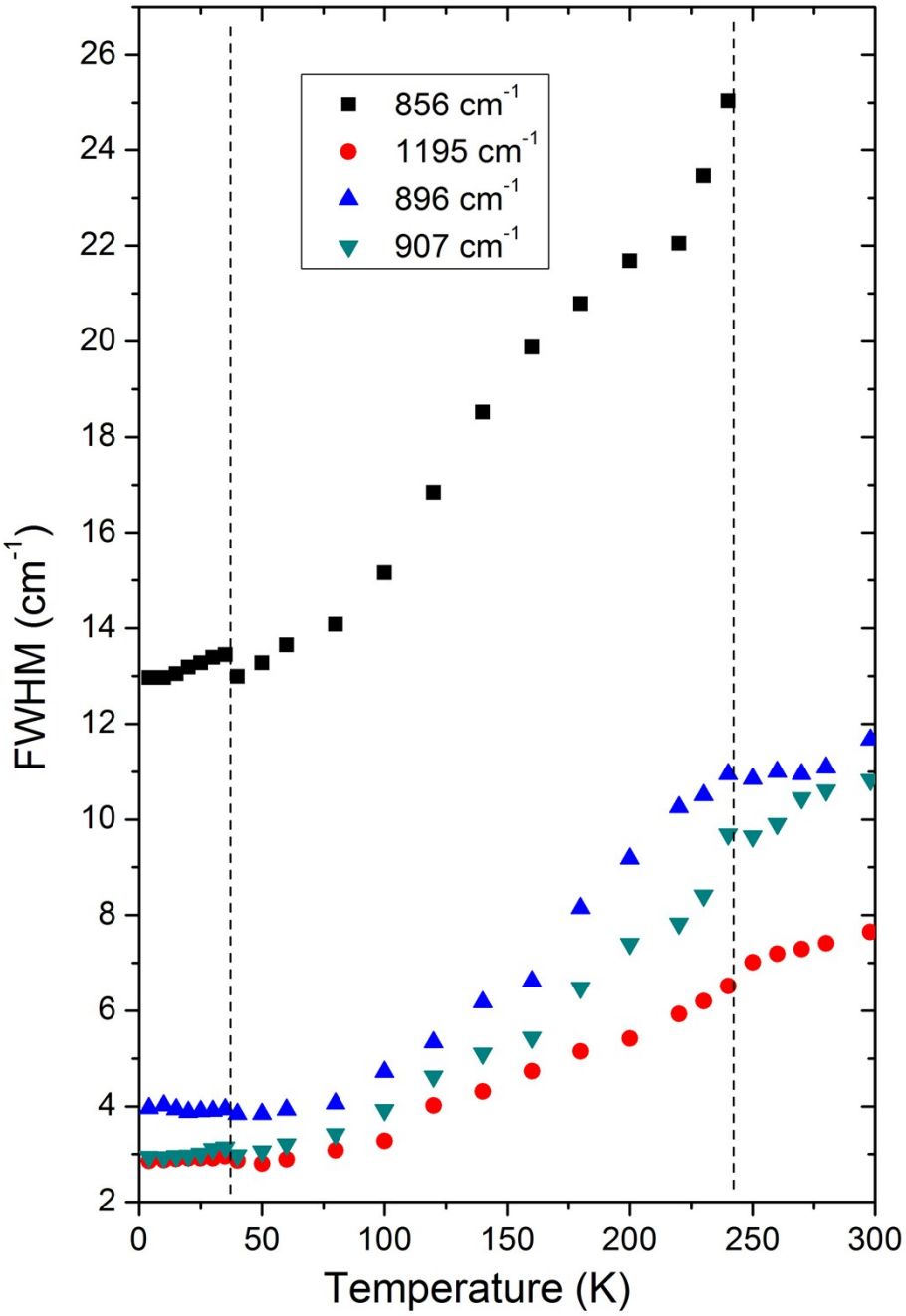


Figure S10. FWHM as a feunction of temperature for a few selected IR modes of **3**. Vertical lines indicate temperatures of the structural and magnetic phase transitions.