

## Single-chain magnet features in 1D [MnR<sub>4</sub>TPP][TCNE] compounds

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**Abstract.** Molecular chains of antiferromagnetically coupled Mn<sup>III</sup>-ion ( $S = 2$ ) and TCNE (tetracyanoethylene) radical moments ( $s = 1/2$ ) show different behaviour depending on group R substituted to TPP (tetraphenylporphyrin) and on the substitution site. The compound with R = F in *Ortho* position is a Single-Chain Magnet (SCM) with blocking temperature  $T_b = 6.6$  K, while that with R = F in *Meta* position shows both blocking ( $T_b = 5.4$  K) and magnetic ordering transition ( $T_c = 10$  K). For bulky groups R = OC<sub>n</sub>H<sub>2n+1</sub>, the magnetically ordered phase is observed ( $T_c \approx 22$  K), which does not however prevent slow relaxation at  $T < 8$  K. Magnetic hysteresis with coercive field  $H_c$  of 2 T at 2.3 K is like that of SCM. The frequency dependent AC susceptibility in the superimposed DC field reveals common features of all systems. The energy of intrachain ferromagnetic coupling between effective spin units  $3/2$ , relevant at low temperatures, is determined for all compounds and the interchain dipolar coupling is estimated. It is concluded that slow relaxation is inherent for all quasi one-dimensional compounds and for the magnetically ordered ones shows up in the high enough magnetic field.

### 1. Introduction

Discovery of slow relaxation and magnetic bistability in anisotropic high spin molecules [1] entered upon the research on molecular nanomagnets. As an analogue to single-molecule magnets (SMM), 1D single-chain magnets (SCM) [2] also show the unique feature of slow magnetic relaxation and magnetic hysteresis without long range order. Slow relaxation of magnetization occurs when the energy barrier  $E_a$  in the Arrhenius law  $\tau = \tau_0 \exp(E_a / k_B T)$  for the thermally activated process is large. The temperature at which relaxation is so slow that no magnetization change can be observed in the laboratory scale, is called the blocking temperature  $T_b$  and reads  $T_b = E_a / (k_B \ln(\tau_m/\tau))$ , where  $\tau_m$  is a characteristic time of the method. The search for SCMs was motivated with the increase of the blocking temperature, in view of potential application of such materials as molecular memory units.

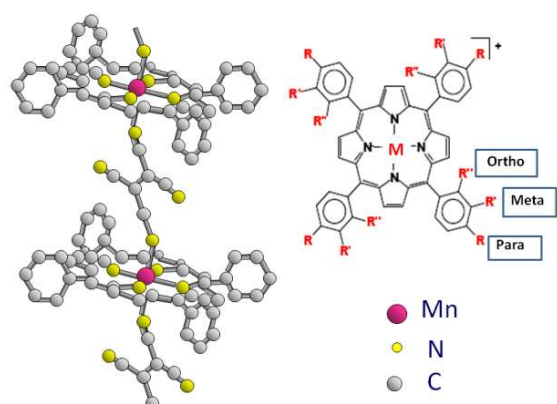
Relaxation of molecular nanomagnets may be compared to that of conventional single-domain particles, which are superparamagnetic at high temperatures, while below  $T_b$  show hysteresis and remanence. The activation energy  $E_a$  for single-domain particles is proportional to the anisotropy of

the material and the volume of the particle. For SMMs  $E_a$  is the well known product  $-DS^2$ , where  $D$  is the easy-axis anisotropy, and  $S$  is the total spin of the molecular cluster. For SCMs, apart from spin and anisotropy, the activation energy is basically proportional to the intrachain exchange integral  $J$ , as it hampers the spin reversal in the ferromagnetically coupled spin array [1,2,3]. The interchain interactions should be negligible to prevent the transition to 3D magnetic ordering. It was also found [4] that the preexponential factor  $\tau_0$  representing the flipping rate of an isolated spin, scales with the size  $L$  of the system, which is a new important property.

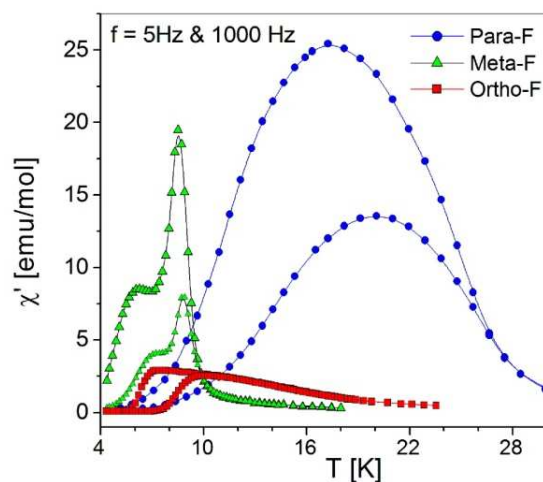
The subject of the paper are the compounds from the family of 1-dimensional charge-transfer chains based on Mn-porphyrin. The  $[\text{Mn}^{\text{III}}(\text{TPP})][\text{TCNE}]\cdot\text{solvent}$  (TPP-tetraphenylporphyrin, TCNE-tetracyanoethylene) was first reported by Miller et al. [5]. Magnetic moments of  $\text{Mn}^{\text{III}}$  cations of spin  $S = 2$  and delocalized moments of  $\text{TCNE}^-$  radicals  $s = 1/2$  are antiparallely coupled by strong kinetic superexchange  $J_{\text{intra}}$ , usually equal to about 100 K [5,6,7]. Magnetic properties of the substance may be tuned using various chemical modifications, e.g. substituting various functional groups  $R$  to the phenyl rings at the periphery of the porphyrin disc. Figure 1 shows the structure of the  $[\text{MnTPP}][\text{TCNE}]$  molecular chain and possible *Para*-, *Meta*- or *Ortho*-position substitution sites. One-dimensional ferrimagnetic behaviour at high temperatures may be evidenced by the fit of magnetic susceptibility  $\chi$  with the Seiden's model [8]. The model deals with an infinite chain of classical spins coupled by the isotropic exchange with alternating quantum spin  $s = 1/2$  according to the Hamiltonian

$$H = -J \sum_{i=1}^{N-1} (S_i + S_{i+1})s_i \quad (1)$$

Seiden's expression for the  $\chi T$  product as a function of  $T$ , allows to determine the intrachain exchange coupling  $J = J_{\text{intra}}$  and the Landé  $g$ -factor. At low temperatures a number of compounds of this type are magnetically ordered what means that besides the interaction along the chain,  $J_{\text{intra}}$ , and the single ion anisotropy  $D$ , the interchain coupling  $J_{\text{inter}}$ , mainly of dipolar origin, is present. A series of  $[\text{MnR}_4\text{TPP}][\text{TCNE}]$  samples using different functional groups  $R$  substituted at *Para*-position was synthesized and investigated [6, 9, 10,11]. Most of them showed transition to the long range order at temperatures about  $\approx 20$  K. The long alkoxy  $\text{OC}_n\text{H}_{2n+1}$  functional groups were substituted to the phenyl rings with the aim to investigate the role of dipolar forces in setting the magnetic order. It appeared that even in the case of 30 Å distant chains the compound could be magnetically ordered and  $T_c$  did not change much with interchain range [11,12]. Magnetic transition detected with AC susceptibility  $\chi_{\text{AC}}$  was very sharp (critical exponent  $\gamma$  close to that of the 3D Ising model), however its strong dependence on the frequency of the oscillating field was astonishing. Applying weak constant field pushed dependence on frequency to lower temperatures, where irreversibility of magnetization was observed [10,12]. The other strange thing was the absence of heat capacity  $C_p$  singularity at  $T_c$  [13] and a large magnetization hysteresis at lowest temperatures. It was also interesting to test the dependence of the intrachain coupling and the Mn(III) anisotropy on the position into which group  $R$  is substituted. To this end a strongly electronegative fluorine ion was chosen. A striking difference in magnetic behaviour, dependent on the substitution site, was observed by us for compounds modified with  $R = \text{F}$ . Figure 2 presents real part of  $\chi_{\text{AC}}$  for three modifications of  $[\text{MnF}_4\text{TPP}][\text{TCNE}]$ . The *Para*-F compound with fluorine in *Para*-position, is a cluster-glass system [10],  $[\text{MnF}_4\text{TPP}][\text{TCNE}]$  with fluorine in *Ortho*-position (hereafter abbreviated as *Ortho*-F compound) is a Single Chain Magnet [7]. *Meta*-F compound with fluorine in *Meta*-position is an intermedium system showing magnetic phase transition and simultaneously SCM-like slow relaxation at low temperature, which can be observed with or without magnetic field.



**Figure 1.** Structure of the [MnTPP][TCNE] molecular chain and possible *Para*-, *Meta*- or *Ortho*-position substitution sites.



**Figure 2.** Real component of AC susceptibility measured with frequency 5 Hz and 1000 Hz for three phases of [MnF<sub>4</sub>TPP][TCNE]: fluorine substituted into *Para*-, *Meta*- and *Ortho*-position.

In light of the data obtained thus far, we are going to discuss magnetic relaxation in the Mn-porphyrin chains and to reveal the Single Chain Magnet features in compounds showing magnetic transition to the ordered phase. All measurements were carried out at the Lake Shore 7225 AC susceptometer / DC magnetometer. We present three compounds of different relaxation and/or magnetic order type, as directly reflected in the dynamic susceptibility result given in Fig. 3. The first system is the Ortho-F Single Chain Magnet (figure 3a); the second one, with fluorine in *Meta*-position (Meta-F) shows both magnetic transition and blocking of relaxation (figure 3b). The third one, [Mn(OC<sub>n</sub>H<sub>2n+1</sub>)<sub>4</sub>TPP][TCNE], represented with compound with OC<sub>12</sub>H<sub>25</sub> group in *Para*-position (hereafter abbreviated as OC<sub>12</sub>H<sub>25</sub>), has a sharp magnetic transition (figure 3c) but reveals slow relaxation of the SCM type at low temperatures in the presence of superimposed DC magnetic field. The common feature of all compounds is the 1D ferrimagnetic character compatible with the Seiden isotropic model [8] in the temperature range ~50 - 300 K. As will be shown, at low temperatures (~20 - 70 K) these systems may be described by the anisotropic Heisenberg model [14], which predicts the ferromagnetic Ising-like behaviour in the limit of zero field. Therefore, at low temperatures (e.g. 20 - 50 K), the chains may be described as composed of effective units of spin  $S = 2 - 1/2 = 3/2$ , which interact ferromagnetically. Exchange integral  $J_{eff}$  of such ferromagnetic (FM) coupling may be determined from the formula

$$\chi = \frac{2Ng^2\mu_B^2}{3J_{eff}} \left( \frac{J_{eff}S}{k_B T} \right)^2 \quad (2)$$

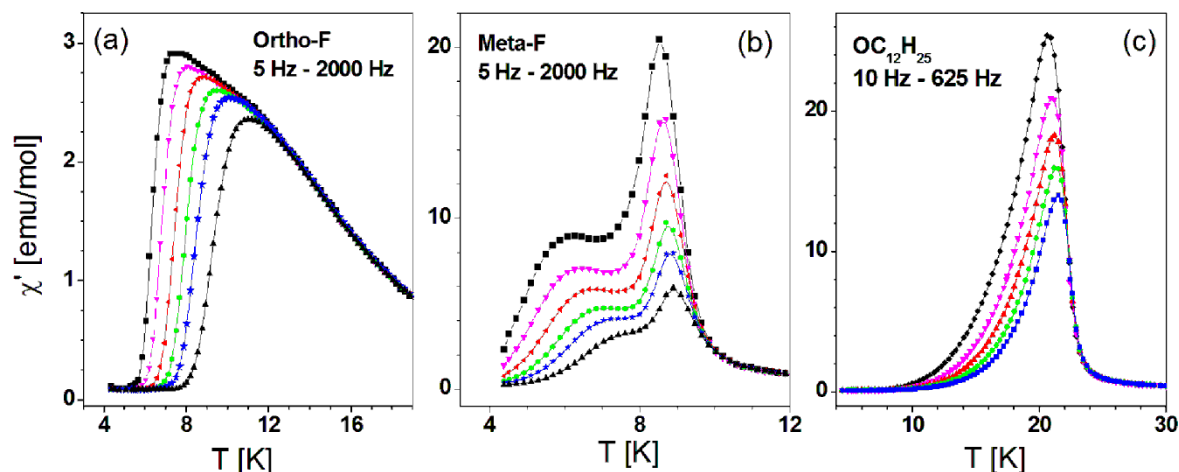
derived in Ref.[14]. Values of  $J_{eff}$  determined from the low-temperature susceptibility will help us to explain the value of activation energy  $E_a$  observed in relaxation measurements.

It is known that parallel magnetic susceptibility for an anisotropic Heisenberg or Ising-like 1D system measured in the limit of zero field is proportional to  $\xi / T$ , where  $\xi$  is the correlation length. This implies the relation

$$\chi T \approx C_{eff} \exp\left(\frac{\Delta_\xi}{k_B T}\right) \quad (3)$$

where  $\Delta_\xi$  is the energy necessary to create a domain wall in the chain and  $C_{eff}$  is the Curie constant of the effective spin unit [15]. In the paper we determine  $\Delta_\xi$  for several [Mn<sup>III</sup>R<sub>4</sub>(TPP)][TCNE]

compounds and use its values for discussion of competition between magnetic order and SCM behaviour (see Table 1.).



**Figure 3.** Comparison of frequency dependent AC susceptibility (real component  $\chi'$ ) for (a) Ortho-F Single Chain Magnet, (b) Meta-F showing magnetic transition and blocking of relaxation and (c) magnetically ordered compound with  $\text{OC}_{12}\text{H}_{25}$  group in *Para*-position. For higher frequency maximum of the  $\chi'$  peak shifts to higher temperature.

## 2. Main characteristics of Ortho-F SCM

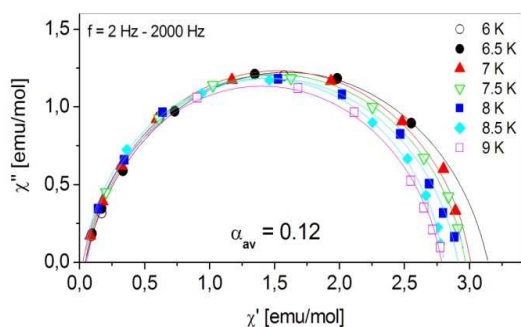
Structural and morphological characterization of Ortho-F compound together with the magnetic properties studied by AC and DC techniques have been already reported in [7]. The intrachain antiferromagnetic exchange integral derived with the Seiden model is  $J_{\text{intra}} = -217$  K. The ferromagnetic intrachain coupling of effective spin units  $3/2$  determined from  $\chi'$  in the temperature region 22 - 68 K using Eq. 2 is  $J_{\text{eff}} = 19.5$  K. The energy  $\Delta_{\xi}$  for domain wall creation determined from Eq. 3 in the range 38 - 5 K is equal to 22.5 K (see Table 1) [16].  $\chi_{\text{AC}}$  of this compound shows strong dependence on frequency in accord with slow time decay of thermoremanence. Slow relaxation evokes the hysteresis loop with the coercive field  $H_c$  equal to 20 kOe at 2 K and decreasing linearly with temperature.

As may be seen from figure 3a and Ref.[7], upon lowering temperature,  $\chi'$  reaches maximum and abruptly falls down, while the imaginary component  $\chi''$  [7] for increased frequencies moves as a whole to higher temperatures. Value of the relative variation of the temperature  $T_p$  of the  $\chi''$  peak per decade of frequency,  $X = (\Delta T_p / T_p) / \Delta(\log_{10} f)$ , is equal to 0.128. This is much bigger than that of spin glasses and points to the blocking phenomenon. Absence of higher harmonics of the  $\chi_{\text{AC}}$  anomaly means that there is no spontaneous magnetic moment in the sample and that no phase transition occurs. The  $\chi''$  vs  $\chi'$  Cole-Cole plots for  $T = 6$  K up to  $T = 9$  K given in figure 4 deviate insignificantly from perfect semicircles and form arcs of size  $(1 - \alpha)\pi$ . Parameter  $\alpha$  represents distribution of relaxation times. In Ortho-F it does not change with temperature and is equal to  $0.120 \pm 0.002$ , which means that in good approximation Ortho-F has a single relaxation time. This result is a fingerprint of the Single Chain Magnet behaviour.

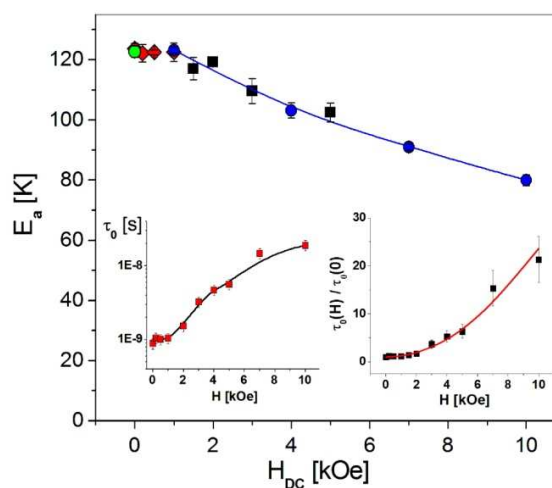
From the frequency shift of the  $\chi''$  maxima one obtains a temperature dependence of the relaxation time  $\tau$  and then, using the fit to the Arrhenius law, the activation energy  $E_a$ . Based on the data of the 6 K÷9.5 K range, one gets  $E_a = (122 \pm 2)$  K, where  $\tau_0 = 1 \cdot 10^{-9}$  s. The field dependence of the activation energy deduced from the  $\chi''(T, f)$  data obtained under static magnetic field is shown in log

scale in figure 5. As seen, for  $H_{DC}$  less than  $\approx 1.5$  kOe,  $E_a$  does not change but for higher field gradually decreases. Simultaneously,  $\tau_0$ , which is the characteristic flipping time for a magnetically isolated spin unit, increases (see figure 5, inset on the left). The ratio of  $\tau_0$  at a given field to that at zero field,  $\tau_0(H)/\tau_0(0)$ , shown in figure 5 (inset on the right) is a quadratic function of  $H$  given:  $\tau_0(H)/\tau_0(0) = 1+(H/H_0)^2$ , with  $H_0 = (2.1 \pm 0.1)$  kOe. This result is consistent with that reported for Mn/Fe and Mn/Ni chains [17].

In the temperature range 6 K–9.5 K the finite-size effects [4,17] are relevant for Ortho-F compound (Figure 7 in Ref.[7]). As follows from the numerical study of the finite chain presented in [18], the highest field (10 kOe) applied by us stays in the low field limit, as  $\tanh(\mu H/k_B T) \leq 0.3$ , where  $\mu$  ( $= 3 \mu_B$ ) is the magnetic moment of one  $[\text{MnF}_4\text{TPP}][\text{TCNE}]$  unit. Therefore, the single-time approximation should be valid. Despite the increase of  $\tau_0$  in the presence of the superimposed magnetic field, the decrease of  $E_a$  results in shortening of the relaxation time, e.g. at  $T = 5$  K from  $\tau = 49$  s to  $\tau = 0.17$ , and at  $T = 8$  K from  $\tau = 0.005$  s down to  $\tau = 0.0004$  s for  $H = 0$  and  $H = 10$  kOe respectively. As reported in [7], the  $E_a$  vs  $H$  dependence determined experimentally for Ortho-F, could be explained as associated with solitary waves, i.e. with creation and propagation of domain walls in this one-dimensional anisotropic Heisenberg system. It is known that the value of activation energy  $E_a$  at zero field is a function of the exchange constant  $J$  between the spin units and of the single-ion anisotropy  $D$ . According to [3], for the infinite chain ( $L \gg \xi$ )  $E_a = (4J + |D|)S^2$ , whereas for  $L \ll \xi$  one has  $E_a = (2J + |D|)S^2$ , because the energy cost to flip the spin in the domain is approximately twice as much as to flip the spin at the end of the chain. In order to estimate these two energy barrier limits we take  $J = J_{eff} = 19.5$  K, obtained above, and the easy axis anisotropy parameter  $D = -3.3$  K determined by means of HFEPR spectroscopy [19] for MnTPPCL complex. We believe that this  $D$  value is adequate here because, as concluded from *ab initio* studies for manganese porphyrin complexes [20], TCNE ligands hardly affect magnetic anisotropy of the manganese porphyrin complex, and they are important only to the ferrimagnetic alignment of the spins. Using the values above, we get  $E_a = 183$  K and 95 K for two cases respectively. In view of this, the experimentally determined  $E_a = (122 \pm 2)$  K attests to  $L \ll \xi$  case relevant for our SCM.



**Figure 4.** Cole-Cole diagrams for Ortho-F. The solid curves represent the least-squares fit to a generalized Debye model with  $\alpha_{av} = 0.12$ .

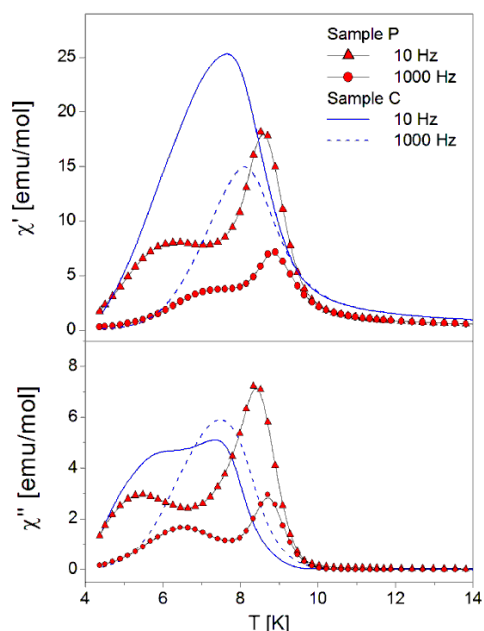


**Figure 5.** Effect of applied magnetic field on activation energy for Ortho-F; the solid line is a guide. Left inset: field dependence of time  $\tau_0$ ; solid line is a guide. Right inset: field dependence of  $\tau_0(H)/\tau_0(0)$ , solid line is the fit to a quadratic dependence (see text).

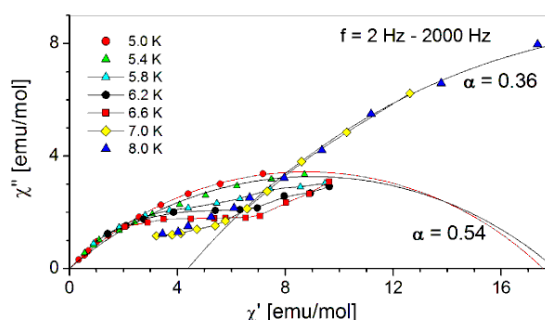
### 3. Blocking and magnetic order in Meta-F compound

Synthesis and crystallographic data of  $[\text{MnF}_4\text{TPP}][\text{TCNE}]$  with fluorine in *Meta*-position have been described in [21]. Meta-F compound crystallizes in the monoclinic system, while that of the Ortho-F compound is the triclinic one [22,7]. Magnetic measurements were performed for two types of the Meta-F sample: the ground crystalline sample (C) and the powder one (P). Both C and P samples show the phase transition to a 3D ordered magnetic state, that is easily suppressed by DC magnetic field. The intrachain antiferromagnetic exchange coupling between  $\text{Mn}^{\text{III}}$  ion and TCNE radical, determined from the fit of the Seiden's expression to the experimental  $\chi T$  data for  $50 \leq T \leq 300$  K, is  $J_{\text{intra}} = -100$  K for both samples. The low temperature fit of  $\chi'$  according to Eq. 3 gives ferromagnetic coupling of spin 3/2 effective units  $J_{\text{eff}} = 28$  K for sample C and only  $J_{\text{eff}} = 21$  K for sample P.

AC susceptibility of the two samples is different. Figure 6 presents data measured with frequency 10 Hz and 1000 Hz for sample C and sample P. As may be seen, the temperature dependence of  $\chi'$  and  $\chi''$  for powder sample is not typical and consists of two anomalies, one at  $T_c = 10$  K ( $\chi''$  onset), reflecting transition to the ordered state, and the other related to blocking of relaxation, with  $T_b = 5.4$  K ( $\chi''$  maximum at  $f = 10$  Hz). The different character of two anomalies was checked by the measurement of susceptibility nonlinear components: the second and third harmonic components accompanied only the peak at  $T_c$ , therefore blocking is not a phase transition in the thermodynamic sense. Parameter  $X$  of frequency shift for phase transition is 0.015, while the one for blocking is much larger and equals 0.058, similarly to that of cluster [23] or fractal spin-glasses [24]. We would like to mention that the complex behaviour of the Meta-F specimen, relying on parallel SCM- and ordered magnet features, is like that recently observed for  $[\text{Mn}(3,5\text{-Cl}_2\text{saltmen})\text{Ni}(\text{pao})_2\text{-}(\text{phen})]\text{PF}_6$  [25] and cobalt-radical coordination magnet [26]. On the other hand, unlike the sample P, the C sample shows one anomaly (Figure 6), whose double nature comes forward only in the applied DC field [21]. Below, we present results obtained for Meta-F powder sample. Samples of all other compounds discussed in this paper were also powders.



**Figure 6.** AC susceptibility measured with frequency 10 Hz and 1000 Hz for sample P and sample C of the Meta-F compound.

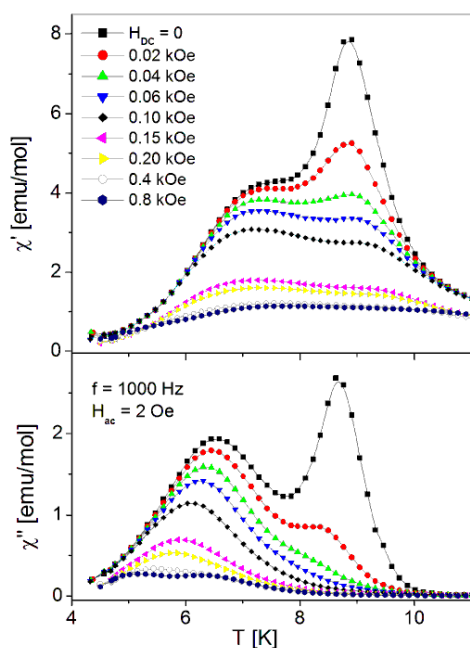


**Figure 7.** Cole-Cole diagram for Meta-F sample P with two distributions of relaxation times:  $\alpha = 0.54$  for blocking,  $\alpha = 0.36$  at phase transition.

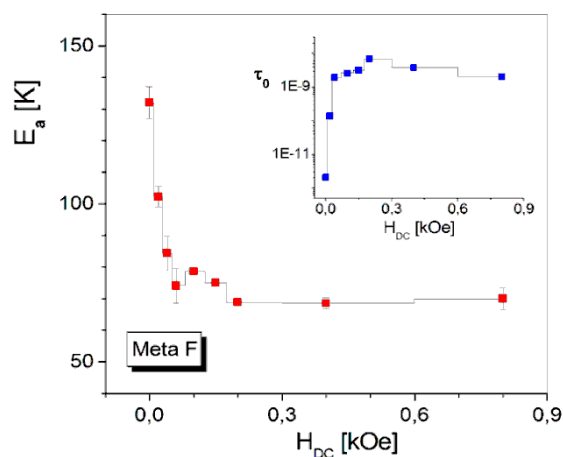


The Cole-Cole diagram obtained from measurements with  $f = 2 \text{ Hz} - 2000 \text{ Hz}$  in the temperature range  $5 \text{ K} - 8 \text{ K}$  is presented in Fig. 7. The two processes are visible with distribution of relaxation times  $\alpha = 0.54$  for blocking and  $\alpha = 0.36$  for phase transition. The flat segments of curves for  $5.8 \text{ K}$ ,  $6.2 \text{ K}$  and  $6.6 \text{ K}$ , where  $\chi''$  does not change, are certainly responsible for simultaneous reversal of all the spins in short segments of the chains. Such relaxation mechanism was observed and theoretically explained for CoPhOMe SCM, highly doped with diamagnetic impurities [4]. Therefore, the magnetically correlated segments of chains in our powder Meta-F sample are short.

Figure 8 shows the influence of the external field on the AC susceptibility. It can be seen that at  $H = 0.8 \text{ kOe}$  the anomaly related to phase transition is completely suppressed, while that coming from blocking is less field sensitive. As the magnitude of the external magnetic field is increased, the  $\chi''$  maximum shifts to lower temperatures, i.e.  $T_b$  decreases. Activation energy determined from the Arrhenius plot is  $E_a = 139(3) \text{ K}$  where  $\tau_0 = 5 \cdot 10^{-13} \text{ s}$ . Despite the similar value of  $E_a$  at zero field to that of Ortho-F, the dependence of activation energy on applied field looks quite different (Figure 9). Already at  $H \approx 200 \text{ Oe}$   $E_a$  drops down to the half value and then stays constant at the value  $E_a = 70 \text{ K}$ , while the preexponential factor increases up to  $\tau_0 \approx 5 \cdot 10^{-9} \text{ s}$  and then does not change. This clear effect undoubtedly reflects crossover between  $L \gg \xi$  and  $L \ll \xi$  case. Magnetic field, which increases the correlation length in chains of parallel (to field) oriented spins, at the same time will reorient the other spins in adjacent chains and will divide magnetic domains into shorter segments. Hence, the interchain dipolar coupling gets attenuated and phase transition disappears.



**Figure 8.** DC applied field effect on AC susceptibility of powder sample of the Meta-F compound.



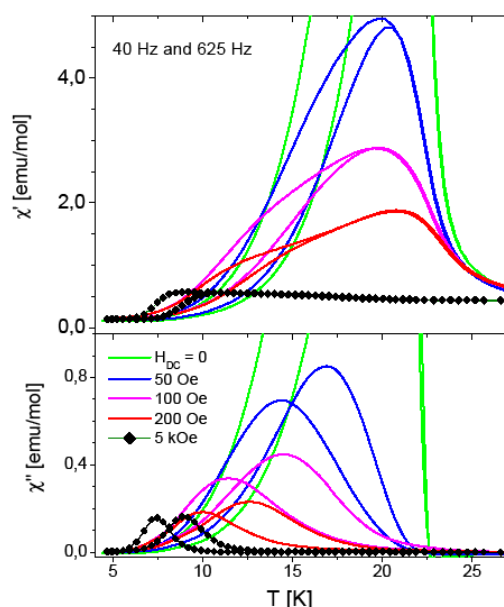
**Figure 9.** Effect of applied magnetic field on activation energy for Meta-F. Inset: field dependence of time  $\tau_0$ . Solid lines are guides.

#### 4. Magnetic phase transition and slow relaxation in the $\text{OC}_n\text{H}_{n+1}$ -substituted compound

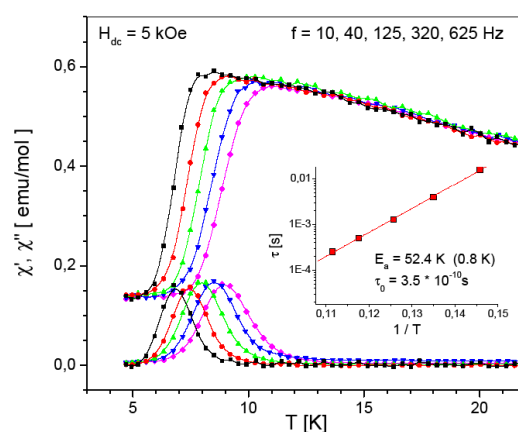
The present paragraph will deal with the properties of  $[\text{Mn}(\text{OC}_n\text{H}_{2n+1})_4\text{TPP}][\text{TCNE}]$  ( $n = 10, 12, 14$ ), which are somehow unique due to the very large (up to  $30 \text{ \AA}$ ) interchain spacing [9,11]. Despite the structural isolation of the chains the compounds show transition to the magnetically ordered state with  $T_c = 21.7 \text{ K}$ ,  $22.0 \text{ K}$  and  $20.5 \text{ K}$  respectively [11,12]. Interestingly, no heat capacity anomaly due to

the onset of the magnetic order was detected [13], like it also occurred for other members of the family of the Mn-porphyrin chains [27]. It was therefore concluded that the most part of the magnetic entropy is retained above the phase transition temperature in the form of the dominant short-range order. At low temperature, the divergence of the in-chain correlation length promotes correlated spin blocks which interact from chain to chain through dipolar forces. As shown in [28], the rate of increase of the correlation length is the essential parameter in order to reach the observed transition temperatures. For the  $T_c$  values above an exponential divergence of the 1D correlation length is required, which implies the existence of single-ion anisotropy, whereas the power-law divergence for 1D Heisenberg coupled spins yields transition temperatures one order of magnitude smaller than observed.

Some results obtained for the samples with  $n = 10$  and  $14$  have been already described in [12]. Here we report investigations for  $n = 12$ , as a representative for alcoxy-substituted modifications, because it shows the highest AC susceptibility at  $T_c$ , equal to  $22 \text{ emu/mol}$  for  $f = 40 \text{ Hz}$  (see Fig. 3c), compared to  $8 \text{ emu/mol}$  and  $9 \text{ emu/mol}$  for  $n = 10$  and  $14$  [12]. The one-dimensional character of these ordered molecular magnets is markedly visible in measurements performed in magnetic field. Figure 10 shows  $\chi'$  and  $\chi''$  of  $\text{OC}_{12}\text{H}_{25}$  measured at two frequencies of the oscillating field for several values of the external static field. When applied field increases, the AC peak reveals its double nature: the anomaly at  $T_c$  gradually disappears and the frequency dependent part is shifted to lower temperatures. As given in figure 11, at  $H = 5 \text{ kOe}$  AC susceptibility is of the SCM-type, yet with the broad distribution of relaxation times ( $\alpha_{av} = 0.22$ , not shown). Activation energy for this process is  $E_a = 52 \text{ K}$ , with  $\tau_0 = 3.5 \cdot 10^{-10} \text{ s}$ . We would like to notice the different in-field behaviour of  $\text{OC}_{12}\text{H}_{25}$  (Figure 10) as compared to that of Meta-F (Figure 8). For the latter, the low temperature  $\chi'$  and  $\chi''$  components responsible for blocking were visible already in zero field and when the field increased, the  $\chi'$  and  $\chi''$  components were getting weaker. For  $\text{OC}_{12}\text{H}_{25}$  in turn, the  $\chi'$  and  $\chi''$  components responsible for blocking developed with the field, which means that applied field attenuates the interchain coupling and brings in the magnetic isolation of the chains.



**Figure 10.** Influence of applied magnetic field up to  $5 \text{ kOe}$  on  $\chi'$  and  $\chi''$  of  $\text{OC}_{12}\text{H}_{25}$  measured for  $f = 40 \text{ Hz}$  and  $625 \text{ Hz}$ .

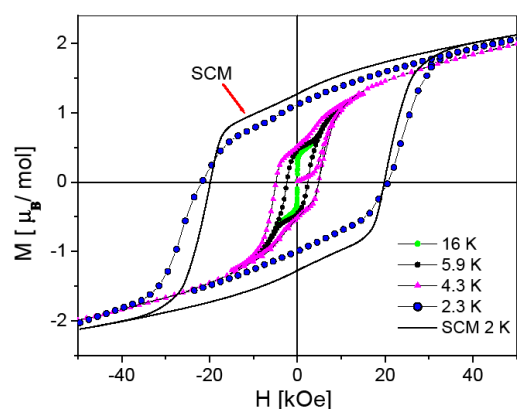


**Figure 11.** AC susceptibility for  $\text{OC}_{12}\text{H}_{25}$  at  $H_{DC} = 5 \text{ kOe}$ , measured for  $f = 10, 40, 125, 320$  and  $625 \text{ Hz}$ . Inset: Arrhenius fit.

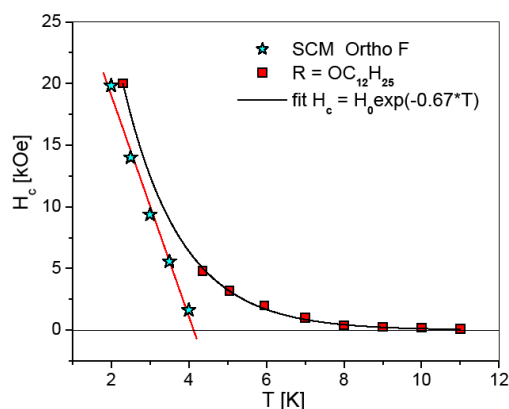


The other striking feature of  $\text{OC}_{12}\text{H}_{25}$  is a large value of the coercivity field  $H_c$  at  $T = 2.3$  K and its quick decrease with temperature. Figure 12 shows hysteresis curves for  $\text{OC}_{12}\text{H}_{25}$  measured with the magnetic sweep rate  $\approx 60$  s per point (1 kOe/min) at several temperatures. The curve for Ortho-F SCM recorded at  $T = 2$  K with the rate  $\approx 100$  s per point (0.6 kOe/min) is shown for comparison [7]. Hysteresis of  $\text{OC}_{12}\text{H}_{25}$  at  $T = 2.3$  K is very similar. The drop in  $H_c$  with temperature is however not the same (see Figure 13). For Ortho-F a fast linear drop is observed, which, at  $T$  approaching zero, leads to  $H_c(T=0) \approx 40$  kOe. The exponential  $H_c(T) = H_0 \exp(-0.67 \cdot T)$  dependence for  $\text{OC}_{12}\text{H}_{25}$  shown in figure 13 suggests much higher value of  $H_0$ , equal to  $\sim 80$  kOe. Upon heating the sample,  $H_c$  markedly decreases and at  $T = 16$  K is equal to 20 Oe.

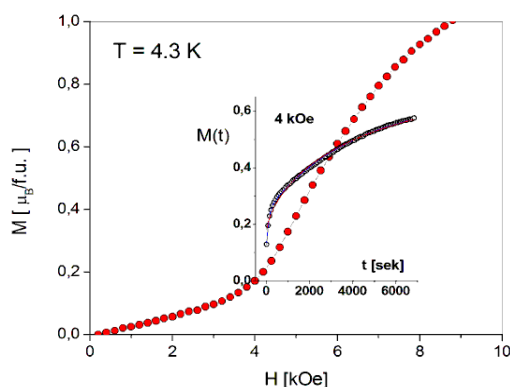
One should notice, that due to metamagnetism and spin flop transition displayed by most of compounds from the family of Mn-porphyrins, the hysteresis loop opens only for the field higher than the critical one  $H_{sf}$ . The value of  $H_{sf}$  at 2.4 K, 3.5 K and 4.3 K is equal to 28 kOe, 14.5 kOe and 5 kOe respectively. Figure 14 shows  $M(H)$  dependence during the spin flop transition at 4.3 K together with the time evolution of magnetization  $M(t)$  measured at  $H = 4$  kOe. The time dependence of magnetization could be fitted with the stretched exponential function  $M(t) = A - M \cdot \exp[-(t/\tau_{av})^\beta]$ , with  $\beta = 0.74$  and mean relaxation time  $\tau_{av} = 4 \cdot 10^3$  s. It was also checked that  $\tau_{av}$  decreased under illumination with light [29].



**Figure 12.** Hysteresis curves at several temperatures for  $\text{OC}_{12}\text{H}_{25}$ . The curve for Ortho-F SCM is shown for comparison. See text for magnetic field sweep rate.



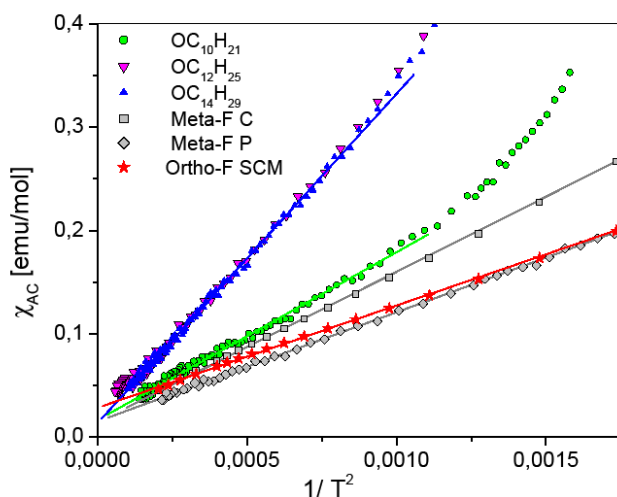
**Figure 13.** Temperature dependence of the coercivity field for Ortho-F (linear fit) and for  $\text{OC}_{12}\text{H}_{25}$  (exponential fit).



**Figure 14.**  $M(H)$  dependence at the spin flop transition at 4.3 K. Inset: Time evolution of magnetization  $M(t)$  measured at  $H = 4$  kOe fitted to the stretched exponential function.

## 5. Discussion

All materials presented above are well approximated by quasi one-dimensional ferrimagnetic Heisenberg chains with small anisotropy. In this group, depending on type of the substituent R and on the substitution site, one finds Single Chain Magnet, magnetic cluster glass, as well as magnetically ordered phases, which show slow relaxation at low temperatures. In case of magnetically ordered compounds, long range correlations along the chains are present above  $T_c$  and phase transition is triggered due to the weak interchain dipolar forces acting between the correlated chain segments. This is the reason why such transitions were not detected by calorimetry despite the big singularity in magnetic susceptibility coming from formation of magnetic domains. As shown above, transition at  $T_c$  undergoes attenuation by the applied DC field (Figure 8 and Figure 10). Two types of magnetically ordered phases were mentioned: the one showing the blocking anomaly below  $T_c$  without applied field (Meta-F P) and the other, in which slow relaxation and blocking could be revealed only in non-zero DC field ( $OC_nH_{2n+1}$ ). The first case (Meta-F P) concerns the sample consisting in some part of magnetically isolated chains, as number of defects prevents formation of long correlated segments, which are necessary for creation the relatively strong interchain dipolar forces. In the second case, the respectively strong DC field is needed to bring in the magnetic isolation of the chains.



**Figure 15.** The  $\chi'$  vs  $T^{-2}$  plots for compounds under study; the tilt angle of the straight line fits is proportional to the effective ferromagnetic intrachain coupling  $J_{eff}$  between the net spin units  $3/2$ .

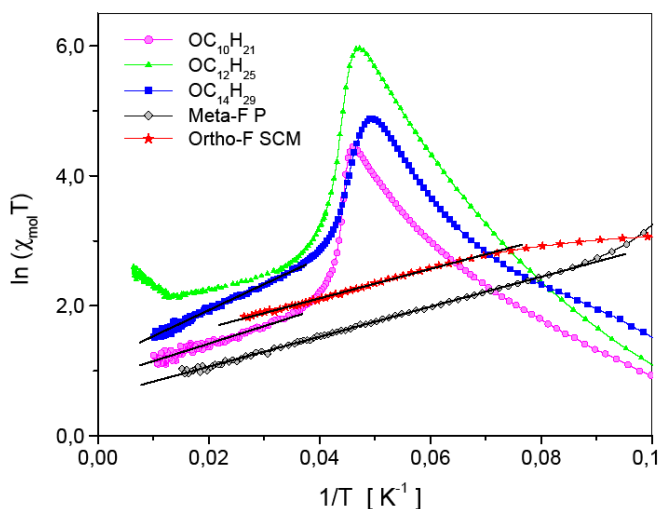
In order to discuss magnetic relaxation in the family of  $[MnR_4TPP][TCNE]$  compounds and the competition between the tendency to ordering vs the tendency to blocking we have determined the coupling constants and other crucial values. Figure 15 shows the  $\chi'$  vs  $T^{-2}$  plots from which the intrachain effective FM coupling  $J_{eff}$  between effective spin units  $3/2$  was obtained according to Eq.2. The results and temperature ranges in which linear fits were carried out are given in Table 1. The dipolar interaction  $J_{dip}$  can be estimated from the ordering temperatures using the relationship developed for anisotropic exchange interaction [30]

$$k_B T_c = 4S(S + 1)\sqrt{J_{eff}J_{dip}} \quad (4)$$

where  $S = 3/2$  is the net spin. The values obtained are dozens of mK (see Table 1.). For the assessment of  $J_{dip}$  in Ortho-F Single Chain Magnet, instead of  $T_c$  in Eq.4, the blocking temperature  $T_b = 6.6$  K, determined from the maximum of the  $\chi''$  maximum for  $f = 10$  Hz, was used.

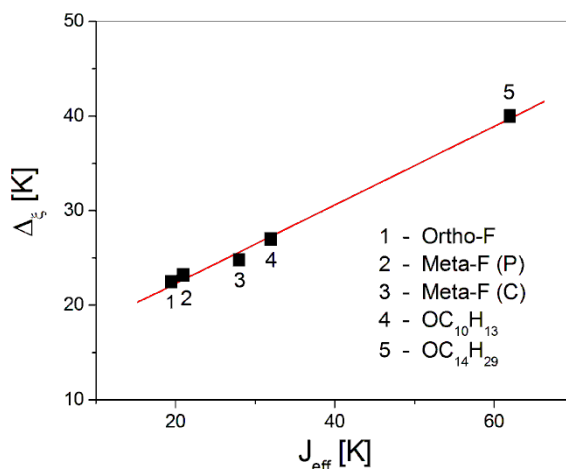
The one-dimensional character of the compounds under study is illustrated in Fig. 16 with the  $\ln(\chi_{mol}T)$  vs  $1/T$  dependences. According to Eq.3, for anisotropic Heisenberg or Ising-like 1D systems in the low temperature region this dependence should be linear with the tilt angle equal to the energy  $\Delta_\xi$  necessary to create a domain wall in the chain [15]. Figure 16 shows such a behaviour down to the lowest temperatures for Ortho-F SCM and for Meta-F, while for the other compounds of the family the linear  $\ln(\chi'T)$  vs  $T^{-1}$  dependence is observed at temperatures much higher than  $T_c$ . The only

exception is the OC<sub>12</sub>H<sub>25</sub> system, for which the  $\ln(\chi_{\text{mol}}T)$  vs  $1/T$  dependence was not linear in a suitably long temperature range. This exception is in accord with the overall appearance of this magnetically ordered compound. On the other hand, the presented above experimental evidence of the in-field slow relaxation in OC<sub>12</sub>H<sub>25</sub> point to the common mechanism of magnetic coupling and relaxation in [Mn<sup>III</sup>R<sub>4</sub>(TPP)][TCNE] molecular compounds.



**Figure 16.** The  $\ln(\chi'T)$  vs  $T^{-1}$  dependences for Ortho-F SCM and for other compounds of the family; the energy  $\Delta_\xi$  needed to create a domain wall in the chain is determined from the Eq.3.

In order to find the characteristic, common for SCM and magnetically ordered compounds, we plot  $\Delta_\xi$  values as a function of intrachain effective FM coupling  $J_{\text{eff}}$  as shown in figure 17. The  $\Delta_\xi$  vs  $J_{\text{eff}}$  dependence obtained is linear and reads  $\Delta_\xi = 14 \text{ K} + 0.416 * J_{\text{eff}}$ . The lowest  $\Delta_\xi$  and  $J_{\text{eff}}$  are observed for Ortho-F Single Chain Magnet. While the intersection point (14 K) may represent the  $|D|S^2$  term, the proportionality factor (0.416) is much less than  $2S^2$  value expected for domain creation in a ferromagnetic Ising chain. Such small value could be expected for quasi one-dimensional ferrimagnetic Heisenberg systems of small anisotropy which possess wide domain walls.



**Figure 17.** Linear dependence of  $\Delta_\xi$  vs  $J_{\text{eff}}$  obtained for the compounds of the [MnR<sub>4</sub>TPP][TCNE] family.

**Table 1.** Characteristic temperatures, magnetic interactions and activation energies for compounds under study:  $T_c$  - ordering temperature;  $T_b$  - blocking temperature,  $T_f$  - freezing temperature,  $J_{intra}$  - intrachain AFM coupling between  $Mn^{III}$  ion and TCNE radical,  $J_{eff}$  - low temperature intrachain effective FM coupling between effective spin units 3/2 (Eq.2),  $J_{dip}$  - interchain dipolar coupling (Eq.4),  $E_a$  - activation energy of Arrhenius relaxation,  $\tau_0$  - prefactor in the Arrhenius law,  $\Delta_\xi$  - the energy of creation a domain wall in the chain (Eq.3).

Compound	Type	$J_{intra}$	$J_{eff}$	$J_{dip}$	$E_a, \tau_0$	$\Delta_\xi$ [K]
Ortho-F	$T_b=6.6$ K	217 K [7]	19.5 K fit 14-60 K	$\leq 0.01$ K	123 K $1 \cdot 10^{-9}$ s	22.5 K
Meta-F (P)	$T_c=10$ K $T_b=5.4$ K	100 K	21 K fit 22-68 K	$\sim -0.02$ K	132 K $2 \cdot 10^{-12}$ s	23.2 K
Meta-F (C)	$T_c=10$ K	100 K [21]	28 K fit 22-68 K	$\sim -0.02$ K		24.8 K
Para-F	$T_f=26$ K	236 K [6]			336 K $1.8 \cdot 10^{-12}$ s	
OC <sub>10</sub> H <sub>21</sub>	$T_c=22.5$ K	117 K [6]	32 K fit 30-100 K	$\sim -0.07$ K		27 K
OC <sub>12</sub> H <sub>25</sub>	$T_c=22$ K	178 K [6]	63 K fit 36-106 K	$\sim -0.04$ K	52 K <sup>a</sup> $3.5 \cdot 10^{-10}$ s	
OC <sub>14</sub> H <sub>29</sub>	$T_c=21.2$ K	148 K [6]	62 K fit 34-100 K	$\sim -0.03$ K		40 K

## 6. Conclusion

On the basis of the presented results we conclude that slow relaxation is an inherent feature for all compounds of the  $[MnR_4TPP][TCNE]$  family. For the magnetically ordered compounds it is apparent in the AC susceptibility as a frequency dependent bump at temperatures below  $T_c$  or may show up in the high enough magnetic field. The superimposed DC magnetic field destroys the antiferromagnetic coupling between the chains and brings in magnetic isolation of the chains. The preexponential factor  $\tau_0$  in the Arrhenius law increases in the applied field, however, as the energy barrier  $E_a$  decreases, the in-field relaxation accelerates. As observed for Meta-F P and Meta-F C samples, the quality of the sample relying on the undefected structure is crucial for setting magnetic order. For the compounds of the  $[MnR_4TPP][TCNE]$  family, including Ortho-F SCM, the linear dependence of the energy  $\Delta_\xi$  on the intrachain effective ferromagnetic coupling  $J_{eff}$  is observed. A strong dependence of the AC susceptibility on frequency, observed in a number of ordered quasi one-dimensional compounds, previously interpreted in the frames of spin (spin-cluster) glass, originates from SCM features. However, the true Single Chain Magnet behaviour is a unique property which rules out any magnetic transition to the collective phase.

### Acknowledgements

The authors acknowledge receiving the samples under investigation from Dr. K. Falk and Dr. K. Griesar (Institute of Physical Chemistry, Darmstadt University of Technology) as well as from Dr. S. Najak (working temporarily in Darmstadt TU, on leave from Bhabha Atomic Research Centre, Trombay, India). M.B. acknowledges partial support from the Polish Ministry of Science and Higher Education within the Research Project No. 0087/B/H03/2008/34. Thanks are also due to Dr. A. Pacyna (INP, Kraków) for his kind assistance in the lab.

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