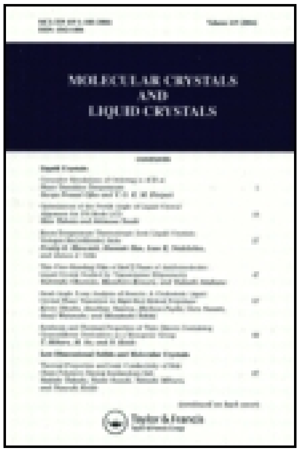

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Magnetism in Nitronyl Nitroxide Radicals and their Ion Radical Salts

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MAGNETISM IN NITRONYL NITROXIDE RADICALS AND THEIR ION RADICAL SALTS

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Abstract We report the results of magnetization, susceptibility and muon spin rotation/relaxation (μSR) measurements and crystal structure analyses of the organic neutral and ion radicals based on nitronyl nitroxide. Magneto-structural correlations in naphthyl and quinolyl nitronyl nitroxides, some of which exhibit ferromagnetic intermolecular interactions, are discussed in terms of intermolecular and interatomic contacts. The temperature dependence of the paramagnetic susuceptibility of sodium 2-sulfonatofuryl nitronyl nitroxide and 2-carboxyfuryl nitronyl nitroxide are interpreted in terms of a combination of ferromagnetic and antiferromagnetic interactions. Of the organic radicals exhibiting ferromagnetic intermolecular interactions, magnetic transitions in the zero-field muon spin relaxation are observed in 1-naphthyl and *p*-cyanophenyl nitronyl nitroxide below 0.10 and 0.17 K, respectively.

INTRODUCTION

Organic molecular magnetism has developed rapidly[1] because a rich variety of neutral and ionic organic radicals and their complexes have been found to be ferromagnets since the first discovery of a purely organic ferromagnet.[2] Of these radical solids, α-nitronyl nitroxide (2-substituted 4,4,5,5-tetramethyl-2-imidazoline-1-oxyl 3-oxide) is an interesting class of molecular crystals because not only numerous derivatives of it are easily synthesized but also it has sufficient chemical stability and crystallinity.[1,3] These features bring about opportunities to investigate magneto-structural correlations and hence the mechanism of ferromagnetic (FM) intermolecular interactions in the organic radical crystals. Muon spin rotation/relaxation (μSR) is a technique which has been successfully used to observe the magnetic transition in a number of organic radical crystals.[4-8] We have therefore been carrying out magnetization measurements, X-ray diffraction structural analyses and μSR studies of nitronyl nitroxide radicals.

In this paper, we first report magneto-structural correlation in two isomeric series of nitronyl nitroxide molecular magnets; 1- and 2-naphthyl nitronyl nitroxide and 2-, 3- and 4-quinolyl nitronyl nitroxide. Next, the magnetic properties of newly synthesized nitronyl nitroxide radicals having carboxyaryl, sulfonatoaryl or imidazole group are described. Finally, magnetic transitions observed in the zero-field μSR experiments are presented.

EXPERIMENTAL

All the organic radicals studied here were prepared according to the reported method[3] and recrystallized from benzene, chloroform or methanol solution.

Magnetization isotherms up to 7 T and magnetic susceptibility χ at 0.1 ~ 0.3 T of a polycrystalline sample were measured by using a Quantum Design MPMS7 SQUID magnetometer. Paramagnetic susceptibility χ_p was obtained by subtracting the diamagnetic contribution, which was estimated from the χ vs. $1/T$ plot at high temperatures.

Low-temperature μSR measurements for polycrystalline pellet samples were carried out at the ISIS muon facility of the Rutherford Appleton Laboratory (U.K.) by using a dilution refrigerator. Details of the experiments and theoretical analyses are described elsewhere.[6-8]

RESULTS AND DISCUSSION

Magnetostructural correlation in two isomeric series of nitronyl nitroxides: quinolyl and naphthyl nitronyl nitroxide

As we have previously shown, among the three structural isomers of quinolyl nitronyl nitroxide (QNNN) and the two isomers of naphthyl nitronyl nitroxide (NAPNN), 2- and 3-QNNN and 1-NAPNN exhibit FM intermolecular interaction, while 4-QNNN and 2-NAPNN show antiferromagnetic (AFM) intermolecular interaction.[9-11] Since the QNNN and NAPNN molecules have almost identical chemical formula, i.e., a N atom of the quinolyl group in QNNN is replaced by a =C–*H* moiety in NAPNN, the remarkable differences between the intermolecular interactions observed in the isomers of QNNN and NAPNN suggest that a closer examination of the magnetic and crystallographic properties of the two isomeric series may afford useful insight into magnetostructural correlations in organic radical crystals.

Temperature dependences of the product of paramagnetic susceptibility and temperature, $\chi_p T$, of 2- and 3-QNNN and 1- and 2-NAPNN are interpreted in terms of an anisotropic three-dimensional (3D) model based on two-dimensional (2D) FM square lattices with FM or AFM interlayer interaction, as shown by the solid lines in Fig. 1.[11] The temperature dependence of $\chi_p T$ for the model is described by the equation $\chi_p T = \chi_p^{2D} T/[1 - zJ'/(2kT)]$ where χ_p^{2D} is the susceptibility for the 2D FM lattice with the intralayer exchange coupling constant J, J' is the interlayer exchange coupling constant, k is the Boltzmann constant and z is the number of neighboring layers.[12,13] The 2D FM square lattice model with $z = 2$ yields $J/k = 0.02$ K and $J'/k = 0.01$ K for 2-QNNN, $J/k = 0.12$ K and $J'/k = 0.03$ K for 3-QNNN, and $J/k = 0.09$ K and $J'/k = 0.03$ K for 1-NAPNN. Since both J and J' are positive, the molecules in these radical crystals form 3D FM exchange paths, while the intralayer FM interaction is two to four times as large as the interlayer FM interactions. In contrast, the anisotropic 3D model yields exchange coupling constants $J/k = 0.14$ K and $J'/k = -0.31$ K for 2-NAPNN. The negative value of J' obtained for 2-NAPNN indicates an AFM interlayer interaction, whereas the intralayer interaction is ferromagnetic.

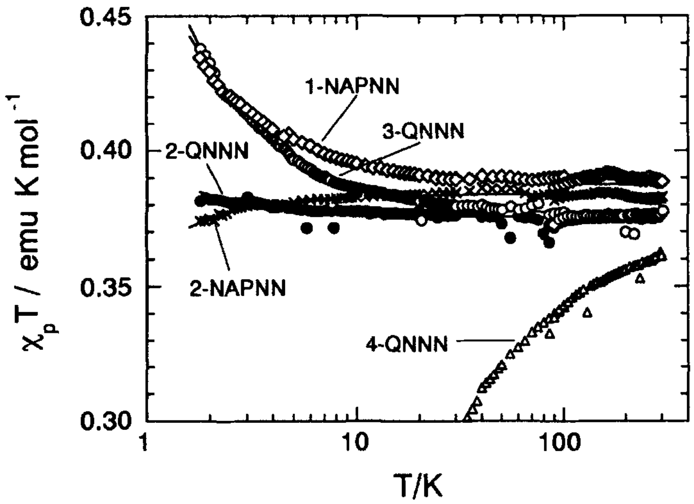


FIGURE 1 Temperature dependence of $\chi_p T$ of the three structural isomers 2-, 3- and 4-QNNN and the two structural isomers 1- and 2-NAPNN. Note the logarithmic scale for temperatures.

By considering magneto-structural correlations in these radical crystals, we found that a small difference between the molecular arrangements results in quite different magnetic interactions, which vary between FM and AFM ones.[11] We show here how the difference of the molecular arrangements observed between 2-QNNN and 2-NAPNN, which have molecular structures very close to each other, yields the remarkably different magnetic interactions in the whole crystals; i.e., FM in the former and AFM in the latter.

The crystal structure of 2-QNNN,[11] projected along the *a* axis, is shown in Fig. 2. The 2-QNNN molecules are oriented in the same direction along the *c* axis making a herringbone-like molecular arrangement. In the *ac* plane, there are interatomic contacts between the O atoms of the ONCNO group and the methyl group as well as between the O atom and the quinolyl ring, as shown by the dashed lines. Since these contacts favor FM intermolecular interactions,[11,14] the 2-QNNN molecules form 2D layers with FM intreractions. The 2D molecular layers parallel to the *ac* plane are connected by the intermolecular contacts between the O atom and the quinolyl ring constituting a 3D molecular network, as shown by the solid lines. Since all the contacts forming this network contribute to the FM interaction, the magnetic exchange paths through the intermolecular contacts in 2-QNNN should result in a 3D FM network, as actually observed in the results of magnetic measurements shown above.

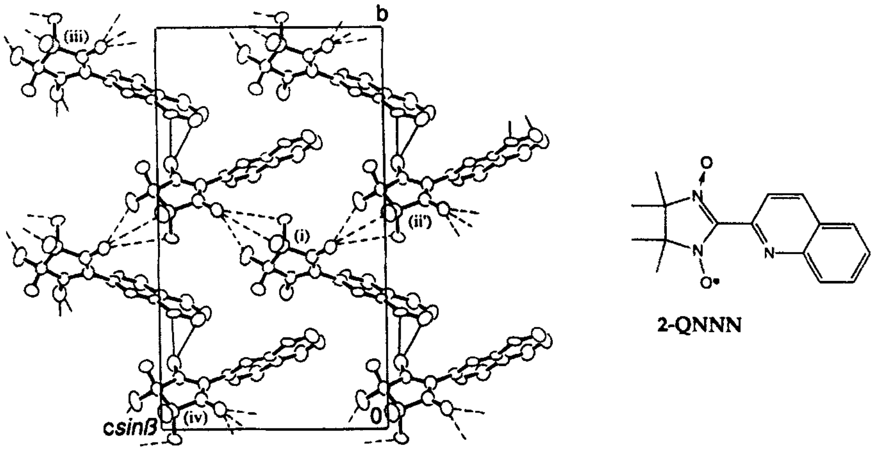
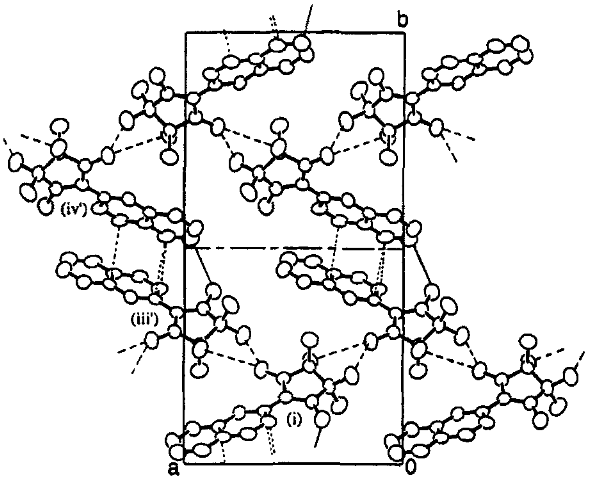
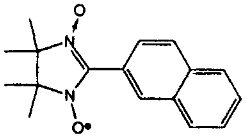


FIGURE 2 Crystal structure of 2-QNNN.

The crystal structure of 2-NAPNN,[8,11] projected along the *c* axis, is shown in Fig. 3. In the half of the unit cell divided at the (020) plane, of which a side view is shown by the dash-dotted line, the 2-NAPNN molecules are oriented in the same direction along the *a* axis making a herringbone-like molecular arrangement. The arrangement of the molecules in the half of the unit cell of the 2-NAPNN crystal is quite similar to that of 2-QNNN. Therefore, the 2-NAPNN molecules form 2D FM layers parallel to the *ac* plane. In contrast to the 2-QNNN crystal, however, the molecular orientations in the other half of the unit cell are reversed. The reversed molecular orientations in 2-NAPNN result in several intermolecular contacts between the naphthyl rings standing opposing one another across the (020) plane, as represented by the dotted lines. Since the contacts between aromatic rings of nitronyl nitroxide may favor AFM interactions,[14] 2-NAPNN exhibits AFM behavior for the crystal as a whole, as observed in the magnetic measurements.





2-NAPNN

FIGURE 3 Crystal structure of 2-NAPNN.

As shown above, the packing of the molecules in the crystals of 2-QNNN and 2-NAPNN presents some very similar features, that is herringbone-like 2D molecular layers, probably due to their almost identical chemical structures. However, eliminating the electronegative N atom from 2-QNNN induces a change of crystal symmetry and hence a partial difference in the overall molecular arrangement because of the reduction of electrostatic attractive forces through the N atom.[11] This small alternation in the molecular packing results in a drastic change in magnetic behavior of the crystal as a whole.

Coexistence of ferro- and antiferromagnetic interactions in carboxy- and sulfonato-aryl nitronyl nitroxide

Carboxy, carboxylato and imidazole groups have the potential to form hydrogen-bonds betwen molecules. Hydrogen-bonds may affect the physical properties of materials. We have therefore synthesized some carboxyaryl, carboxylatoaryl and imidazolyl derivatives of nitronyl nitroxide and measured magnetizations and susceptibilities of them in order to study the effects of hydrogen-bonds on the intermolecular magnetic interactions. For the same reasons, we have also synthesized anion radical salts of sulfonatoaryl derivatives of nitronyl nitroxide.

Figure 4 shows the temperature dependence of $\chi_p T$ of 2-carboxyfuryl nitronyl nitroxide (2-CAFNN) and sodium 2-sulfonatofuryl nitronyl nitroxide [Na(2-SAFNN)]. The temperature dependence of $\chi_p T$ of both radical crystals is not totally reproduced by the Curie-Weiss law $\chi_p = C/(T - \Theta)$. Upon lowering the temperature, the experimental data deviate towards values which are larger than those calculated theoretically by using the Curie-Weiss law with negative (AFM) Weiss constants $\Theta = -2.2$ K for 2-CAFNN and $\Theta = -1.8$ K for Na(2-SAFNN), as shown by the dotted lines in Figure 4. Since any AFM model predicts deviations towards smaller values from those calculated by the Curie-Weiss law, the deviation towards larger values implies that a minor FM intermolecular interaction coexists with a major AFM interaction. We have therefore analyzed the experimental data by assuming that there is a coexistence of FM and AFM interactions.

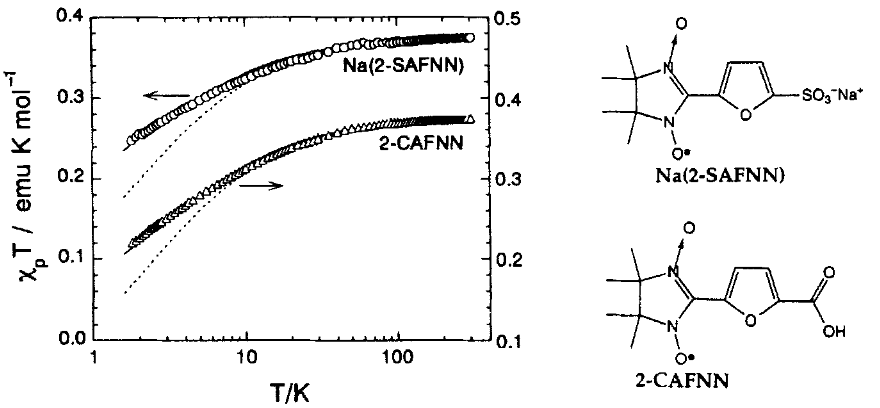


FIGURE 4 Temperature dependence of $\chi_p T$ of Na(2-SAFNN) and 2-CAFNN. Note that the vertical scale for 2-CAFNN is offset for clarity. The dotted lines show $\chi_p T$ calculated by the Curie-Weiss law and the solid lines represent $\chi_p T$ calculated based on a coexistence of FM and AFM interactions (see the text).

Although the crystal structures of 2-CAFNN and Na(2-SAFNN) are not yet known, we have examined the anisotropic 3D model applied to the NAPNN and QNNN radical crystals to interpret the temperature dependence of $\chi_p T$. The model with $z = 2$ yields sufficient fits and the intra- and interlayer exchange couplings $J/k = 0.33$ K and $J'/k = -2.2$ K for Na(2-SAFNN) and $J/k = 0.40$ K and $J'/k = -3.0$ K for 2-CAFNN. The results clearly indicate the coexistence of FM and AFM intermolecular interactions in 2-CAFNN and Na(2-SAFNN), although crystal structure analyses are needed to discuss further the exchange paths in these radical crystals.

Figure 5 shows the temperature dependence of χ_pT of *p*-carboxyphenyl nitronyl nitroxide (*p*-CAPNN) and 2-imidazolyl nitronyl nitroxide (2-IMNN). In these radical crystals, χ_pT is interpreted in terms of the modified singlet–triplet molecular dimer model,[15] as shown by the solid lines in Fig. 4. In contrast to *p*-CAPNN which shows rather weak AFM intradimer intermolecular intraction with an exchange coupling $J/k = -2.1$ K,[16] 2-IMNN exhibits quite strong AFM interactions with the intradimer exchange coupling $J/k = -86$ K. To the best of our knowledge, this is the largest AFM coupling for the nitronyl nitroxide derivatives and comparable to $J/k = -74$ K reported for the cation radical salt, *N*-methyl-*p*-pyridiniumyl nitronyl nitroxide iodide.[17]

Magnetic transition observed in zero-field μSR of naphthyl and *p*-cyanophenyl nitronyl nitroxide with ferromagnetic intermolecular interaction

Since zero-field (ZF) μSR measurements directly probe the local magnetic field which is quasistatic on a microsecond time-scale and can be carried out down to a few tens of mK, we have investigated the low-temperature magnetic behavior of three nitronyl nitroxide derivatives, 1- and 2-NAPNN and *p*-cyanophenyl nitronyl nitroxide (*p*-CNPNN), through the measurements of ZF-μSR.[8,18]

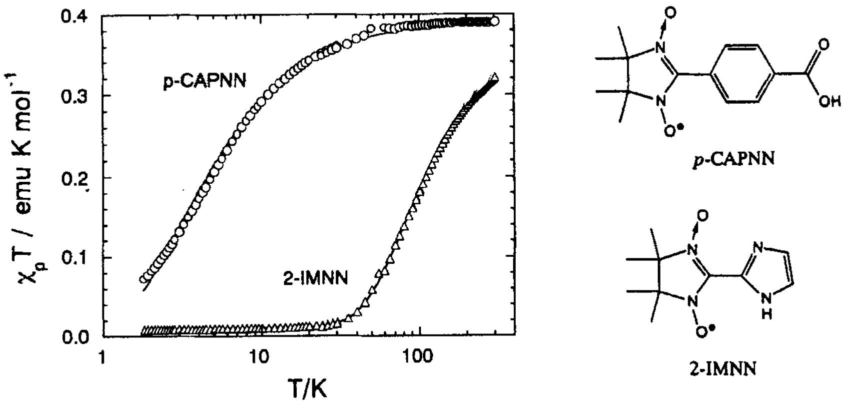


FIGURE 5 Temperature dependence of χ_pT of p-CAFNN and 2-IMNN. The solid lines represent χ_pT calculated on the basis of the singlet-triplet dimer model.

Figure 6 shows ZF-μSR data for polycrystalline pellet samples of 1- and 2-NAPNN.[8] A clear transition is observed via changes in the relaxation function in 1-NAPNN at temperatures below 100 mK. The observed asymmetry below this transition temperature is well fitted by two terms, one fast-decaying oscillatory term which dominates the initial relaxation and a second slowly relaxing exponential which dominates the long-time behavior. Above the transition the asymmetry can be described by a single-exponential decay. The relaxation function is almost independent of temperature in 2-NAPNN and is also well described by a single slow exponential.

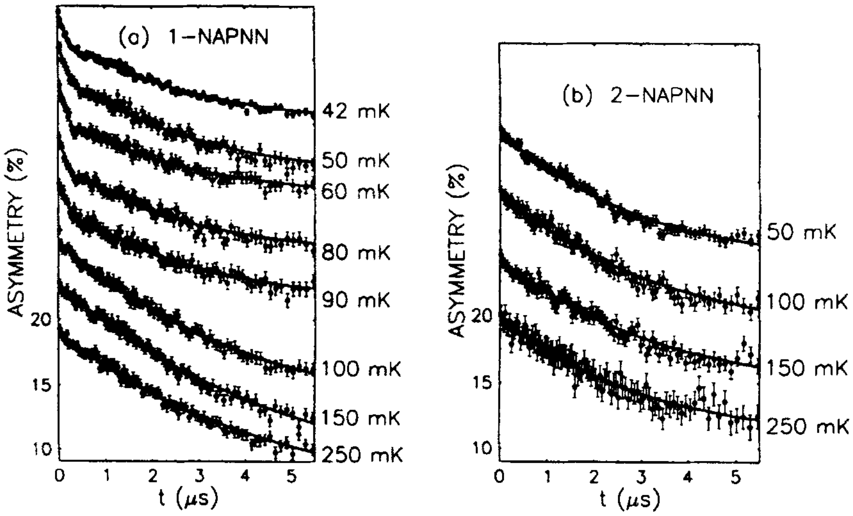


FIGURE 6 Time evolution of ZF-μSR of 1- and 2-NAPNN as a function of temperature. The ordinate scale refers to the lowest trace in each case. The other traces are all vertically offset for crality.

The frequency of the fast-decaying oscillatory term observed in 1-NAPNN is near 1 MHz and corresponds to a local field of about 75 G, comparable with values obtained for other nitronyl nitroxide.[4-7] The slow relaxation disappears at about 20 G of longitudinal field. These values are consistent with typical magnetic dipole fields calculated for these nitronyl nitroxide system.[8] Although the precise origin of the two relaxations in 1-NAPNN is not clear at present, we suspect that a distribution of magnetically inequivalent muon sites leads to the observed complicated relaxation behavior. In 1-NAPNN we are observing very weak oscillations which are even more strongly damped. However, the sudden change of relaxation function below 90 mK suggests clearly the magnetic transition in 1-NAPNN around 0.10 K which may be due to the onset of magnetic order. No magnetic transition is observed in 2-NAPNN down to 0.05 K. The difference in magnetic behavior of these two chemical isomers is remarkable. 1-NAPNN shows FM intermolecular interactions and a magnetic transition, while 2-NAPNN exhibits AFM interactions without a transition. The slight change of molecular geometry induces quite different molecular arrangements and consequently a large difference in the magnetism.[8,10,11]

Figure 7(a) shows ZF-μSR data for a polycrystalline pellet sample of *p*-CNPNN. Below 0.17 K the data can be well fitted by two exponentials, one with a fast relaxation rate and the other with a slow relaxation rate. At temperatures higher than 0.2 K, only the slow relaxation term is observed. This is reminiscent of the behavior observed in 1-NAPNN.

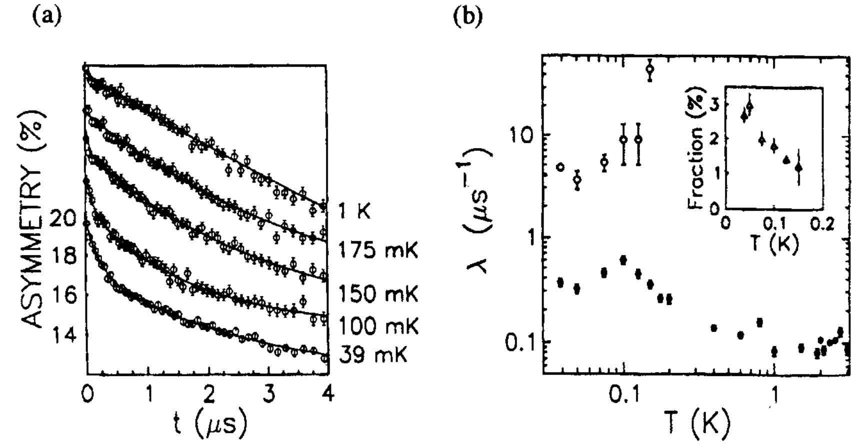


FIGURE 7 Time evolution of ZF-μSR of a polycrystalline sample of *p*-CNPNN as a function of temperature. The vertical scale refers to the lowest temperature trace and the others are all vertically offset for clarity.

The temperature dependence of the two relaxation rates is shown in Fig. 6(b). The inset shows the amplitude of the fast relaxing component which decreases as the temperature increases and disappears above 0.17 K. This suggests that the fast relaxation is related to the presence of magnetic order in the *p*-CNPNN crystals and a magnetic transition takes place at 0.17 K. No oscillations are observed even below the transition temperature. The fast relaxation is, however, characteristic of magnetic order in some other nitronyl nitroxide radicals.[5,6,8]

In summary we have observed magnetic transitions at 0.10 K and 0.17 K in 1-NAPNN and *p*-CNPNN which exhibit FM intermolecular interaction.[8,10,11,19] In contrast no magnetic transition is found for 2-NAPNN showing AFM intermolecular interaction in the crystal as a whole.

ACKNOWLEDGEMENTS

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