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Photosensitive magnetism of radicals coupled with carbon nanotubes

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Abstract

The magnetic coupling of spin-bearing moieties is a recurrent problem of molecular magnetism. We present electron spin resonance results showing that carbon nanotubes could serve this purpose. Moreover, the association of nitroxide radicals (TEMPO) with carbon nanotubes, either covalently or non-covalently, yields a material with slightly photosensitive magnetism. Wrapping a conjugated polymer (PmPV) [1] around the nanotubes increases the observed effect.
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1. Introduction

Molecular magnetism is a promising yet challenging field of research [1]. Molecules offer the enticing promise of a magnetic material possessing optical or electrical supplementary properties [2]. Some materials like Prussian blue analogues permit rational if not predictive synthesis [3,4], but in most cases serendipity is unfortunately the rule. Amongst untackled problems is the question of coupling between radicals, which ultimately governs the bulk behaviour. Intramolecular coupling is usually the fact of delocalised π electrons, whereas intermolecular coupling comes from short-range contacts between neighbouring molecules. As electrons in overlapping orbitals have a natural tendency to be antiparallel, antiferromagnetic interactions result in most cases of such contacts. High temperature ferromagnetism remains the holy grail for researchers in the field, the highest Curie temperature for an organic material being today 6.7 K [5]. This can certainly be ascribed to the lack of a good understanding on how intermolecular coupling works. Mixing of fullerene C_{60} with tetrakis(dimethylamino)ethylene has led to a crystalline complex exhibiting ferromagnetism below 16 K [6]. This result exemplifies the potential role of π electrons as transmitters of ferromagnetic exchange interaction in organic materials.

Single-walled carbon nanotubes (SWNTs) have original electronic properties because of their

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[1] Poly(m-phenylene-co-2,5-dioctyloxy-p-phenylene-vinylene). $M_w = 20000$ g/mol, $M_w/M_N = 2$.

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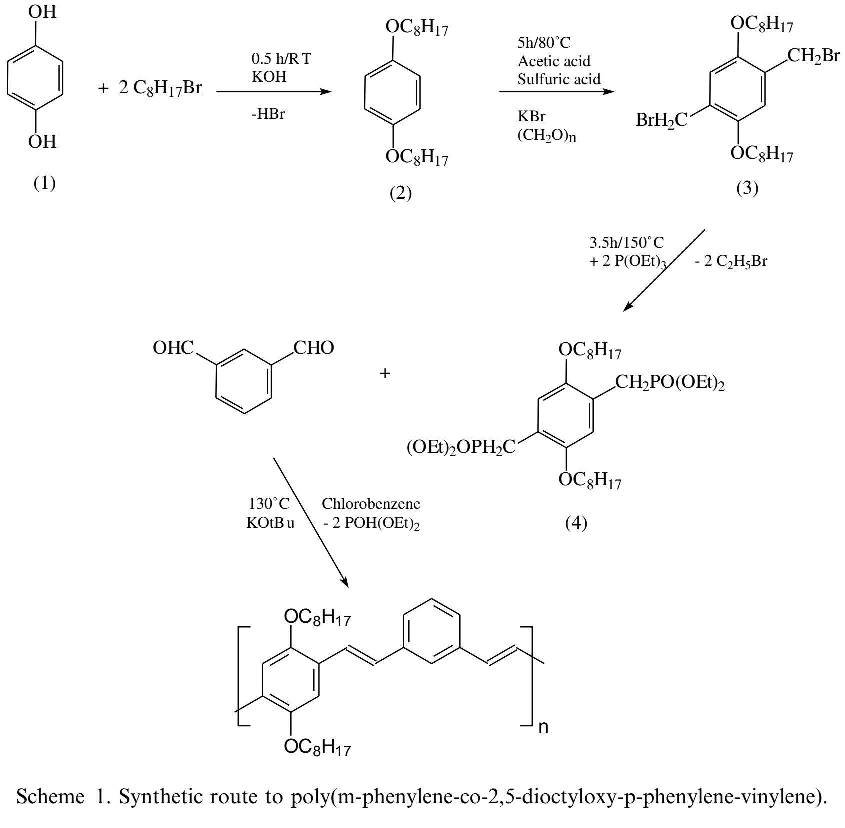
peculiar structure [7,8]. Based on this fact, some achievements have already been reported [9,10]. It has also been shown that nanotubes can coherently transport spin-polarized electrons over long distances (250 nm) [11]. In this context we decided to investigate SWNTs as magnetic couplers between radicals. The commercially available TEMPO radical (nitroxide family), chosen mainly because of its stability, has been easily grafted to SWNTs. As the first measurements had revealed some photosensitivity of the electron spin resonance (ESR) signal we tried wrapping conjugated polymers around the SWNTs, following the work of Star et al. [12]. These authors having shown that such a wrapping enabled the gating of the SWNTs conductivity, we saw a possibility of modifying the interradical coupling. Light switching of the intramolecular coupling of radicals has already been demonstrated but with photochromic couplers [13,14]. It will be seen below that associating PmPV to the SWNT-TEMPO system enhances the photosensitivity. Moreover, the photosensitivity is kept even when the radicals are not covalently attached to the nanotubes, which is surprising.

2. Experimental

Purified SWNTs (>95% weight) were used as purchased from MER Corp. (Tucson, AZ, USA). Free radical 4-amino TEMPO (4-amino-2,2,6,6-tetramethyl-piperidine-1-oxyl) has been used as purchased from Aldrich (97% pure). The polymer, (PmPV), was made by a Horner–Emmons polycondensation [15] of isopthalaldehyde and 2,5-di-n-octyloxy-1,4-xylene-bis(diethylphosphonate) in dry chlorobenzene (cf. Scheme 1). The phosphonate ester was prepared in a three-steps procedure [16]. First octyloxy side groups were introduced by a Williamson reaction of hydroquinone (**1**). The re-



Scheme 1. Synthetic route to poly(m-phenylene-co-2,5-dioctyloxy-p-phenylene-vinylene).

sulting 1,4-di-n-octyloxybenzene (**2**) was bromomethylated to give 2,5-di-n-octyloxy-1,4-bis(bromomethyl)-benzene (**3**) and this was converted to 2,5-di-n-octyloxy-1,4-xylene-bis(diethylphosphonate) (**4**) by an Arbuzov reaction with triethylphosphite.

Covalent grafting of the radicals to the SWNTs was a three-steps process. SWNTs were first cut and polished following the procedure of Liu et al. [17]. The carboxylic acid groups present at the ends of the tube after this step were then converted to the acid chloride by treatment with oxalyl chloride [18]. The final step consisted in reacting these functionalised tubes with 4-amino-TEMPO. Samples without covalent grafting of the radical to the nanotubes were prepared as follows: preparation of samples without polymer consisted in sonicating a mixture of SWNTs and TEMPO (10:1 by weight) in dichloromethane for ≈1 h. The solutions flocculated and sedimented rapidly. For the samples with polymer, PmPV was added to the solution before sonication (SWNTs and PmPV in equal amount). These suspensions were dark green in colour and stable for many days. Before performing ESR measurements (X band) under light irradiation, a few drops of either suspension were sprayed on fused silica plates and the solvent left to evaporate. Inside the ESR cavity the sample was irradiated with the light from a broad spectrum Hg lamp (Olympus). The light was fed into the cavity through a fused silica fiber and an anticaloric filter was placed in the light path. For low temperature measurements the tube containing the sample was placed in a stream of liquid helium. Temperature was not controlled for room temperature measurements but we checked with a miniature thermocouple that the sample did not get heated when irradiated with light.

3. Results and discussion

3.1. ESR of SNWTs with covalently grafted TEMPO radicals

The magnetic properties of the functionalised nanotubes have been probed using X-band ESR. The spectrum of a suspension in dichloromethane is given in Fig. 1. The room temperature spectrum exhibits the characteristic triplet of a nitroxide radical in solution, with a hyperfine constant $a_N = 15.5$ G. When the solution is brought to liquid helium temperature only a single line remains, with a Landé factor $g = 2.0078$ and the lineshape is Lorentzian. [2] These observations unfortunately imply that the radicals are either very weakly coupled, or that no coupling is present.

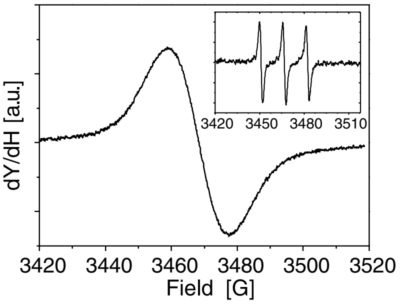


Fig. 1. ESR signal of SWNTs with covalently linked TEMPO radicals in frozen dichloromethane solution (4 K). Inset: room temperature spectrum showing the well-known nitroxide triplet.

Several reasons can be put forward which could explain this state of things. Let us start with the reasons that would impede the expected coupling. If this coupling of the radicals is to take place along the nanotube, then maybe the length of the tube exceeds some limit. In the case of di-radicals bond to classical molecules, the influence of the length of the coupler has been discussed [21] and intramolecular coupling at distances over 40 Å have been reported [22], but these systems are far too different from the one discussed here for any useful comparison to be made. The functionalisation of SWNTs occurs mostly at the ends [17,23] and to a lesser extent on the sidewalls [24]. It is therefore expected that radicals are essentially located in bunches near the extremities which can be ~100 nm to ~1 μm apart, depending on the synthesis of the nanotubes and of the subsequent treatments. In the present case, even though the conduction electrons can reach the ballistic regime

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[2] We did not observe any ESR signal for the pure nanotubes (solid state), neither at room temperature nor at 4 K, as did Bandow et al. [19] but contrary to the observations of Thess et al. [20].

[25], they do not seem to efficiently couple the radicals located at both ends. A finite size effect on the axial nanotube conductance [26] is not relevant here, as it would require an unrealistic uniformity in nanotubes lengths to be observed in our samples. If distance is a problem, one could then wonder why the radicals attached at one end—hence very close together—should not be coupled. Finite size effects on radial conductivity could interfere and here again prevent efficient coupling. This point could maybe receive confirmation from theoretical calculations. A more trivial reason could be that steric hindrance takes place at the extremities of the nanotubes and prevents the attachment of more than one radical. SWNTs have a typical diameter of 1–2 nm, an open end has therefore a perimeter of 3–6 nm. The TEMPO radical has roughly a diameter of 0.6 nm, small enough for several to fit at the end of a nanotube, but not all sites possess a –COOH group where a covalent bond can form.

It still cannot be totally excluded that some minor degree of coupling takes place. This fact is notably supported by our observation of a photosensitivity of the ESR signal (see below). This coupling could either be very small—hence hard to observe—because of the excessive length of the nanotubes, or it could also be that not all nanotubes are properly grafted with radicals. Consequently the big ESR signal coming from numerous uncoupled radicals would mask the small signal from a minority of coupled radicals.

It occurred to us during the course of the experiments that the ESR signal was light-sensitive. Fig. 2 shows the relative variation of the doubly integrated ESR signal as a function of light irradiation. Going from darkness to full light induces a small (2%), but clear and reproducible decrease of the signal. The ESR signal of the pure radical remained constant whether in dark or light, pure nanotubes did not give any ESR signal, neither in the dark nor in the light (see footnote 2). The area below the integrated ESR signal is a measure of the total number of spins present in the ESR cavity. The irradiation of the sample therefore causes a diminution of the number of single unpaired electrons in the sample. Two processes can be envisaged which would explain this observation: (1) the photoexcitation of the nanotubes promotes electrons in a higher energy level where they can pair with the single electron of a radical, therefore causing the loss of a spin, (2) two radicals couple with the mediation of a photoexcited nanotube, the pairing of the two single electrons again causes a diminution of the ESR signal. We currently are unable to tell which mechanism is the active one, both could even be acting simultaneously. The results of the experiments described in the next section nevertheless indicate that, rather than altering the coupling of radicals present at one end of a nanotube, light irradiation influences the coupling between both ends of a nanotube.

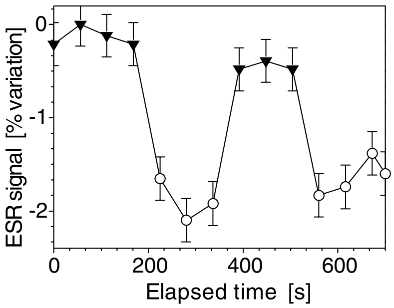

Fig. 2. SWNTs with covalently grafted radicals. Variation of the integrated ESR signal as a function of time under intermittent irradiation with light. (▼) in darkness, (○) under white light. The line is a guide to the eyes.

3.2. *ESR of polymer-wrapped SNWTs mixed with TEMPO radicals*

The paper of Star et al. gives evidence that wrapping a conjugated polymer such as PmPV around SWNTs provides a means of switching the conductivity of the nanotubes with light. Their results show that the photoexcited polymer, in intimate electrical contact with the nanotubes, bears a dipole moment that locally alters the electric field at the surface of the tubes. In view of this result it was interesting to check whether the same process would be efficient in our system in modifying the interradical coupling.

Fig. 3 gives a summary of the spectroscopic characterization of our systems. The absorption spectrum (inset in Fig. 3) of the polymer-wrapped

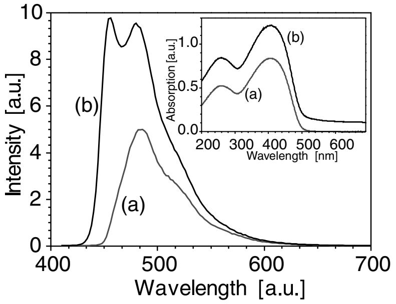

Fig. 3. Luminescence spectra of pure PmPV (curve a) and PmPV-wrapped nanotubes (curve b), in dichloromethane. The inset is a UV–VIS absorption spectrum of the same samples.

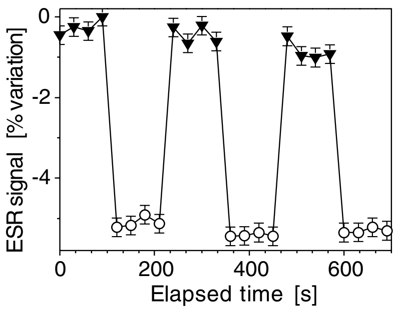

Fig. 4. PmPV-wrapped SWNTs with covalently grafted radicals. Variation of the integrated ESR signal as a function of time under intermittent irradiation with light. (▼) in darkness, (○) under white light. The line is a guide to the eyes.

nanotubes is almost identical to that of the pure polymer, except for an additional continuous background. We do not observe the considerable broadening of the bands reported by Star et al. Yet we are confident that there is indeed an interaction of the polymer with the nanotubes because of the observed changes in the luminescence spectra. As can be seen in Fig. 3, the pure PmPV spectrum has two broad bands centered at 480 and 520 nm, whereas the spectrum of the PmPV-wrapped nanotubes has an additional sharper band at 455 nm. Another proof of the efficient association of the polymer to the nanotubes is the increased solubility: when dispersed in dichloromethane pure nanotubes flocculate and sediment within a few minutes, whereas the polymer-wrapped nanotubes yield suspensions stable for many days.

We studied the photomagnetic properties of these samples either in frozen solutions or in solid state (films cast on fused silica plates). Both types of samples gave similar results, except for the response time which was faster in the solid state. Fig. 4 shows that modulating the light on such a sample induces a change in the integrated ESR signal which is roughly two times bigger than in the previous case of unwrapped SWNTs. This observation confirms that SWNTs actually couples radicals and that this coupling can be acted on, for example with light. We did check that the effect was not an artifact due to the light heating the sample. A miniature thermocouple showed to increase of the temperature (which would decrease the paramagnetic susceptibility, hence the ESR signal) of the sample under light irradiation, and in any case the ESR signal of the pure TEMPO radical remained constant when the light was turned on and off.

Rather surprisingly, if the ESR sample is prepared from a solution where the polymer, the nanotubes and the radicals are just mixed together (see experimental section) without covalent attachment of the radicals to the nanotubes, the same effect—although slightly smaller—is observed, as can be seen in Fig. 5. This unexpected behaviour is neither observed in SWNTs + PmPV mixtures nor in PmPV + TEMPO ones and is therefore due to the synergetic contribution of all three compounds. The following mechanism can be put forward as a working hypothesis. PmPV and nanotubes bind together, allowing for a stable suspension of SWNTs to form. This association makes the nanotubes sensitive to light variations

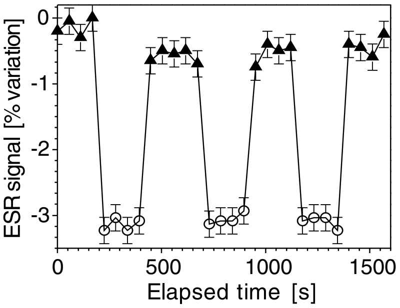

Fig. 5. PmPV-wrapped SWNTs mixed with radicals. Variation of the integrated ESR signal as a function of time under intermittent irradiation with light. (▲) in darkness, (○) under white light. The line is a guide to the eyes.

by a change in their electronic configuration. Because of their length, the nanotubes are certainly not entirely covered with polymer, so sections remain exposed. It has been observed that nanotubes have affinity for amides [27] and amines [28]. We can therefore reasonably assume that the 4-amino TEMPO has some natural inclination to interact with the nanotubes or at least that it can sit close enough for electron transfers to occur. Consequently, radicals stuck to a nanotube can be magnetically coupled and this coupling is light-dependent because of the conjugated polymer.

4. Conclusion

We have carried out a study of the magnetic properties of TEMPO radicals attached to or mixed with single wall carbon nanotubes. Our results show that SWNTs do magnetically couple the radicals, but no direct evidence could be obtained from the ESR lineshape that remains unchanged. Still, an indirect proof comes from the light-induced variations which have been observed on the integrated ESR signal. Wrapping a conjugated polymer around the nanotubes did not modify the magnetic behaviour, but did increase the efficiency of the response to light. Interestingly, the covalent attachment of the radicals to the tubes did not bring much of a difference as compared to the simple mixing up of the materials. We are currently investigating other polymers and radicals mixed and attached to nanotubes.

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References

[1] O. Kahn, Molecular Magnetism, Wiley-VCH, 1993.

[2] J.S. Miller, M. Drillon (Eds.), Magnetism: Molecules to Materials, Wiley-VCH, 2001.

[3] M. Verdaguer, Polyhedron 20 (2001) 1115.

[4] K. Hashimoto, S. Ohkoshi, Philos. Trans. R. Soc. Lond. A 357 (1999) 2977.

[5] A transition to a ferromagnetic state occuring at 6.7 K has been recently observed in a gallium salt complex: W. Fujita, K. Awaga, Chem. Phys. Lett. 357 (2002) 385.R;
See also Chiarelli, M.A. Novak, A. Rassat, J.L. Tholence, Nature 363 (1993) 147.

[6] B. Narymbetov, A. Omerzu, V.V. Kabanov, M. Tokumoto, H. Kobayashi, D. Mihailovic, Nature 407 (2000) 883.

[7] P.M. Ajayan, Chem. Rev. 99 (1999) 1787.

[8] C.N.R. Rao, B.C. Satishkumar, A. Govindaraj, M. Nath, Chem. Phys. Chem. 2 (2001) 78.

[9] H.W.C. Postma, T. Teepen, Z. Yao, M. Grifoni, C. Dekker, Science 293 (2001) 76.

[10] A. Bachtold, P. Hadley, T. Nakanishi, C. Dekker, Science 294 (2001) 1317.

[11] K. Tsukagoshi, B. Alphenaar, H. Ago, Nature 401 (1999) 572.

[12] A. Star, J. Fraser Stoddart, S.D.M. Diehl, A. Boukai, E.W. Wong, X. Yang, S.W. Chung, H. Choi, J.R. Heath, Angew. Chem. Int. Ed. 40 (9) (2001) 1721.

[13] K. Matsuda, M. Irie, J. Am. Chem. Soc. 122 (2000) 8309.

[14] K. Matsuda, M. Irie, J. Am. Chem. Soc. 122 (2000) 7195.

[15] H.-H. Hörhold, H. Rost, A. Teuschel, S. Pfeiffer, Synth. Met. 84 (1997) 269.

[16] A.P. Davey, A. Drury, S. Maier, H.J. Byrne, W.J. Blau, Synth. Met. 103 (1999) 2478.

[17] J. Liu, A.G. Rinzler, H. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, A. Lu, T. Iverson, K. Shelimov, C.B. Huffman, F. Rodriguez-Macias, et al., Science 280 (1998) 1253.

[18] J.E. Riggs, Z. Guo, D.L. Carroll, Y.P. Sun, J. Am. Chem. Soc. 122 (2000) 5879.

[19] S. Bandow, S. Asaka, X. Zhao, Y. Ando, Appl. Phys. A 67 (1998) 23.

[20] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, et al., Science 273 (1996) 483.

[21] M. Minato, P.M. Lahti, J. Am. Chem. Soc. 119 (1997) 2187.

[22] P. Wautelet, A. Bieber, P. Turek, J. Le Moigne, J.J. André, Mol. Cryst. Liq. Cryst. 305 (1997) 55.

[23] V. Georgakilas, K. Kordatos, M. Prato, D.M. Guldi, M. Holzinger, A. Hirsch, J. Am. Chem. Soc. 124 (5) (2002) 760.

[24] M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weiss, F. Jellen, Angew. Chem. Int. Ed. 40 (21) (2001) 4002.

[25] C.T. White, T.N. Todorov, Nature 393 (1998) 240.

[26] J. Wu, W. Duan, B.L. Gu, J.Z. Yu, Y. Kawazoe, Appl. Phys. Lett. 77 (16) (2000) 2554.

[27] K.D. Ausman, R. Piner, O. Lourie, R.S. Ruoff, M. Korobov, J. Phys. Chem. B 104 (38) (2000) 8911.

[28] Y. Sun, S.R. Wilson, D.I. Schuster, J. Am. Chem. Soc. 123 (2001) 5348.