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Invited Review

Ferromagnetism in Metallocene-Doped Fullerenes

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Summary. Ferromagnetism in fullerene-based systems doped with metallocenes is reviewed. These compounds form a ferromagnetic state by spin-coupling between π electrons on fullerene units, while the metallocene molecules do not contribute to the spin ordering. One of these compounds has the highest critical temperature (19 K) for this class of compound. The magnetic properties of these materials are very strongly dependent on the crystallization conditions.

Keywords. Fullerene; Ferromagnetism; Adducts; Metallocene; Cobaltocene.

1. Introduction

The discovery of high-T_c fullerene magnetism is presenting an exceptional challenge to our understanding of magnetic phenomena the solid state. Indeed *p*-electron magnetism has been considered unlikely, ever since *Heisenberg* considered it essential to have atoms (or ions) with *d*-electron orbitals to form a ferromagnetic state. Magnetic behaviour in fullerene compounds was first discovered in 1991 by *Fred Wudl* and collaborators [1]. Their discovery of ferromagnetism in tetrakis-dimethylamino-ethylene-fullerene [60] (*TDAE*-C_{60}) with a *Curie* temperature of 16 K was quite a surprise. The critical temperature signifying the onset of a magnetic state was an order of magnitude higher than the previous record and this brought the research field from the realms of the esoteric into the mainstream.

Inspired by the discovery of *TDAE*-C_{60}, several research groups immediately started to work on synthesis of new fullerene ferromagnetic compounds. A logical step was to replace the donor *TDAE* with other organic or organometallic donors. Unfortunately this approach to our knowledge so far did not result in any new reproducibly synthesised ferromagnetic compounds [2–4]. Charge-transfer salts

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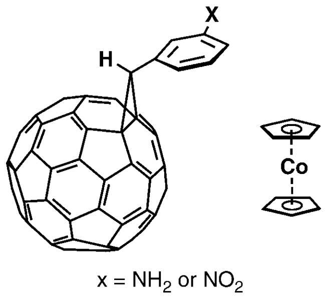

Fig. 1. The building blocks of cobaltocene-doped fullerene-based ferromagnets

of C_{60} with donors other then *TDAE* proved – without exception – to be paramagnetic, as were doped higher fullerenes [5].

Another approach was to functionalise the C_{60} molecule and change its properties slightly and subsequently to dope it with the same set of donors [6]. This direction was more promising and recently, the compound 1-(3-aminophenyl)-1*H*-methanofullerene C [60] doped with cobaltocene (*APHF-CO*) was discovered [7] with the highest reported *Curie* temperature of $T_c = 19\,\mathrm{K}$ (3 K higher then *TDAE*-C_{60}). Within two years this compound could be reproducibly synthesised in a way which would reliably exhibit a low-temperature magnetic phase. A related compound, 1-(3-nitrophenyl)-1*H*-methanofullerene (*NIPHF-CO*), also doped with cobaltocene was also found to exhibit clear signs of ferromagnetic behaviour [8]. The difference between the two compounds is that the aminophenyl adduct on the fullerene is replaced by a nitrophenyl group. The structural units of these compounds are shown schematically in Fig. 1.

In this review we discuss the synthesis, electronic structure and magnetic properties of these materials, emphasizing the connection between synthesis conditions and magnetic properties.

2. Synthesis

The 1-(3-nitrophenyl)-1*H*-methanofullerene-[C_{60}]-cobaltocene (*NIPHF-CO*) and 1-(3-aminophenyl)-1*H*-methanofullerene[C_{60}]-cobaltocene (*APHF-CO*) are synthesised in a two-step procedure. First, the fullerene derivative (*APHF* and *NIPHF*) is synthesised and purified. Subsequently they are doped with organic dopant by similar methods as *TDAE* C_{60}. [7, 8]. The detailed procedure for preparation of these compounds and chemical characterisation data for these compounds are reported by *Mrzel et al.* [6] and *Umek et al.* [8].

It was found that the temperature at which the doping is performed plays a crucial role in determining the magnetic properties of these materials. A detailed study revealed the optimum conditions, particularly the temperature for the synthesis of ferromagnetic material. Only after a prolonged systematic study was the reproducibility of the synthesis sufficiently reliable to be able to seriously examine the magnetic properties of these materials. A number of attempts to determine the crystal structure of the materials were not successful, indicating that the degree of crystallinity of these materials is rather small. The nanocrystallinity of the materials seems to be the cause of a small magnetic moment at saturation, which is always much smaller than would be expected if all the spins were ferromagnetically aligned. Attempts to grow single crystals of these materials were so far not successful.

3. The Electronic Structure

Upon formation of a charge transfer complex, the organic donor such as *TDAE* or cobaltocene transfers one electron to the fullerene. This results in a charge transfer state with a *Jahn-Teller* distorted C_{60} molecule [9]. In the case of the fullerene derivatives, an additional distortion is also caused by the presence of the adduct. The donor itself is also in a charged state, and also changes conformation upon CT. In the case of *TDAE*, this has been studied in some detail [10]. In the case of metallocene-doped fullerenes, it is important to note that the cobaltocene dopant molecule has no net spin (*i.e.* has a closed shell) in the $+1$ charge state and thus does not contribute to the magnetic properties of cobaltocene-doped fullerene ferromagnets. Previous to the discovery of ferromagnetic state in cobaltocene-doped fullerene derivatives, it was not clear how important was the role of the *TDAE* itself (with $S = 1/2$) in the formation of a ferromagnetic state. The fact that cobaltocene has no spin in the case of *APHF-CO* or *NIPHF-CO* provided conclusive evidence that the spin ordering takes place primarily on the fullerenes and not on the dopants.

The main signatures of a charge transfer between the donor and the fullerene acceptor are a) the appearance of a near-infrared absorption due to the new HOMO-LUMO transitions and b) the appearance of shifted vibrational bands of the fullerene in the infrared spectrum. In order to ascertain that the electrons on $\mathrm{Co}Cp_2$ do not participate in the magnetic interactions, it is important to show that a *complete* charge transfer from the donor to the fullerene acceptor has taken place.

Optical spectra of *APHF-CO* and *NIPHF-CO* show a clear absorption peak near 1.1 eV (1100 nm). In Fig. 2 we compare the optical absorption spectra for *TDAE*-C_{60} and *APHF-CO*. This absorption is a characteristic signature of the fullerene in the -1 charge state and corresponds to dipole allowed transitions between the new t_{1u}-derived occupied HOMO and the unoccupied t_{1g}-derived LUMO of *APHF* or *NIPHF*. We note that although the spectral shape (including the vibrational sidebands) and intensity of this feature is similar to $C_{60}{}^{-}$ (in $TDAE^{+}C_{60}{}^{-}$), the t_{1u}–t_{1g} absorption peak of the $APHF^{-}$ is blue-shifted from 1080 nm in $C_{60}{}^{-}$ to 1020 nm in $APHF^{-}$, suggesting an increased HOMO-LUMO spacing in the latter. On the other hand the absorption spectra of *APHF* and pure C_{60} in the visible and UV spectral range (190–500 nm) are virtually indistinguishable (see insert to Fig. 2), indicating that the electronic structure of *neutral APHF* is *very* similar to C_{60}.

Evidence for a *full* CT comes from vibrational spectroscopy. The mid-infrared transmittance spectra of *APHF-CO* as well as neutral $Cp_2\mathrm{Co}$ and *APHF* in the region of the four main C_{60}-derived IR-active vibrational modes of *APHF* are shown in Fig. 3. In addition to the four C_{60}-derived modes at 526, 573, 1184 and 1427 cm^{-1}, *APHF* shows a large number of additional weaker vibrational modes, which are assumed to be partly a result of the broken icosahedral symmetry of the fullerene by the adduct and partly due to the adduct itself. As expected, in

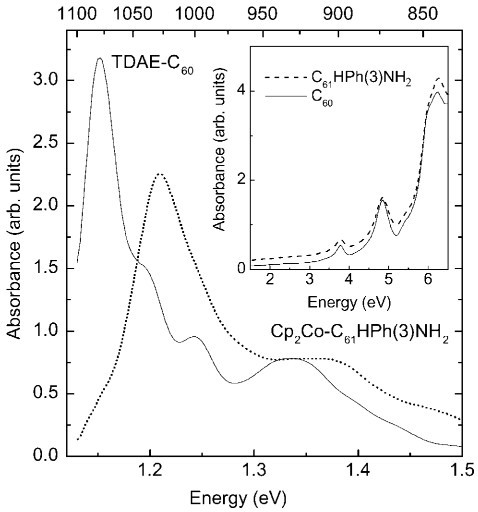

Fig. 2. The optical spectra of *APHF-CO* in comparison with *TDAE*-C_{60}. The peak near 1.2 eV corresponds to the HOMO-LUMO transition. The insert shows that the spectra of the monoadducts themselves are virtually identical

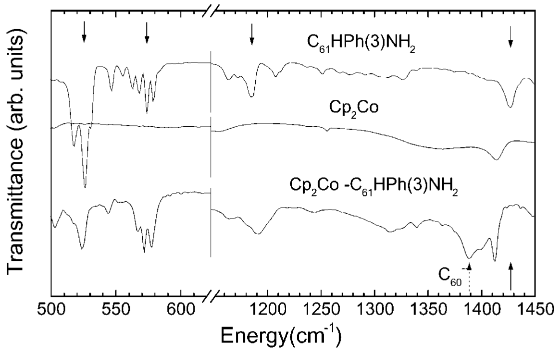

Fig. 3. The infrared vibrational spectra of *APHF*, cobaltocene and *APHF-CO*. The characteristic bands of the fullerene are shown by arrows

APHF-CO the four main fullerene-based modes are distinctly frequency shifted to 524, 572, 1191, and 1388 cm^{-1} respectively (Fig. 3), in excellent agreement with shifts in C_{60}^- anions in other doped fullerenes [11]. Careful examination of the *APHF-CO* spectra reveals no presence of the 1427 cm^{-1} peak corresponding to *neutral APHF*. This implies that there are no remaining unpaired electrons on the donor molecules and the ferromagnetic properties can be attributed entirely to the fullerene spins in these compounds.

4. Magnetic Phenomena

When the magnetic properties of *TDAE*-C_{60} were first measured at low temperatures [1], the researchers found a rather unusual cusp in the susceptibility with an onset at $T_c = 16$ K, indicating that below this temperature some kind of spin ordering was taking place. The behaviour was not typical for a ferromagnet, however, and only later, when single crystal data could be compared, it was shown that the unusual behaviour could be attributed to the nano-crystalline nature of the powder samples. The problem with powder samples is that the surface-to-volume ratio of the nano-crystalline particles is very large: up to 30% of all the buckyballs could be in the first few layers of each nano-particle (these were found by electron-microscopy to be typically of the order of 50 nm in diameter). This could lead to some unusual magnetic properties, resembling superparamagnetism. Since the dopants are sensitive to air, the surface could also be chemically degraded. As a result it is difficult to determine whether the observed behaviour is intrinsic or not.

Subsequent measurements have confirmed the existence of a magnetically ordered state at low temperatures: it was established by low-field radio-frequency ESR [12] that in the absence of external field there is a small, but finite internal field which is present only below T_c. The presence of such an internal field was confirmed later by muon spin resonance [13] and so the fact that there is a net ferromagnetic component to the spin order was established.

The magnetic behaviour of powder samples of *APHF-CO* and *NIPHF-CO* is qualitatively similar as with *TDAE*-C_{60} nanopowder. There are no single-crystal data yet available for the metallocene-doped fullerenes, but they may be expected to show similar differences between powder samples and single crystals as *TDAE*-C_{60}.

The magnetization of all the mentioned metallocene-doped powder samples measured so far show a non-linear curve as a function of magnetic field such as is found in soft ferromagnetic materials. (In these, there is little or no remnant magnetization in the absence of external field.) These properties together with an observed increase of T_c with magnetic field – another property typical of ferromagnets – lead to the belief that these materials are proper ferromagnets.

The low-temperature magnetic susceptibility $\chi(T)$ of *APHF-CO* measured by an AC susceptometer is shown in Fig. 4a). $\chi(T)$ shows an abrupt increase near 19 K and saturates rapidly, reaching a near-constant value $\chi \sim 2.7$ emu/mol at 17 K. A peculiar feature of the material is that the critical temperature of the transition to a ferromagnetic state appears to decrease with time and eventually disappears after a year or so (Fig. 4b). Although this could be attributed to chemical instability, the fact that T_c decreases is not trivial: such degradation would be expected to lead to a lower magnetisation, but not to such a marked change in the critical temperature.

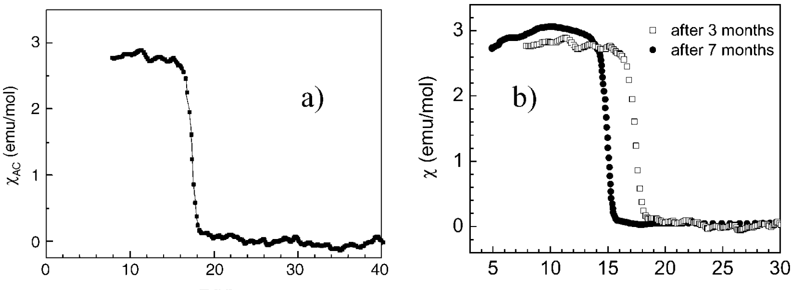

Fig. 4. a) The AC susceptibility χ_{AC} of *APHF-CO* as a function of temperature. b) χ_{AC} as a function of time after synthesis. T_c is clearly reduced with time

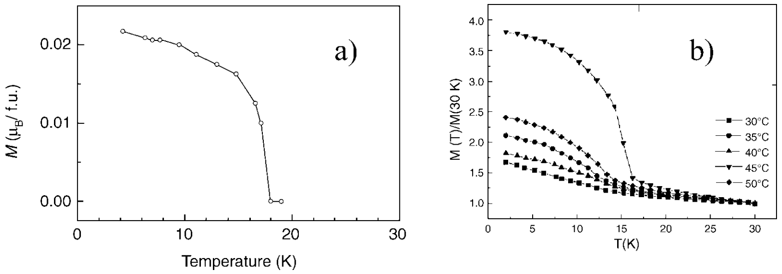

Fig. 5. a) The magnetisation of *APHF-CO* as a function of temperature measured by SQUID magnetometer. b) The magnetisation *M*(*T*) for *APHF-CO* synthesised at different temperatures. The highest *M* and T_c are achieved with synthesis at 45°C

It is an indication that the exchange coupling is strongly dependent on the structure and chemistry of the material.

The DC magnetization $\mathbf{M}(T)$ measured with a SQUID at $H = 30$ Oersted (Fig. 5a) also shows a rather characteristic rise below 18.5 K. The typical saturation moment of $\sim 0.021\,\mu_B$/f.u. measured by SQUID magnetometer (Figs. 5a and 6a) and $\sim 0.045\,\mu_B$/f.u. in AC magnetization measurements (Fig. 6b), shows that typically only a few percent of the sample is ferromagnetically ordered. The effect of synthesis temperature (at the doping stage) is shown in Fig. 5b. A temperature dependence of the magnetisation was measured in a static magnetic field of 50 Oe for five *APHF-CO* samples synthesised at five different temperatures between 30°C and 50°C. The magnetisation of the samples differs markedly both in magnitude and in critical temperature T_c. The magnetisation is highest when the synthesis is performed in the vicinity of 45°C and falls off rapidly on either side of that temperature. The critical temperatures range from 13 K and 17 K. The low-temperature magnetisation of the samples in a weak external field (the spontaneous magnetisation) can vary approximately by a factor of 3 among the different samples. The results shown are normalised by the value of magnetisation at 30 K (the temperature at which all samples were in the paramagnetic phase and so their magnetic moment at low temperature is directly proportional to the quantity of magnetic material present).

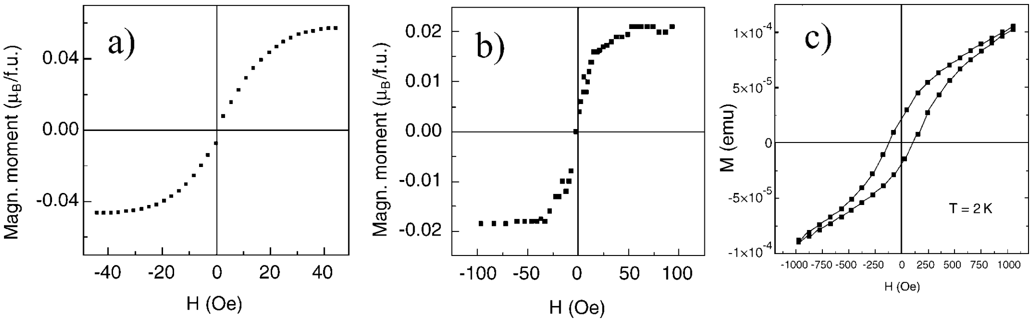

Fig. 6. The magnetisation curves of *APHF-CO* measured by a) AC susceptometer, b) SQUID magnetometer, c) SQUID measurement shows a hysteresis loop for samples synthesised under certain conditions (see text)

The magnetization curves measured directly using a SQUID magnetometer (Fig. 6b) and indirectly with an AC susceptometer and calculated from $M(H) = \int \chi_{AC}\, dH$ (Fig. 6a) both show complete saturation at $\mathbf{M} \sim 0.045\, \mu_B/\text{f.u.}$ at a relatively low field of $H = 40$ Oersted. These data appear to exclude the possibility of spin-canted antiferromagnetism, since application of higher fields above 40 Oe does not increase **M**, as expected for a proper ferromagnet.

In Fig. 6c we show the magnetisation data for *APHF-CO* synthesised by a different route [8] – for the sample with the highest low-field/low-temperature magnetisation, the magnetisation curve at 2 K in fields $-$ 1 kOe $< H <$ 1 kOe is shown. The magnetisation curve shows clear hysteretic behaviour with a coercitive field of $H_c \sim 100$ Oe, and a remanent magnetisation M_r which is about 0.1 per cent of the expected saturation magnetisation M_s. The magnetisation did not show saturation in fields up to 1 kOe. Repeating the measurement at 2 K up to fields of 50 kOe also did not produce saturation. A sample of approximate weight 10 mg and a molar mass of 1000 g/mol when magnetically saturated should have a magnetic moment of ~ 0.05 emu. The measured value in the highest experimentally accessible field is ~ 50 times smaller. Thus, in common with most other organic ferromagnets *APHF-CO* shows a very small, or no hysteresis, which is clearly very sample-dependent and is shown to depend on the synthesis conditions. The critical parameters determining this behaviour are not known at present.

In the X-band ESR spectra of *APHF-CO* above 26 K, a *single* strong symmetric line is observed with $g = 2.00$, whose intensity is consistent with one spin per formula unit, confirming the absence of spins on the donor. No other line is visible at high temperature, which indicates that there is no neutral $\text{Co}Cp_2$ with $s = 1/2$ present. The width of the ESR line decreases monotonically from 16 Oe at 300 K, to 2 Oe at 26 K, and shows no visible anomalies at intermediate temperatures. Below $T \sim 26$ K, an additional line appears, which grows in intensity upon reducing the temperature (Fig. 7). The susceptibility χ calculated from the intensity of this line is plotted as a function of T in Fig. 8. χ_0 shows a slight increase already at $T = 25 \sim 30$ K. In addition to the increase in static susceptibility, the T-dependent ESR line also shifts and broadens at low temperature. The shift in resonance field

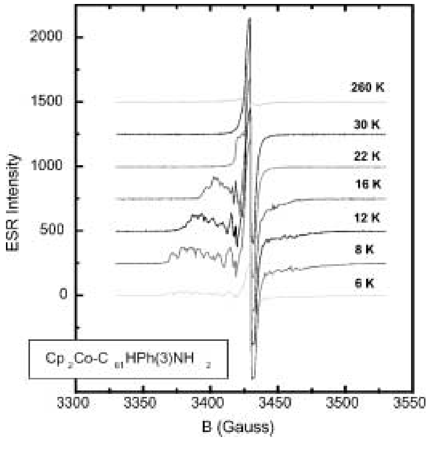

Fig. 7. The ESR signal of *APHF-CO* at different temperatures

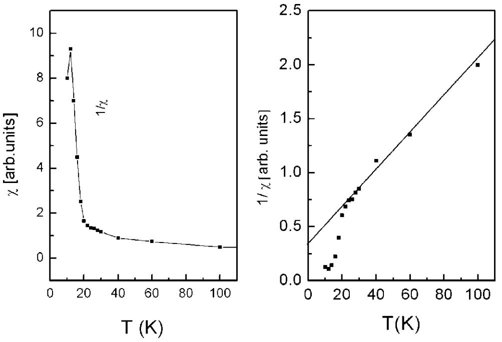

Fig. 8. a) The static susceptibility χ_0 as a function of T from the ESR intensity. b) The inverse susceptibility $1/\chi_0$ as a function of T shows a negative intercept implying AF spin correlations

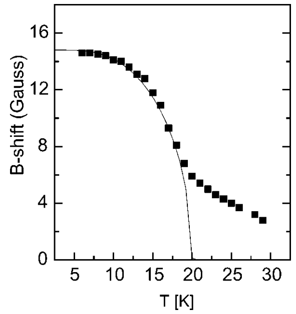

Fig. 9. The shift of the ESR resonance field with temperature is attributed to the existence of an internal field

(Fig. 9) is interpreted to be due to the appearance of an internal field below T_c. Although the broadening is difficult to measure accurately above T_c, a lineshift is clearly evident well above T_c, at least up to 30 K, which together with the increase in χ_0 could be interpreted as an onset of FM well above T_c. However, since no such increase in M or χ_{AC} is observed above T_c which are done at zero applied field, we attribute this effect to the external 3.4 kOe field of the ESR apparatus. (Such a field-induced enhancement in T_c and broadening of the transition is indeed expected for a ferromagnet.) The inverse ESR susceptibility ${\chi_0}^{-1}(T)$ of the FM line, shown as a function of temperature shown in Fig. 8b, suggests *Curie-Weiss* (*CW*) behavior above T_c with a negative temperature intercept of ${\chi_0}^{-1}(T)$ at $T \sim 30$ K. Below 26 K, χ_0 starts to depart significantly from the *CW* law, suggesting a changeover from AFM to FM spin correlations.

The low-temperature magnetic properties of 1-(3-nitrophenyl)-1*H*-methanofullerene C_{60} doped with cobaltocene (*NIPHF-CO*) are very similar to those of the amino compound. A measurement of the temperature dependence of the magnetization (Fig. 10) reveals an onset of the magnetic ordering at temperatures around 15 K. The magnetisation curve at 2 K (insert of Fig. 5) has non-linear behaviour with hysteresis which is narrower than in the amino compound but still clearly observable. Similarly as for the amino compound, M_s does not saturate in fields up to 50 kOe.

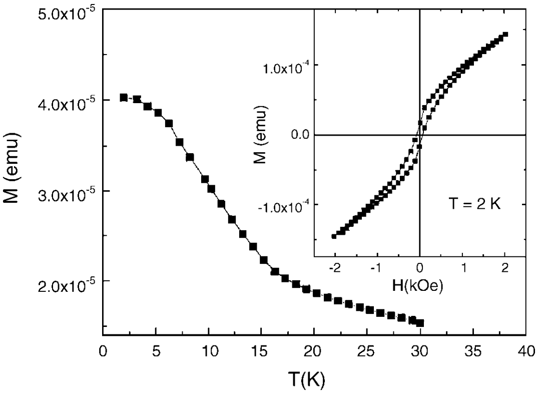

Fig. 10. The magnetisation $\mathbf{M}(T,H)$ as a function of temperature and magnetic field (insert) for *NIPHF-CO*

5. Discussion

There are some distinct and important differences in the magnetic behavior of *APHF-CO* compared to *TDAE*-C_{60}. First, *APHF-CO* shows a clear field-saturation of **M** below T_c in some samples, whereas *TDAE*-C_{60} powder samples typically do not show full saturation [14]. Secondly, the susceptibility χ_{AC} below T_c is temperature-*independent* in *APHF-CO* for $H = 0$, while *TDAE*-C_{60} shows a distinct spin-glass-like cusp at low temperatures [15] and finally in *APHF-CO* there is a conspicuous absence of anomalies in the ESR spectra for $100 < T < 200$ K which are a characteristic feature in *TDAE*-C_{60} [16]. Some of these effects in *TDAE*-C_{60} have been attributed to the molecular rotation of the C_{60} molecules [17, 18], which are believed to lead to a competition between spin-glass and FM interactions at low temperatures. *APHF-CO* and *NIPHF-CO* have inhibited rotational degrees of freedom because of the amino-phenyl or nitro-phenyl adduct, which may explain the absence of the glass-like behaviour and absence of anomalies related to the orientational ordering at intermediate temperatures.

To emphasize the importance of the structure for achieving a FM state, we mention that Co*Cp*$_2$ salts of *ortho*- *para*-isomers of *APHF* also exhibit a full CT and, judging by their vibrational, NIR and UV-Vis spectra compared to the *meta*-isomer, show no detectable difference in electronic structure. However, repeated attempts at obtaining a FM phase with these isomers have so far proved unsuccessful, the *ortho*- and *para*-isomers showing antiferromagnetic ordering down to 4 K.

The magnetic properties of *APHF-CO* and *NIPHF-CO*, such as the transition temperature, values of the spontaneous magnetisation and the coercive field strongly depend on the details of the preparation procedure, different for each material. The effect of ageing shown in Fig. 4b is particularly unusual and cannot be understood in a simple way. All samples studied so far show a characteristic low value of magnetisation and in some cases an absence of magnetisation. Further, the magnetisation curve is non-linear and hysteretic at low fields (few kOe) and linear at higher applied fields, but this linear part can be small and clearly depends on synthesis conditions. Full saturation has been obtained in *APHF-CO*, with a magnetisation which is saturated already in very low applied fields (< 50 Oe) but with no hysteresis. This was not found to be easily reproducible however. It is too early to speculate whether these compounds are proper ferromagnets with a full saturation of one μ_B per doped spin in crystalline form. In the case of *TDAE*C_{60} this was proven only after high quality single crystals were synthesized.

A systematic study of the choice of synthesis procedure of the fullerene based ferromagnets in correlation of their magnetic properties clearly shows that crystallisation conditions – for example temperature – play a crucial role in determining the magnetic properties.

To conclude, the saturation of the magnetization in both AC susceptibility and SQUID magnetization measurements together with infrared absorbance measurements enables us to classify *APHF-CO* and *NIPHF-CO* as π-electron molecular ferromagnets whose magnetic lattice is composed of single molecular species. *APHF-CO* and has the highest *Curie* temperature $T_c = 19$ K to date for this kind of compound. In contrast to *TDAE*-C_{60}, no spin-glass properties have so far been observed in these materials, but rather distinct characteristics of a proper soft ferromagnet. The antiferromagnetic nature of other cobaltocene doped isomers of *APHF* appears to suggest that the main challenge of synthesizing new organic FM compounds is related to achieving appropriate self-assembly of the D-A pairs into a molecular crystal structure favoring FM over AFM interactions at low temperatures.

6. Outlook

There are very good reasons for finding new organic ferromagnets with higher T_c. Organic materials in general do not require high-temperature synthesis and are soluble in organic solvents, making processing easier for magnetic storage media for example. Moreover they are very light, which makes them potentially very interesting for applications. At present it seems that molecular magnets utilising high spin states of transition-metal ions embedded in an organic matrix are more likely to meet that challenge than fullerene materials.

However, in spite of the fact that common knowledge supposes that the spin–spin interactions are weak in organic materials, there is no *a priori* reason to suppose that ferromagnetism in molecular organic materials based on fullerenes should exist only at low temperatures. The recent report of ferromagnetism at high temperatures in a fullerene compound [19] show that the aims of achieving high T_cs in fullerene-based ferromagnets may indeed be achievable.

The fundamental challenge remains of understanding a spin correlated state composed of entirely *p* electrons still remains. It is clear that a good understanding of the origin of the inter-molecular exchange interactions in disordered molecular materials is essential for designing new organic magnetic materials.

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