Magnetic and Electrochemical Properties of a Diradical TEMPO-substituted Disulfide in Solution, Crystal and on Surface.


Abstract: We report a study of the magnetic and electrochemical properties of a diradical TEMPO-substituted disulfide in three different environments: in solution, crystal and as a SAM on Au(111) substrate and explore the relationship between them. In solution, this flexible diradical shows a strong spin exchange interaction between the two nitrooxides that depends on the temperature and solvent. Structural, dynamical, and thermodynamical information are extracted from the EPR spectra of this dinitroxide. The magnetic interactions in the crystal include intra- and intermolecular contributions, which have been studied separately and shown to be antiferromagnetic in both cases. Finally, we demonstrate the magnetic as well as the electrochemical properties are preserved upon the chemisorption of the diradical on the gold surface. The resulting SAM presents anisotropic magnetic properties; and angle-resolved EPR spectra of the monocrystal enabled us to make a rough determination of the orientation of the molecules in the SAM.

Introduction

The spin-spin interactions between unpaired electrons in organic diradicals (and polyradicals) are of crucial importance in many areas such as organic magnetism,[1−3] molecular charge transfer,[4] and multiple spin labeling in structural biology.[5] When unpaired electrons are in close proximity, the dominant interaction is likely to be the electron spin-spin exchange coupling, which is the basis for bulk magnetic phenomena. In flexible di- or polyradicals spin exchange coupling is mainly mediated by intramolecular nitroxide collisions.[6,7] However, polynitroxide with rigid scaffolds, which are too constrained to allow intramolecular nitroxide collisions, can also show spin exchange coupling by through-bond and/or through-space mechanisms.[8]

Among organic radicals, nitroxides have the advantage that they are stable under ambient conditions and can be easily synthesized, functionalized, and manipulated. Nitroxide radicals have been widely used as probes of molecular dynamics, including motion of spin labels on polymers and biomolecules, as probes in membranes, and providing details of molecule tumbling in liquids.[9] Dir- and poly-nitroxides have shown improved properties with respect to mononitroxides as contrast agents in magnetic resonance imaging (MRI),[10] or radiation protectors during brain radiotherapy.[11] When used as electron spin agents for dynamic nuclear polarization (DNP), dir- or poly-nitroxides can enhance the sensitivity of nuclear magnetic resonance signals by several orders of magnitude.[12] The origin of magnetic interactions in dir- and poly-nitroxides can be intra- and/or intermolecular, i.e. between the radicals of the same molecule and/or radicals anchored to different molecules. Such magnetic interactions can be either ferromagnetic or antiferromagnetic, depending upon the topology and conformation of the coupling pathway connecting the radicals.[1,2,3,13,14] It is very important to differentiate between these two interaction pathways in polyradical systems as the net magnetic behavior and hence their properties could be entirely different[13,15] influencing in many kinds of applications.[10,16,17,18,19]

We thought interesting to study the flexible TEMPO-substituted disulfide diradical 3 (Scheme 1) under different constrains and environments like in solution and in crystal as well as when it is grafted on gold surfaces in order to determine if the resulting supramolecular assemblies confer new properties to the systems. Here, we report a comparative study of disulfide 3 properties in four distinct environments: (i) in a fluid solution where conformational flexibility and intramolecular collisions determine the spin exchange, (ii) in a single crystal where molecular alignment makes it possible to accurately measure anisotropic magnetic properties, (iii) in a SAM on a flat Au(111) surface where magnetic interactions are determined by the packing of the molecules in two dimensions, and (iv) in a SAM on the surface of Au NPs where packing density is reduced due to high curvature. Supramolecular assemblies of nitroxide radicals have been built using a range of different scaffolds such as polymers,[20] dendrimers,[7] calix[4]arenes,[8] flat metallic surfaces,[21] or nanoparticles.[22] Gold nanoparticles (Au NPs) functionalized with organic radicals were first reported in 2002, using the stable diradical TEMPO-substituted disulfide[3] as electron spin agents for dynamic nuclear polarization (DNP),[23] or radiation protectors during brain radiotherapy[24]. These spin-labelled nanoparticles were prepared via the exchange reaction of Au NPs protected by n-butylthiol ligands with disulfide 3.[25,26] However, the properties of disulfide 3 anchored to a 2D Au(111) substrate forming a SAM, in the solid state, have not been explored yet. Only few works of TEMPO SAMs on gold are described in the literature, where the kinetics of the functionalization of gold,[27] the distribution of...
electroactive centers on the surface and the electrocatalytic activities toward primary alcohols oxidation were reported. All these works are based on electrochemical studies.

Of particular interest is the deposition of organic radicals (e.g., nitroxides) on surfaces as SAMs since it makes them magnetically responsive. Such hybrid inorganic-organic systems offer suitable platforms to study the influence of the surface on the paramagnetic species as well as the intermolecular interactions present between radicals. On the other hand, nitroxides are electroactive, yielding reversibly the corresponding oxoammonium cation by electrochemical oxidation. Therefore, the chemisorption of diradical 3 on Au(111) substrate as a SAM could provide a hybrid material showing a combination of magnetic and electrochemical properties with potential use in electronic devices such as nonvolatile memory device.

Results and Discussion

Synthesis

Disulfide 3 was synthesized using Steglich conditions. 3,3'-dithiopropionic acid 1 was coupled with 4-amino-TEMPO 2 using DCC/DMAP, obtaining a 37% yield (Scheme 1).

![Scheme 1. Synthesis of disulfide 3 using Steglich conditions.](image)

Structure and magnetic properties of diradical 3 in the solid state

Single crystals of diradical 3 were grown from CH₂Cl₂/toluene and used for X-ray analysis. The data collection conditions and parameters of refinement process are listed in Table S1. The molecular conformation and packing of diradical 3 are described in Supporting Information.

We performed the EPR analysis of a single crystal of compound 3 with external magnetic field aligned along each of the three directions of the crystal (a, b and c, Figure 1). When the monocystal was in a vertical position in the holder and at 0°, the magnetic field was parallel to the b axis (Figure 1, upper spectrum), at 90° to the a axis (Figure 1, middle spectrum) and when the crystal was in a horizontal position at 0°, the field was parallel to the c axis (Figure 1, lower spectrum). A Lorentzian line was observed when the static field was along the b axis (g = 2.0092; ΔHpp = 11.6 G) and when it was along the a axis (g = 2.0062; ΔHpp = 12.7 G) whereas when the static field was parallel to the c axis, significant broadening of the signal was observed (g = 2.0031; ΔHpp = 22.5 G). Interestingly, the g values obtained in the three directions (2.0092, 2.0062 and 2.0031) coincide exactly with the g values of a TEMPO radical unit (2.0090, 2.0060 and 2.0027, see Figure 2). Therefore, each of the three TEMPO axis of all the TEMPO units inside the bulk crystal should be oriented parallel to one of the three directions of the crystal. The N-O axis of all TEMPOs should be parallel to the b axis of the crystal, the axis passing through the centre of the six-membered ring parallel to the c axis of the crystal, and the third axis across the ring to the a axis of the crystal. We used the same nomenclature for the crystallographic axis and the TEMPO molecular axis.

Another feature determined by EPR is that the main axis of growth or packing of the molecules inside the crystal is the c axis (whereas the longest crystallographic axis of the unit cell is the a axis). In order to develop understanding of the crystal growth and verify these features, a morphology prediction of diradical 3 crystal was proposed using the molecular modeling software Materials Studio. The aim of morphology prediction is to simulate the habit of a single crystal of a crystalline material using its internal crystal structure via molecular modeling-based simulation techniques. We used Bravais-Friedel Donnay-Harker, BFDH Method and Growth Morphology Method. The BFDH laws are based on the crystal lattice and space group symmetry to generate an ordered list of possible growing faces versus their appearance importance and their relative growth rate. The Growth Morphology Method considers the role of intermolecular forces in crystallization and tries to find relations between crystal structure and crystal morphology on an energy basis. It attempts to provide a rough estimate of a generic morphology determined by the interactions between the molecules in the crystal. Before performing any morphology prediction that involves energetic considerations, it is very important to select an appropriate energy expression and verify that it is able to accurately describe the crystal cell parameters, the molecular fragments and the intermolecular interactions in the crystal. In this case, five available force fields were tested: COMPASS, COMPASS 26, COMPASS 27, Universal, and Dreiding. The cell parameters predicted by geometry optimization with the different force fields are presented in Table S2 along with the errors in reproducing the experimental values. The best job in reproducing the experimental cell of diradical 3 was done by Dreiding and COMPASS 27. Both the BFDH Method and the Growth Morphology Method using the two best force fields indicated that the c axis was intrinsically the fastest growing direction and predicted similar morphology. However, the orientation of the molecules along the a and c axes of the crystal was better reproduced in the BFDH method.
Method. Figure 3 presents the optimized cell using BFDH Method. For the optimized cell by means of the Growth Morphology Method using Dreiding and COMPASS 27 force fields see the Supporting Information. The strong intermolecular N–H⋯O hydrogen bonds make the crystals grow in that direction. The simulation of the packing of the molecules in the crystal and the prediction of the crystal elongated along the c axis are in good agreement with the EPR data obtained. The predicted morphology was in quite good agreement with the experimental morphology.

**Figure 1.** Top: three axes of the monocrystal of diradical 3. Bottom: EPR spectra of the monocrystal of diradical 3 in the three directions of the crystal (a, b, and c). We used the same nomenclature for the crystal axis and the crystallographic axis.

**Figure 2.** g anisotropy of TEMPO radical. We used the same nomenclature for the TEMPO molecular axis and the crystallographic axis.
Figure 3. Theoretical simulation of crystal growth of diradical 3 by means of BFDH Method.

We also performed several rotations of the single crystal inside the EPR cavity at different angles, both with the monocrystal in a vertical and a horizontal position on the holder from 0 to 360° (every 45°) to collect EPR data from intermediate directions of the molecules inside the crystal (Figure 4 and 5, respectively). When the monocrystal is in a vertical position on the holder, the $g$ value varies from 2.0092 (parallel to $b$ axis) to 2.0062 (parallel to $a$ axis) and the width of the EPR signal is very similar. By contrast, when the monocrystal is in a horizontal position on the holder the width of the signal changes significantly when turning the crystal from $g = 2.0031$ (parallel to $c$ axis) to $g = 2.0063$ (parallel to $a$ axis) (Figure 5), indicating an important anisotropy in these directions.

The magnetic properties of a polycrystalline sample of diradical 3 were investigated by SQUID magnetometry in the temperature range 2-300 K. The temperature dependence of the molar magnetic susceptibility $\chi_M$ is given in Figure 6. The $\chi_M T$ value of 0.75 cm$^3$Kmol$^{-1}$ at 300 K corresponds to the expected contribution of two noncorrelated $S = \frac{1}{2}$ spins. The $\chi_M T$ value remains constant from 300 K to ca. 80 K and then decreases sharply. This behaviour is indicative of antiferromagnetic interactions between the spin carriers. The $\chi_M T$ vs $T$ curve fit gives $\theta = -10.4 \pm 0.35$ K (see the Supporting Information). When disulfide 3 was anchored onto Au NPs forming high coverage of radicals on the surface, antiferromagnetic interactions were also present and dominant but a contribution of ferromagnetic ones at low temperature was also observed.

Taking into account the packing of the X-ray crystal structure, the unpaired spins on TEMPO groups are coupled antiferromagnetically probably through the TEMPOs oriented antiparallel along the $c$ axis from different columns (Figure S2), which correspond to the shortest distance between two N-O units.
Spin exchange in solutions of diradical 3

The EPR spectrum of monoradical 2 (Scheme 1) in toluene solution showed three lines with relative intensities 1:1:1 from the coupling of the unpaired electron with the $^{14}$N atom$^{[39]}$ and this pattern was independent of the temperature (see Figure S3). In contrast, the EPR spectrum of diradical 3 shows five lines, indicating that there is a strong intramolecular spin exchange interaction $|J| >> |a_N|$ between the two nitroxides.$^{[24,25b,25c]}$ In addition, the relative intensity and linewidths change upon cooling from 380 to 240 K (Figure 7). This clearly shows that the intramolecular exchange interaction is modulated by the temperature.

In flexible diradicals like 3, magnetic exchange interactions $|J|$ critically depends on the frequency of collisions of the spin-bearing functional groups.$^{[40]}$ Consequently, the EPR spectra are dependent on the conformational space that can be accessed the two nitroxides, and the relative energies of the effective conformations and the rates of conformational changes. The EPR spectra are thus affected by the temperature, viscosity and the nature of the solvent. In the case of a flexible N-containing diradical, with only a through-space spin exchange mechanism between the two radicals, we may have two limit cases: a) In conformations with the two nitroxides far away from each other (“far” conformation) with a magnitude of $J$ smaller than the hyperfine coupling constant with nitrogen nuclei, $a_N$, i.e. $|J| << |a_N|$, where the spectrum of the biradical is similar to that of two independent monoradicals exhibiting three lines separated by the hyperfine coupling constant $a_N$ with relative intensities of 1:1:1. b) In conformations with the two nitroxides close to each other (“close” conformation) and therefore $|J| >> |a_N|$, the spectrum consists of a five-line hyperfine pattern with $a_N/2$ separations between the lines and relative intensities of 1:2:3:2:1. Commonly, the dynamics of thermally activated intramolecular electron-spin exchange in flexible nitroxide biradicals in low viscosity solutions are simulated in terms of this three-conformation model (or the cage model),$^{[6]}$ firstly proposed by Luckhurst$^{[41]}$ and further developed by Parmon et al.$^{[42]}$ where three main molecular states are considered: conformation A, $|J| << |a_N|$ or $|J| = 0$ and two other conformations (B and C), where the radical centers are exchange coupled. This is necessary to explain the deviation of the relative intensities in the hyperfine pattern (e.g. from the 1:2:3:2:1 ratio) when the widths of all lines become equal. However, the spectra of diradical 3 in toluene are simpler and can be explained by the co-existence of just two conformations: one with $|J| >> |a_N|$, and another one with $|J| << |a_N|$, with different rates of interconversion between them. This is the minimum number of effective conformations that is sufficient to adequately describe the lineshape, corresponding to the two limiting cases described above.

At 380 K (Figure 7), the rate of interconversion between the two conformations is fast and hence the frequency of radical collisions is high. In these conditions, the electron-spin exchange interaction is rapidly modulated (fast exchange, $|J| >> |a_N|$), and we are very close to the fast exchange limit$^{[43]}$ because the spectrum shows five lines with almost identical linewidth and close to the 1:2:3:2:1 intensity ratio. As the temperature is gradually lowered from 380 to 240 K, the alternate (2nd and 4th) lines broaden and disappear. At low temperatures, molecular motions slow down and hence the rate of interconversion between effective conformations becomes slow. At 240 K the frequency of collisions is very low and the spectrum is not affected by spin exchange interactions showing only three lines with 1:1:1 relative intensities.
The EPR spectra of diradical 3 were simulated using a two-conformation model from the Quantum Chemistry Program Exchange package. This program simulates the exchange-broadening of isotropic EPR spectra and is restricted to intramolecular exchange. First-order rate constants for the thermally activated process were extracted by fitting the experimental EPR spectra (Figure 7). The simulation led to a linear Arrhenius plot over the 240–380 K temperature range (see Figure S4), which gave the activation parameters: $E_{a} = 2.97 \text{kcal.mol}^{-1}$; $\log A = 10.03 \text{ (} \Delta G_{300K} = 5.7 \text{kcal.mol}^{-1}; \Delta H = 2.37 \text{kcal.mol}^{-1}; \Delta S = -11.1 \text{cal.K}^{-1}.\text{mol}^{-1}).$ The value of $\Delta H$ is positive, which means that the transition from the “far” to the “close” conformation is endothermic and the conformation in which radicals do not interact is consequently more stable. Taking into account the crystallographic data, a plausible conformation of the “far” conformation (in which radicals are not colliding) could be compatible with the syn-like conformation observed in the x-ray crystal structure. In this conformation the radical units are not pretty close to each other to lead spin exchange coupling by collision, and the interspin distance is about 8 Å, which implies a distance too large to observe spin exchange coupling mediated through-space. Thus, the proposed conformation is compatible with the lack of spin exchange interaction observed ($|J| << |\Delta m| \text{ or } |J| = 0$) neither by intramolecular collisions nor through-space. This conformation is also proposed to be adopted in frozen solution because of the detection of half-field $|\Delta m_s| = 2$ transition (see below). A schematic representation of the dynamic process between the “far” and “close” conformations could be the one represented in Scheme 2.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>1.3x10$^9$</td>
</tr>
<tr>
<td>260</td>
<td>9.6x10$^8$</td>
</tr>
<tr>
<td>280</td>
<td>7.1x10$^8$</td>
</tr>
<tr>
<td>300</td>
<td>5.3x10$^8$</td>
</tr>
<tr>
<td>320</td>
<td>3.9x10$^8$</td>
</tr>
<tr>
<td>340</td>
<td>2.9x10$^8$</td>
</tr>
<tr>
<td>360</td>
<td>2.1x10$^8$</td>
</tr>
<tr>
<td>380</td>
<td>1.2x10$^8$</td>
</tr>
</tbody>
</table>

**Figure 7.** Experimental (left) and simulated (right) EPR spectra of diradical 3 at different temperatures in toluene at 5x10$^{-4}$ M. $k$ value is the frequency of collisions between both radicals.

![Scheme 2](image-url)
In frozen solutions, the EPR spectra are sensitive to the dipole-dipole interaction between the neighbouring nitroxides which substantially alters the shape of the spectrum. The empirical ratio of peak heights $d_1/d_2$ (Figure S5) is a measure of the strength of the dipolar interaction.\textsuperscript{25b} The spectrum of diradical 3 at 120 K (Figure S6) shows significant contribution of electron-electron dipolar interaction because the $d_1/d_2$ parameter is 0.75, while for monoradical 2 $d_1/d_2 = 0.53$ is found (Figure S5).\textsuperscript{25b} Moreover, under these conditions, a $|\Delta m_s| = 2$ (half-field) transition was observed for diradical 3. The observation of a half-field transition is characteristic of dipolar coupled spins\textsuperscript{46} and gives direct evidence for the presence of a triplet state. In order to establish if the origin of such interaction was intra- or intermolecular, we made an EPR concentration study. A series of EPR spectra of diradical 3 at different concentrations, from $10^{-2}$ M down to $5 \times 10^{-4}$ M, were recorded at 120 K (Figure 9). We observed transitions at half-field $|\Delta m_s| = 2$ even in very dilute conditions, indicating an intramolecular origin of such interaction between the two radicals of the disulfide. Therefore, in frozen solution the two TEMPO radical units are not far away from each other.

Most molecules in the frozen solution probably adopt a conformation similar to the crystal structure where the two branches are in a syn-like conformation in relation to the disulfide group, bringing the TEMPO radical units closer than in a linear conformation. In fact, in frozen solutions the EPR spectra are sensitive to the dipole-dipole interaction: CW EPR measurements are sensitive to dipole-dipole interactions between nitroxides for distances up to $2 - 2.5$ nm.\textsuperscript{47} The proposed conformation could be compatible with the stable conformation found in the solid state in the X-ray crystal structure as it has an interspin distance of 0.8 nm letting an observation of a dipolar coupling. In addition, this assignment supports the suggestion previously made of this conformation to be adopted as the “far” conformation in the dynamic process (Scheme 2). As the temperature decreases the transition from the “far” to the “close” conformation is slower and when the molecule freezes could adopt the “far” conformation, which is the most thermodynamically stable ($\Delta H > 0$). The spectra recorded at 300 K at these different concentrations are depicted in Figure S7.
As diradical 3 shows intramolecular dipolar interactions, the SQUID data for the polycrystalline sample (Figure 6), included the contribution from both intra- and intermolecular magnetic exchange interaction pathways. However, it is very important to differentiate between intra- and intermolecular exchange interactions in diradical (or polyradical) compounds as the net magnetic behavior could be entirely different. For example, Rentschler et al. prepared magnetically diluted samples by embedding the compounds in a poly(vinyl chloride) film to suppress intermolecular exchange interactions and study separately intra- and intermolecular exchange interactions, observing completely different behavior in some complexes.\(^\text{[15]}\) To overcome this problem we prepared a dilute frozen solution of diradical 3 and studied it by EPR following the half-field transition signal intensity at different temperatures to examine only the intramolecular magnetic interaction contribution. In this way the magnetic interactions in diradical 3 can be semi-quantitatively assessed by EPR as the intensity of the forbidden EPR transition signal is proportional to the imaginary part of the magnetic susceptibility.\(^\text{[48]}\) Therefore, the plot of \(I\cdot T\) vs. \(T\) (where \(I\) is the spectrum intensity of the \(|\Delta m_s| = 2\) transition) shows the same shape of the curve as in the usual representation of \(\chi\cdot T\) vs. \(T\) as measured by SQUID. According to the shape of the curve obtained, we can assess the type of predominant magnetic interactions in the sample. In addition, we can determine whether the triplet state is the ground state. The intensity of the \(|\Delta m_s| = 2\) transition signal \(I\) was measured in the 4-110 K temperature region. The corresponding \(I\cdot T\) vs. \(T\) curve is shown in Figure 10. We observe a decrease of the \(I\cdot T\) value as the temperature decreases. This behaviour is indicative of predominantly antiferromagnetic interactions between the spin carriers and demonstrates that the singlet is the ground state, with the triplet state thermally accessible. Thus, intramolecular magnetic interactions in diradical 3 are antiferromagnetic. As the SQUID measurement also showed antiferromagnetic interactions, the intermolecular magnetic interaction contribution should be antiferromagnetic as well.

\[\text{Figure 10. Dependence of the intensity of the half-field transition band } |\Delta m_s| = 2 \text{ with temperature for a frozen solution of diradical 3 at } 1.5\times10^{-3} \text{ M.}\]

Cyclic voltammetry (CV) of our target molecule was carried out with 0.02 M tetrabutylammonium hexafluorophosphate in CH\(_3\)CN as an electrolyte (versus Ag\(_{\text{g}}\)) and using Pt\(_{\text{w}}\) as a working electrode. The cyclic voltammogram showed one reversible redox wave at \(E_{1/2} = 0.77 \text{ V, with } \Delta E = 69 \text{ mV (Figure 11). This electrochemically reversible process corresponds to two-electron oxidation of the two TEMPO moieties (one-electron oxidation of each moiety). This result suggests very weak or null electronic interactions between the TEMPO units of the diradical, otherwise two electrochemical waves would be anticipated.}\]
Figure 11. Cyclic voltammogram of diradical 3 in CH3CN with 0.02 M nBu4NPF6 (vs Ag) at 100 mVs⁻¹.

SAMs of diradical 3 on Au(111) substrate

Diradical 3 was chemisorbed on Au(111) in order to form a self-assembled monolayer (SAM)⁴⁹. The preparation of SAMs was achieved by immersing a freshly cleaned gold substrate in a 1 nM THF solution of diradical 3 for 18 h at room temperature. After this time, the monolayer was rigorously rinsed with abundant THF, to ensure that there was no physisorbed material left on the substrate and dried under a N₂ stream (Scheme 3).

Scheme 3. Scheme of the SAM of TEMPO derivative 3 on gold.

SAMs of diradical 3 on Au(111) substrate

Diradical 3 was chemisorbed on Au(111) in order to form a self-assembled monolayer (SAM)⁴⁹. The preparation of SAMs was achieved by immersing a freshly cleaned gold substrate in a 1 nM THF solution of diradical 3 for 18 h at room temperature. After this time, the monolayer was rigorously rinsed with abundant THF, to ensure that there was no physisorbed material left on the substrate and dried under a N₂ stream (Scheme 3).

Scheme 3. Scheme of the SAM of TEMPO derivative 3 on gold.

The resulting SAM was characterized by contact angle, X-Ray Photoelectron Spectroscopy (XPS), and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The electrochemical and magnetic properties of this SAM was investigated by cyclic voltammetry (CV) and EPR, respectively.

Contact angle value was 76.1 ± 2 °, showing the high hydrophobicity of the layer. The XPS spectrum of the SAM showed a doublet at 162 eV and 163.2 eV assigned to S2p₃/₂ and S2p₁/₂ respectively, with an intensity ratio of 1.9 : 1 (very close to the expected value of 2 : 1) and a splitting of 1.2 eV⁵⁰ attributed to the S–Au bond (Fig. S8 of the Supporting Information). Additionally, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was performed (Fig. S9 and S10, ESI). ToF-SIMS is a highly sensitive and powerful surface characterization technique employed to determine the composition and structure of molecules on surfaces through mass spectral analysis.⁵¹ We observed two peaks at 258 and 455 m/z, which correspond to the molecular ion peak (M⁺) for SC₁₂H₂₁N₂O₂ and the AuM cluster, respectively, verifying the adsorption and integrity of the molecules.

As in solution, the electrochemical properties of the resulting SAM were investigated by CV using the functionalized gold substrate as a working electrode, and revealed that the redox properties of the molecules in solution were also displayed when they were bound to gold. Indeed, a stable and reversible redox process at E₁/₂ = 0.89 V (vs. Ag wire) was observed (Figure 12) which is in agreement with the redox potential of these molecules in solution. This was thus assigned to the oxidation of TEMPO units. The cyclic voltammogram shows one reversible redox wave with an oxidation peak at 918 mV and a reduction peak at 870 mV at a scan rate of 100 mVs⁻¹ (ΔE = 48 mV). A reduction of 21 mV in ΔE (i.e. the voltage difference between the oxidation and reduction peaks) compared to the redox wave obtained for 3 in solution (ΔE = 69 mV) was observed. This is an additional indication that the electroactive molecules are adsorbed on the surface. However, one would expect no splitting between the oxidation and reduction peaks for an ideal situation⁵² because diffusion should not have any influence on the process as electroactive centres are all close to the electrode surface, and should be non-interacting and in rapid equilibrium with the electrode. In our case, although the value of ΔE is very small, it is still perceptible. This could be explained by the interaction between the TEMPO moieties.

The robustness and stability of the SAM was elucidated by the reversibility of the process and the fact that after performing many consecutive voltage cycles, completely identical redox waves without showing any sign of loss of current intensity were observed, indicating that the two redox states are stable. In addition to this, we also observed that increasing the scan rate resulted in an increase in the intensity of the peak (inset of Figure 12), which is characteristic for surface-confined electroactive species.⁵³
The magnetic properties of the SAM were investigated by EPR. The signal observed in the EPR spectrum of the SAM (Figure 13) unambiguously demonstrates that the magnetic properties of the TEMPO-substituted disulfide 3 were preserved on the surface. In addition, we observed a dependence of the EPR spectra with the orientation of the substrate with respect to the external magnetic field. We measured the EPR spectra of the SAM on the 2D substrate oriented either parallel or perpendicular with respect to the magnetic field and we observed that the position (g value) and linewidth of the spectra were different for different orientations. When the substrate was oriented parallel to the magnetic field the spectrum showed a broader line (13.5 G) at g-value 2.0063 (Figure 13a) whereas in the spectrum obtained with the substrate perpendicular to the magnetic field, the linewidth was 9.4 G and the g-value 2.0049 (Figure 13b). Interestingly, the g-value of the former spectrum (parallel direction) coincides with the one obtained for the a direction of the crystal (Figure 4 and 5) i.e. parallel to the axis across the TEMPO ring. On the other hand, the g-value of the latter spectrum (perpendicular direction) coincides with the one obtained at 45º with respect to the c axis of the crystal (Figure 5) i.e. the axis passing through the centre of the TEMPO ring.

It’s worth mentioning that apart from the g values in the SAM coinciding with those in the monocrystal, the linewidths are similar too. Therefore, we are detecting different EPR spectrum depending on the direction of the magnetic field over the SAM, suggesting an anisotropy in the magnetic behavior of the surface-anchored molecules. This is only detectable if most molecules anchored on the Au(111) substrate are oriented in the same way which suggests uniform packing. The N–H···O hydrogen bonds among the neighbouring branches are probably playing an important role in the packing of the SAM. Taking into account the results of the angle-resolved EPR study of the monocrystal, we can estimate the orientation of the radical centres on the SAM. Thus, the molecules are presumably oriented in the SAM as shown in the schematic representation of Figure 14.

**Figure 12.** Cyclic voltammograms of the SAM in CH$_3$CN with 0.02 M nBu$_4$NPF$_6$ (vs A$_{Ag}$) at different scan rates; from lower to higher intensity: 50 (dotted line), 100 (dash-dot line) and 200 mVs$^{-1}$ (solid line). Inset: Plot of the current intensity vs scan rate.

**Figure 13.** EPR spectra of the SAM of TEMPO derivative 3 on gold, oriented parallel to the magnetic field (a) and perpendicular to it (b).
The linewidth of exchange-narrowed EPR spectra is sensitive to the distance between adjacent radicals, e.g., their packing density.\cite{25a} At high coverage and tight packing of radicals, the line becomes narrower.\cite{54} As expected, the packing of spin labels in the crystal was tighter than in the SAM. However, the EPR lines in the SAM were only slightly broader than in the crystal (in the same orientation) indicating a very tight, nearly crystal-like, packing in our SAM. On the other hand, the linewidths observed in the EPR of gold nanoparticles with high coverage of TEMPO derivative 3\cite{26} are slightly higher than the ones observed in the SAM. This suggests more uniform and tight packing in the SAM than in the Au NPs. Although the arrangement of underlying gold layer in Au NPs is different from planar SAMs,\cite{55} the looser packing of the organic layer (as compared to SAMs) is probably mostly due to the curvature of the 3D gold NP.

Taking into account that both intra- and intermolecular magnetic interactions in diradical 3 are antiferromagnetic, the interactions between the spin carriers in the SAM are probably also antiferromagnetic.

To summarize, the TEMPO-modified substrate has shown interesting anisotropic magnetic properties. The optimization of this kind of magnetic nanostructures could play a key role in the further development of magnetic local probe techniques for the characterization of molecular based magnetic materials.\cite{56} In addition, it is a multifunctional surface since it combines magnetic and electroactive properties. The reported results show high potential of this material for the fabrication of surface molecular devices on surfaces with potential use in electronic devices. For example, as memory devices, since they are electrically commutable in a reversible way between two easily accessible, stable, and persistent redox states (i.e., TEMPO radical and TEMPO oxoammonium cation), which reveal distinct magnetic and optical\cite{57} properties that can be employed as read-out mechanisms. Indeed, TEMPO radical is a paramagnetic species with a maximum absorbance centered at 425 nm, while the oxoammonium cation is diamagnetic with a maximum absorbance at around 476 nm. On the other hand, it also can be explored the electrocatalytic activities of this SAM toward primary alcohols.\cite{27,29} 

Conclusions

TEMPO-substituted disulfide 3 shows a strong intramolecular spin exchange interaction between the two nitroxide groups in solution that depends on the temperature and solvent. The simulation of the dynamics of the thermally activated process has been explained by the co-existence of just two main conformations: one with $|J| >> |\alpha_N|$ ("close" conformation), and another one with $|J| << |\alpha_N|$ ("far" conformation). The observation of a half-field $\Delta m_s = 2$ transition by EPR in dilute frozen solution suggested an intramolecular origin of the dipolar interaction between the two radicals. It was therefore proposed that the molecules adopt a syn-like conformation similar to the X-ray crystal structure. This conformation is also proposed to be adopted as the "far" conformation of the dynamic process. In addition, intra- and intermolecular magnetic interactions were studied separately showing antiferromagnetic interactions in both cases, with a singlet state as the ground state and the triplet state thermally accessible. Structural, dynamical, and thermodynamical information are extracted from the EPR spectra of this dinitroxide compound.

Finally, we demonstrate that the magnetic as well as the electrochemical properties of diradical 3 in solution are preserved upon its chemisorption on Au(111) substrates. In addition, a dependence of the EPR spectra on the magnetic direction was observed suggesting an anisotropy in the magnetic behavior of the radicals forming the SAM. The combination of these EPR spectra and the information on the magnetic properties of diradical 3 obtained from the angle-resolved EPR study of a monocrystal enabled us to make a rough determination of the orientation of molecules on the Au(111) support. The reported results could help to the further development of magnetic local probe techniques for the characterization of molecular based magnetic materials. Bringing together the data from several different molecular assemblies of diradical 3 (solution, monocrystal, SAMs on planar Au(111) and Au NP) was instrumental in developing better understanding of magnetic interactions in these systems. We hope that this systematic approach will be applicable to other related systems which facilitate fabrication of surface molecular devices.

Experimental Section
Methods and chemicals

Solvents and starting materials were purchased from Aldrich. Thin layer chromatography was done with aluminium sheet covered with silica 60 F 254 Merck. Silica column chromatography was carried out using silica gel 60 (35-70 mesh). Melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. Electrospray mass spectra (ESI-MS) were recorded on a Bruker Daltonics Esquire 3000 ion trap Mass Spectrometer. IR spectra were recorded in the attenuated total reflectance mode (ATR) in a Perkin Elmer Spectrum One Fourier transform spectrometer. EPR spectra were obtained with an X-Band Bruker ELEXYS E500 spectrometer equipped with a TE102 microwave cavity, a Bruker variable temperature unit and a field frequency lock system Bruker ER 033 M; line positions were determined with an NMR Gaussmeter Bruker ER 035 M. The modulation amplitude was kept well below the linewidth, and the microwave power was well below saturation. The cyclic voltammetric measurements were performed on a QUICELTRON potentiosstat/galvanostat controlled by a personal computer and driven by dedicated software. Cyclic voltammetry was performed with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode. Magnetic measurements down to 2 K were carried out in a Quantum Design MPMS-SS SQUID magnetometer. The molar susceptibility was corrected for the sample holder and for the diamagnetic contribution of all atoms by means of Pascal’s tables.[58,59]

Crystal structure was determined by Dr. Klaus Wurst at the Innsbruck University. The diffractometer used was a Nonius Kappa CCD, equipped with monochromatic Mo Kα (λ = 0.71073 Å) radiation. The structure was solved by direct methods and refined by full-matrix least squares method with SHELXTL software. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens at carbon atoms were refined with constraints at calculated positions, except hydrogen atom at N(2), which was localised and refined with an isotropic displacement parameter. The ToF-SIMS measurements were reordered with a TOF-SIMS (Time of Flight Secondary Ions Mass Spectrometer) under the following specific analysis conditions: primary gun energy of 25 KV, extractor energy of 8.5 KV, an emission current of 1.05 µA, employing Bi3+ with an intensity of the primary ions of 0.25 pA. The experiments were performed in vacuum at 8.3E-9 mbar. The experiments were performed at 2E-7 mbar. For the general spectra a pass energy of 200 eV, a dwell time of 50 ms and an energy step size of 1 eV were employed. For the general spectra a pass energy of 200 eV, a dwell time of 50 ms and an energy step size of 1 eV were employed. The morphology prediction of diradical was proposed using the molecular modeling software Materials Studio, version 6.0. We used Bravais-Friedel Donnay-Harker, BFDH Method and Growth Morphology Method. In the Growth Morphology Method we tested five available force fields: COMPASS, COMPASS 26, COMPASS 27, Universal, and Dreiding, and the best job in reproducing the experimental cell of diradical was done by Dreiding.

Synthesis of the TEMPO-modified disulfide 3

3,3’-Dithiodipropionic acid (1.05 g, 4.99 mmol) was dissolved in dry THF (50 mL). A solution of dicyclohexylcarbodiimide (DCC) (2.27 g, 11.0 mmol) in dry DCM (50 mL) was added to the stirred solution of dithiodipropionic acid followed by a solution of 4-amino-TEMPO (1.94 g, 11.0 mmol) in dry DCM (50 mL). A catalytic amount of 4-dimethylaminopyridine (1.00 mg) was added to the reaction mixture and the solution was stirred under argon for 14 h. The reaction mixture was filtered, and excess 4-amino-TEMPO was removed by extraction with distilled water (2 × 50 mL). The crude product was purified by flash chromatography using 12:1 DCM:MeOH mixture (Rf = 0.30). Yield: 1.048 g (37%); m.p. 199°C; IR (ATR): ν bar = 3305, 3078, 2997, 2978, 2941, 1648, 1548, 1462, 1440, 1357, 1300, 1269, 1242, 1178 cm⁻¹; ESI-MS: m/z: 539.2 [M + Na]+; EPR (toluene): g = 2.0060, aN = 7.78 G.

Acknowledgements

This work was supported by CSIC-PIF RAPCAM (PIF-08-017-3), the DGI grants CONSOLIDER (CTQ2006-60333), POMAs (CTQ2010-19501) and BeWell (CTQ2013-40480-R), and AGAUR (2009-SGR-00516 and 2014-SGR-17). CIBER-BBN is an initiative funded by the VI National R&D&I Plan 2008-2011, Iniciativa Ingenio 2010, Consolider Program, CIBER Actions and financed by the Instituto de Salud Carlos III with assistance from the European Regional Development Fund.

Keywords: diradical • intramolecular spin exchange interaction • EPR • X-ray diffraction • SAM on Au(111)


