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LETTER TO THE EDITOR

Magnetic order in poly(1, 3-dithienyl-5-phenylverdazyl)

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Abstract. Electropolymerization of 1, 3-dithienyl-5-phenylverdazyl with hexafluorophosphate as the counter anion gives solid materials with a high concentration of radical spins. A portion of the magnetic moments show magnetic order with spontaneous magnetization at temperatures of 10 K and below. The samples are characterized by measurement of field- and temperature-dependent static magnetic susceptibility, electron spin resonance and low-temperature magnetization curves (hysteresis loops).

The search for organic and eventually polymeric materials with ferromagnetic properties is currently an area of very intense research activity [1]. A well characterized, chemically stable organic ferromagnet, obtained via a reproducible synthetic route, whose ordering temperature is well above room temperature and whose magnetization is large enough for applications, is not yet available. Nevertheless, important steps forward have been achieved in recent years both in the chemical preparation of promising new materials and in elaborating the theoretical models for possible routes to ferromagnetic interactions [1, 2]. As a possible attempt to manufacture polymeric magnets, several years ago we introduced stable free radicals into the polymers polyacetylene and polypyrrole [3-5]. It proved to be difficult, however, to raise the spin concentration to the level necessary for a substantial exchange interaction. One of the free radicals introduced as a counter ion into polypyrrole [4] was the well known triphenyl-verdazyl (TPV) radical [6].

Recently, we started to modify the TPV molecule, as did others [7, 8], in order to optimize its exchange interaction in the solid state [9-11]. However, the carbon and nitrogen p-like orbitals give rise preferentially to a quasi-one-dimensional intermolecular overlap of the wave functions and exchange interaction. Since it may be assumed that the d-like wave functions, accessible by the incorporation of sulphur into the molecular units, enable a two- or three-dimensional overlap and possibly exchange interaction, we added thiophene units to the central verdazyl radical part in order to support three-dimensional magnetic order in subsequently polymerized materials. We show below that magnetic ordering was indeed achieved for a non-negligible portion of the poly-(dithienylphenylverdazyl) samples.

1, 3-dithienyl-5-phenylverdazyl (DTPV, see inset to figure 1) was synthesized along the lines described in [9]. The samples of poly-DTPV/PF₆ analysed in this letter were obtained by electropolymerization using hexafluorophosphate (PF₆) as the counter anion. Chemical elementary analysis supports a 1:1 composition of DTPV and PF₆. The static magnetic properties of a powder sample have been characterized by SQUID magnetometry (Quantum Design MPMS, -55 to +55 kOe, 1.8 to 300 K). During the measurements the sample was surrounded by a low-pressure helium atmosphere. For the analysis of the measured magnetic moments a molar mass of 483 g mol⁻¹ was taken into account. Variable temperature

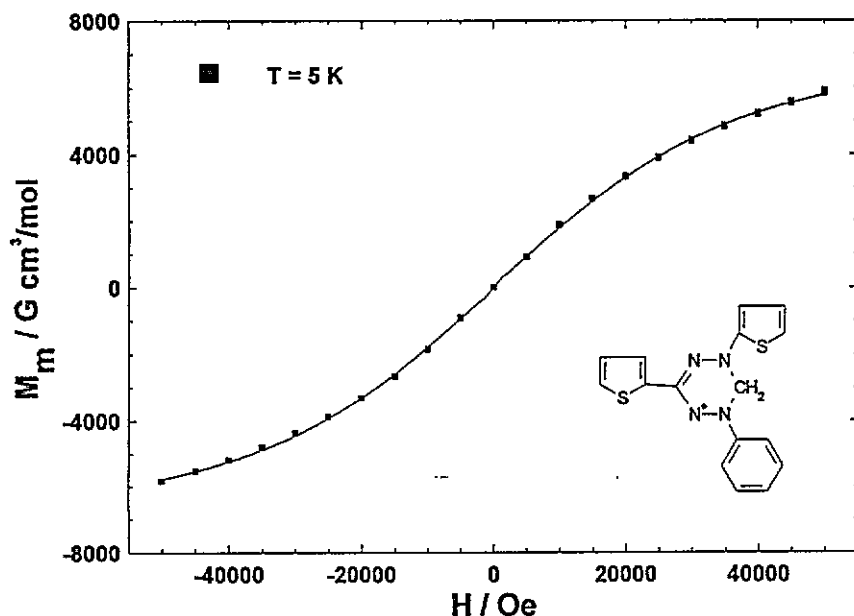


Figure 1. The molar magnetic moment as a function of external magnetic-field strength for the powder sample of poly-DTPV/PF₆ at $T = 5$ K. The experimental data were corrected for the contribution of the magnetically ordered sample portion, shown in figure 2. The fit with a Brillouin function ($S = 3/2$) is shown for comparison. The inset shows the 1,3-dithienyl-5-phenylverdazyl (DTPV) monomer unit.

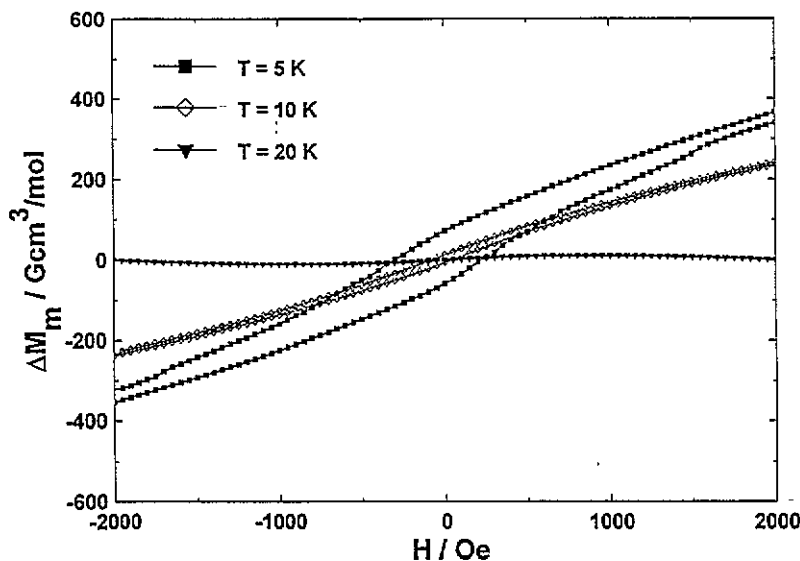


Figure 2. Partial magnetic moment of poly-DTPV/PF₆ obtained from the experimental data after correction for the Brillouin-like contribution (figure 1), showing the low-temperature hysteresis loops on a magnified scale.

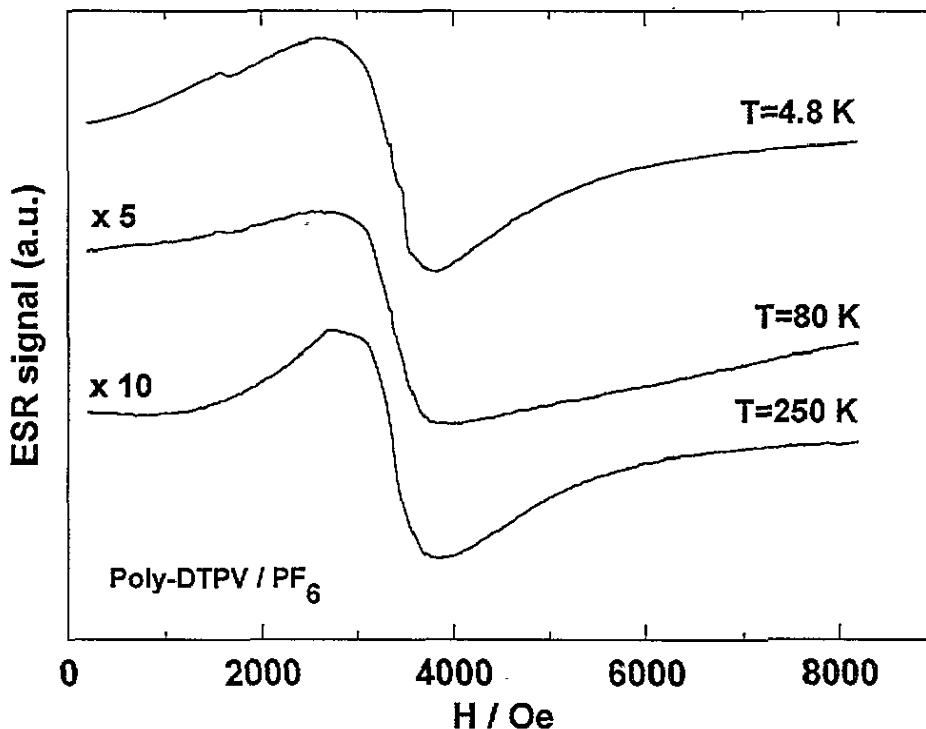


Figure 3. ESR absorption-derivative signals of poly-DTPV/PF₆ for different temperatures ($\nu_L = 9.45$ GHz).

ESR spectra were recorded at 9.5 GHz (Bruker ESP 300 E spectrometer), for additional characterization of the actual impurity content of the sample.

For temperatures above 20 K our sample of poly-DTPV/PF₆ shows a predominance of temperature-dependent paramagnetism. The detailed analysis of the temperature and field dependence of the product of molar magnetic moment and temperature (i.e. $M_m \times T$) allows us to estimate the actual content of ferro- or ferrimagnetically ordered impurity phases, such as Fe₃O₄, in the sample. From the portion of $M_m \times T$ increasing linearly with temperature, a relative portion of at most 100 ppm (weight) of Fe₃O₄-like phases is derived for the sample. The large value of the high-temperature Curie constant ($C = 3$ emu K mol⁻¹) of the sample indicates that on average clearly more than one spin $S = \frac{1}{2}$ resides at each formula unit. This indicates that, besides the verdazyl radicals, a considerable part of the thiophene units carry an additional free spin. A fit to the temperature dependence of the paramagnetic susceptibility indicates a weak average exchange interaction with antiferromagnetic asymptotic Curie temperature $\Theta_p = -10$ K. However, the low-temperature magnetic saturational behaviour shown in figure 1 and compared with the Brillouin function for $S = \frac{3}{2}$ [12] reveals that at least three spins $S = \frac{1}{2}$ must be correlated ferromagnetically in order to account for the ease of low-field magnetic saturation. It has to be taken into account that one spin $S = \frac{1}{2}$ per formula unit allows for a saturation moment of 5582 emu mol⁻¹ only. The low-temperature low-field part shown in figure 2 has been obtained after subtraction of the paramagnetic Brillouin-like contribution (presented in figure 1) from the experimental data. The hysteresis loop proves that about 5% of the low-temperature magnetic moment originates from a magnetically ordered portion of the sample.

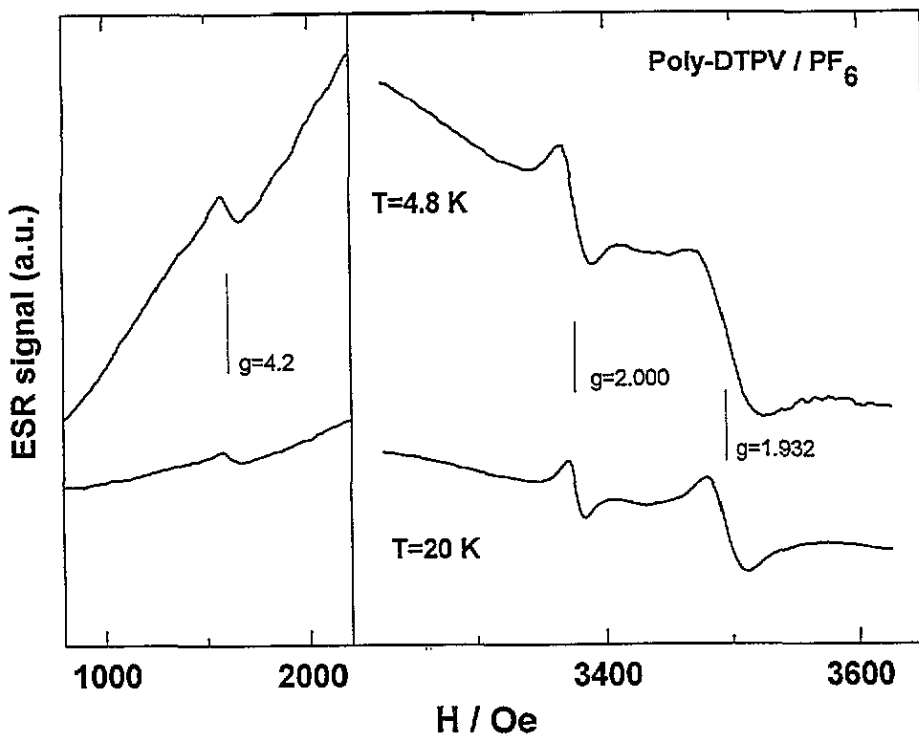


Figure 4. Magnified regions of the ESR absorption-derivative signals revealing impurity contributions of the poly-DTPV/PF₆ sample.

Remanent and spontaneous magnetization at 5 and 10 K, which vanishes between 10 and 20 K, can clearly be seen. Thus the static magnetic characterization gives clear evidence for ferro- or ferrimagnetic order in a relevant portion of the sample of poly-DTPV/PF₆ prepared here.

Additional information on the magnetic properties of the sample was obtained by electron spin resonance (ESR) analysis (figures 3 and 4). Figure 4 magnifies the narrow-line features barely visible in figure 3. In keeping with the large spin concentration, but low average exchange interaction mentioned above, the ESR spectrum is dominated by a strong ESR line centred at $g = 2.0 \pm 0.1$ with rather large width (1 kOe peak-to-peak at 300 K) whose intensity varies with roughly Curie-like properties. Decomposition of the line shape reveals the superposition of several components differing in their temperature dependences. The width of the most prominent line broadens with decreasing temperature from about 1.3 kOe at 250 K to 2 kOe at 150 K and 3.5 kOe at 60 K. In contrast, the width of the ESR line contribution that is the next most important one at 250 K (about $(5 \pm 4)\%$ of the former's intensity) varies only by a small amount from about 0.5 kOe at 250 K to 0.7 kOe at 150 K and 0.7 kOe at 60 K. These ESR data thus provide evidence for the different arrangements of the electron spins with different strength and symmetry of their dipolar interactions and exchange couplings, as is not unreasonable for any presumably polymeric sample.

Weak additional ESR lines, resolved for temperatures below 100 K and shown on a magnified scale in figure 4, give information on the small but non-negligible impurity content of our sample. The lines at about $g = 4.20$, 2.000 and 1.932 contribute at most $(4.2 \pm 0.3) \times 10^{-4}$, $(4.1 \pm 0.6) \times 10^{-5}$ and $(3.1 \pm 0.7) \times 10^{-4}$, respectively, to the total

ESR intensity. Whereas the $g = 4.2$ ESR signal might be related to a small concentration of paramagnetic iron impurity ions [13], the interpretation for the other two lines is less clear. The width of the narrow line at $g = 2.000 \pm 0.001$ increases from 9.6 Oe at 100 K to 16 Oe at 10 K and 23 Oe at 4.8 K. According to its g value, it might originate from an organic-radical electron spin with no close-by paramagnetic neighbours. However, its weak structure consisting of six equidistant lines barely resolved at 4.8 K ($\delta H \approx (4.5 \pm 0.7)$ Oe) points to the importance of isotropic hyperfine interaction with five equivalent nuclear spins $I = \frac{1}{2}$, or with one nuclear spin $I = \frac{5}{2}$ together with $I = 0$ isotopes. The latter situation might result from titanium impurities and the isotope $^{47}\text{Ti}^{3+}$. The well known anisotropy occurring for Ti^{3+} in trigonal surroundings, i.e. $g_{\parallel} = 2.00$ and $g_{\perp} = 1.93$ [14], favour this interpretation. Thus these ESR results prove once again the importance of a careful search for 3d transition-elemental impurities in the analysis of magnetic properties in organic polymeric materials. The impurities identified here cannot explain, however, the magnetic order and spontaneous magnetization shown in figure 2.

In conclusion, we have presented evidence for magnetic order with spontaneous magnetization and hysteresis loops in electropolymerized samples of poly-(1,3-dithienyl-5-phenylverdazyl) with PF_6 counter anions. According to the analysis presented above, these samples have only a low content of possible inorganic impurity phases. Thus it is tempting to systematically optimize the magnetically ordering portion of this new dithiophen-verdazyl based magnetic material.

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References

- [1] Gatteschi D, Kahn O, Miller J S and Palacio F 1991 *Proc. Conf. on Molecular Magnetic Materials (NATO ASI Series E 198)* (Deventer: Kluwer)
- [2] Gatteschi D 1994 *Europhys. News* 25 50
- [3] Winter H, Sachs G, Dormann E, Cosmo R and Naarmann H 1990 *Synth. Met.* 36 353
- [4] Winter H, Gotschy B, Dormann E and Naarmann H 1990 *Synth. Met.* 38 341
- [5] Cosmo R, Dormann E, Gotschy B, Naarmann H and Winter H 1991 *Synth. Met.* 41-43 369
- [6] Kuhn R and Trischmann H 1963 *Angew. Chem.* 75 294; 1964 *Monatsh. Chem.* 95 457
- [7] Allemant P-M, Srdanov G and Wudl F 1990 *J. Am. Chem. Soc.* 112 9391
- [8] Allemant P-M, Srdanov G and Wudl F 1991 *Synth. Met.* 41-43 3245
- [9] Dormann E, Winter H, Dyakonow W, Gotschy B, Lang A, Naarmann H and Walker N 1992 *Ber. Bunsenges. Phys. Chem.* 96 922
- [10] Dormann E, Dyakonow W, Gotschy B, Lang A, Naarmann H, Pilawa B, Walker N and Winter H 1993 *Synth. Met.* 55-57 3273
- [11] Dormann E, Winter H, Gotschy B and Naarmann H 1993 *Phys. Scr.* T 49 731
- [12] Kittel Ch 1976 *Introduction to Solid State Physics* (New York: Wiley)
- [13] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
- [14] Carrington A and McLachlan A D 1969 *Introduction to Magnetic Resonance* (New York: Harper & Row) p 157