Magnetic Communication through Functionalized Nanotubes: A Theoretical Study

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ABSTRACT

Functionalized nanotubes are good candidates to promote communication between paramagnetic centers at large distances through a highly delocalized $\pi$ system. Our study using theoretical methods based on density functional theory predicts the presence of surprisingly strong coupling at very large distances for this kind of system. To reach such strong couplings the system has to fulfill two conditions, the presence of highly charged metal cations and a metallic character of the nanotube.

The singular structural and electronic properties of nanotubes make them ideal candidates for their use in fuel cells, catalysts, and electronic devices.¹ Single-wall carbon nanotubes (SWNTs) have attracted an increasing interest in the field of molecular electronics since they provide unidimensional wires enabling the fabrication of a whole family of electronic devices.² ³ In addition, the functionalization of nanotubes opens up a wide variety of synthetic possibilities expanding the potential applications of the pristine nanotubes.⁴ ⁵ Probably, the best-known functionalization procedure for carbon nanotubes consists of their treatment with strong oxidizing agents, such as a HNO₃/H₂SO₄ mixture,⁶ that usually open the nanotube-generating carboxylato groups at the terminal carbon atoms. The presence of the carboxylato groups improves the solubility of the nanotubes and makes them amenable to chemical reactions characteristic of the functional group.⁷ These terminal carboxylato ligands can coordinate to metal complexes, as shown in the pioneering work of Wong et al. with [IrCl(CO)(PPh₃)₂].⁸ Even if the work in this area has focused so far only on diamagnetic metal atoms,⁵ the coordination to paramagnetic metal atoms would allow their application as magnetic devices. To make some progress in that direction, it is essential to investigate the ability of functionalized nanotubes to "communicate" two paramagnetic centers.⁹ During the last years several papers have been devoted to the electronic properties of nanotubes,¹⁰ and different procedures have been adopted for the separation of semiconducting and metallic SWNTs,¹⁰ but the exchange coupling using nanotubes as bridging ligands is still an unexplored field. The main goal of this paper is to study the magnetic properties of dinuclear metal complexes with semiconducting or metallic SWNT systems as bridges, using theoretical methods based on density functional theory.

During the last years, we have extensively studied the magnetic properties of transition metal complexes using theoretical methods based on density functional theory. Despite the small energy differences involved, the exchange coupling constants calculated using the hybrid B3LYP functional and Gaussian basis sets are in excellent agreement with the experimental data.¹¹ ¹² However, the application of such an approach to very large systems is not straightforward,¹³ ¹⁴ since these calculations are severely limited by the number of atoms, and molecules with 200—300 atoms can be handled only with a huge computational effort. To circumvent such a limitation, we have adopted recently an alternative approach that consists of using a computer code that employs numerical rather than Gaussian basis sets.¹⁵ ¹⁶ This difference, together with the inclusion of some approximations in the calculation of the Coulomb term and with the use of generalized-gradient approximation (GGA) functionals, results in a considerable reduction of computer time, thus allowing for the treatment of very large systems, such as an Fe₁₈ ferric wheel with 714 atoms.¹⁷ Although the results are not as accurate as those obtained with methods based on hybrid functionals, our experience indicates that the sign of the exchange coupling and the relative values of the different coupling constants are correctly reproduced.¹⁸ Hence, this numerical approach is especially appropriate to study the exchange interaction in a system with a large number of atoms, such as metal complex—SWNT systems that we explore here.

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Electronic structure calculations were performed using the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code. \(^{15,16,19,20}\) The generalized-gradient approximation (GGA) functional expression of Perdew, Burke, and Erzehof (PBE)\(^{21}\) was employed, and pseudopotentials were generated according to the procedure suggested by Trouiller and Martins\(^ {21}\) (see ref 22 for a more detailed description). We have employed a triple-\(\zeta\) numerical basis set with polarization functions for the iron and manganese atoms and a double-\(\zeta\) one with polarization functions for the other elements. The values of 50 meV for the energy shift and 250 Ry for mesh cutoff provide a good compromise between accuracy and the computational cost required to estimate the exchange coupling constants according to a previous study.\(^ {18}\) This approach provides good results despite the use of a GGA functional, which is well-known to give \(J\) values that are too large due to an overestimation of the spin delocalization,\(^ {23}\) because the use of pseudopotentials partially compensates this problem.\(^ {18}\) For the calculation of the exchange coupling constants, we have employed the Heisenberg Hamiltonian \(H = -J\hat{S}_1\hat{S}_2\), and a detailed description of the procedure used to obtain the exchange coupling constants can be found elsewhere.\(^ {23,24}\) The orbital and spin density plots were done using the Molekel code.

To study the exchange coupling between paramagnetic centers through nanotubes, we have selected one metallic (5,5) nanotube and one semiconducting (10,0) nonchiral nanotube combined with the Fe\(^ {III}\) and Mn\(^ {II}\) cations, both having a high spin d\(^5\) configuration. We added ammonia molecules to complete the coordination sphere of the transition metal atoms and assumed that the carboxylato groups act as chelating ligands. The models employed in the calculations are represented in Figure 1. We adopted tubes of finite length containing 146 and 142 carbon atoms to model the (5,5) and (10,0) nanotubes, respectively, saturating the dangling bonds with hydrogen atoms. Since a simple model based on the spin polarization of the \(\pi\) system of the nanotube would associate ferro- and antiferromagnetic interactions with odd and even number of atoms (spacers), respectively,\(^ {25}\) three different models can be selected in the case of the (5,5) nanotube to study such an effect (1–3) while, due to the chirality of the system, only one model can be drawn for the (10,0) nanotubes (4). The number of intervening carbon atoms is even for 1 and 3 and odd for 2 (Figure 1).

The calculated exchange coupling constants \(J\) for the Fe\(^ {III}\) systems are very similar for the three models, i.e., \(-208.9\), \(-204.1\), and \(-255.6\) cm\(^{-1}\) for 1, 2, and 3, with Fe–Fe distances of 24.7, 24.3, and 25.2 Å, respectively. The calculated \(J\) values indicate that these kinds of functionalized nanotubes are excellent bridges to communicate the two paramagnetic centers, taking into account that the Fe–Fe distance is around 25 Å. However, we must pay attention to the fact that in all cases the coupling is antiferromagnetic regardless of the number of spacers in the exchange pathway. In previous studies, we found a strong dependence of the exchange coupling with the oxidation state for some dicyanobenzene compounds.\(^ {26}\) Hence, we have performed the same calculations with the isolectronic Mn\(^ {II}\) cation, obtaining very weak coupling with \(J\) values of \(-4.8\) and \(-0.9\) cm\(^{-1}\) for 1 and 2, respectively, showing that an increase in the metal oxidation state favors the mixing of the d orbitals with the \(\pi\) system of the bridging ligands, thus enhancing the antiferromagnetic character of the exchange coupling.

A question that arises from these results is, which is the dependence of the exchange coupling on the length of the nanotube. In search of an answer, we have performed calculations for analogues of 3 with nanotubes that have two and four times its length, still obtaining \(J\) values of \(-108.3\) and \(-89.0\) cm\(^{-1}\), despite the very long Fe–Fe distances of 42.0 and 76.1 Å, respectively. Hence, there seems to be an exponential dependence of the \(J\) value with the distance but a relatively strong exchange coupling remains at very long distances, as shown by the \(J\) value obtained for the longest nanotube with 576 carbon atoms.

On the other hand, we selected the (10,0) nanotube as an example of a semiconducting nanotube. As mentioned above, due to the chirality of the (10,0) nanotubes, it is not possible to build up a model with an odd number of atoms in the exchange pathway (4). In this model the distance between...
the two Fe$^{III}$ cations is 21.31 Å and the calculated coupling constant is $-115.7 \text{ cm}^{-1}$. This value is significantly smaller than those obtained for the (5,5) nanotube complexes (but still large and negative) suggesting that the metallic nanotubes are more efficient in communicating the paramagnetic centers than the semiconducting ones, a point that will be discussed below.

To understand the influence of the electronic structure on the magnetic coupling found above, we have analyzed the interaction between the orbitals of the Fe$^{III}$ cation and those of the functionalized nanotubes. According to Figure 2, the main changes upon metal–ligand interaction in the case of the ferromagnetic solution of model 2 (called hereafter 2–Fe (FM)) are as follows: (i) the presence of a significant contribution of the $\beta$-Fe$^{III}$ d orbitals below the Fermi level (around $-7.2 \text{ eV}$) that empty some $\pi$ bonding orbitals of the nanotube, thus inducing the presence of positive spin density along the nanotube, as seen from the shape of the plotted orbital, (ii) The mixing of the $\alpha$-Fe$^{III}$ d orbitals with the $\pi$ system of the nanotube appears in many molecular orbitals between $-10$ and $-12 \text{ eV}$ (see, e.g., the extensive mixing in the molecular orbital shown in Figure 2). This interaction broadens the peaks corresponding to the d orbitals and is responsible for the spin delocalization. The interaction is stronger in the case of the Fe$^{III}$ model than for the Mn$^{II}$ one where sharper peaks corresponding to the interacting d orbitals appear between $-7$ and $-4 \text{ eV}$ in a region close to the Fermi level of the nanotube with a low density of states of the $\pi$ system. The weaker interaction of the Mn$^{II}$ ion with the nanotube and the larger delocalization in the Fe$^{III}$ complexes is also reflected in the atomic spin density values of 4.6 and 3.8 e$^{-}$ for Mn$^{II}$ and Fe$^{III}$ cations, respectively. A comparative study of the position of the peaks corresponding to the interacting $\alpha$-Fe$^{III}$ d orbitals between metallic and semiconducting nanotubes (see Figure S1, region between $-10$ and $-12 \text{ eV}$, Supporting Information) indicates a larger down-energy shift for the metallic ones and, consequently, a larger interaction that explains the stronger antiferromagnetic coupling. Preliminary results in chiral semiconducting (8,4) and metallic (8,2) nanotubes show the same trend, a larger antiferromagnetic interaction in the metallic nanotube. It is worth noting stronger interactions in the nonchiral nanotubes probably due to a larger delocalization along the exchange pathway.

From the results presented above, a point that deserves a closer look is the predominant mechanism of spin density distribution in such models$^{28}$ and, consequently, why the Fe$^{III}$ model with an odd number of spacers in the bridging ligand is antiferromagnetic. To clarify this point, we plot first the spin density distribution for a model containing only one paramagnetic center with the metallic (5,5) nanotube (see Figure 3). Two main features can be extracted from the analysis of the spin density of such a model: (i) the existence of a relatively strong spin delocalization in some carbon atoms along the nanotube resulting in larger positive values than the negative ones, mainly due to the two interactions between the Fe$^{III}$ d orbitals and $\pi$ system of the nanotube observed previously in the analysis of the density of states (Figure 2) and (ii) the presence of spin polarization along the nanotube, as clearly shown by the sign alternation at the carbon atoms of the nanotube. These two effects are summarized in Scheme 1.

Spin density plots for some selected dinuclear complexes are collected in Figure 4. It is worth noting that an antiferromagnetic distribution described with a single-determinantal wave function does not correspond to a spin state...
of the system; however, those corresponding to the models 1–4 present, as expected, alternating signs of the spin density (see Figure S2, Supporting Information). Hence, we will focus our analysis on the ferromagnetic distributions. The spin distribution corresponding to the ferromagnetic solutions of the FeIII models (1–Fe (FM) and 2–Fe (FM), Figure 4) shows for 1 a positive spin density in practically all the carbon atoms of the nanotube, for 2 only alternate atoms have a significant positive spin density, and for the other atoms it is smaller or negative. Such spin distributions can be understood as the result of the superposition of the spin density of the two models with only one iron atom (Figure 3) where the positive spin values in the carbon atoms are larger than the negatives ones due to the presence of some degree of spin delocalization, derived from the two FeIII–nanotube interactions detected in the analysis of the density of states (Figure 2).

In the 1–Fe (FM) case, due to the even number of carbon atoms in the pathway, there is a “destructive” combination of the spin densities from the two iron atoms, resulting in a positive value for most carbon atoms (see Scheme 2 for a simplified smaller model). This fact is due to the larger positive spin densities from delocalization of two iron cations with the same spin in the nanotube than the negatives ones induced by the polarization mechanism (see Figure 3, 1–Fe (FM) and Scheme 1). For model 2, with an odd number of atoms in the exchange pathway, the situation is the opposite, i.e., there is a “nondestructive” combination that enhances the positive values in alternate atoms, because of the large delocalization (see Scheme 2). However, for the same model with MnII cations, we find sign alternation between neighboring carbon atoms (see Figure 4, 2–Mn (FM)). The reason for the different behavior is the larger delocalization of the FeIII systems in comparison with the MnII case, which can be attributed to the higher charge of the FeIII cations producing a larger mixture of the d orbitals bearing the unpaired electrons with the π system of the nanotube. This effect is also shown by the smaller spin density values along the nanotube for the MnII complex than for the FeIII ones. The presence of this larger delocalization in the FeIII systems gives a strong interaction between the two paramagnetic centers resulting in an antiferromagnetic interaction in all cases, independently of the number of atoms in the exchange pathway. Consequently, in all the FeIII systems the exchange coupling is strongly antiferromagnetic while in the MnII ones it is almost negligible due to a poor spin delocalization.

The spin density distribution for the ferromagnetic solution of the functionalized (10,0) semiconductor nanotube (Figure 5) highlights a different behavior from that obtained with the metallic (5,5) nanotube (Figure 4, 1–Fe (FM) and 2–Fe (FM)) showing now a decay of spin density with the distance to the metal. The lesser delocalization of the spin density is probably due to a weaker interaction between the FeIII d orbital and the π system of the nanotube than for the metallic nanotubes, as we have seen above.

In summary, the calculated exchange coupling constants for the metal-functionalized SWNTs show that very strong coupling can be obtained at very large distances between
the paramagnetic centers. Two key parameters control the strength of the coupling, the oxidation state of the metal cations, and the metallic nature and chirality of the nanotube. A higher oxidation state of the cation results in stronger interactions of the Fe d orbitals with the $\sigma$ system of the nanotubes producing a large spin delocalization. Hence, the calculated $J$ values for the Fe$^{III}$ complexes are 2 orders of magnitude larger than those of the Mn$^{II}$ ion, even if both have a d$^5$ electronic configuration. For the same reason, the Fe$^{III}$ complexes, independent of whether the number of semiconductor (10,0) nanotube of a similar length. The (5,5) nanotube are approximately twice those obtained for a semiconductor (10,0) nanotube of a similar length. The calculated coupling constants of the functionalized metallic (5,5) nanotube are approximately twice those obtained for a semiconductor (10,0) nanotube and for the equivalent model of the semiconducting $\alpha$-Fe d orbitals or the iron atoms of the 2-Fe model with the metallic (5,5) nanotube and for the equivalent model of the semiconducting (10,0) nanotube and representation of the spin distributions for some metal complex-(5,5) SWNT models. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information Available: Representation of the density of states corresponding to the $\alpha$-Fe d orbitals or the iron atoms of the 2-Fe model with the metallic (5,5) nanotube and for the equivalent model of the semiconducting (10,0) nanotube and representation of the spin distributions for some metal complex-(5,5) SWNT models. This material is available free of charge via the Internet at http://pubs.acs.org.

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