Abstract: The new di-imine fluorescent ligand ACRI-I based on a central acridine yellow core is reported along with its coordination complex [Co$_2$(ACRI-1)$_2$] (I), a fluorescent weak ferromagnet. Due to the strong fluorescence of the acridine yellow fluorofoe, this is not completely quenched when the ligand is coordinated to Co(II). The magnetic properties of bulk complex I and its stability in solution have been studied. Complex (I) has been deposited on highly ordered pyrolitic graphite (HOPG) from solution. The thin films prepared have been characterized by AFM, ToF-SIMS, GIXRD, XAS, XMCD and theoretical calculations. The data show that the complex is robust and remains intact on the surface of graphite.

Keywords: molecules on surfaces • Cobalt(II) complexes • fluorescent ligands • magnetic properties •

Introduction

The limit imposed by the superparamagnetic regime present in nanoparticle-based inorganic systems for spintronics sets a miniaturization limit for these systems.[1] At this point, there is a major trend for spintronics: the design of molecular analogues of the inorganic spintronic structures, presenting the possibility of designing cheaper spintronic devices compatible with plastic technology.[2] and the evolution towards molecular spintronics which take advantage of the possibility to tailor molecules with control down to the single spin. Basically, these approaches present the following advantages in front of inorganic spintronics: electron spins can be preserved for longer times and distances, low density, transparency, chemical versatility, flexibility, processability and novel added functionalities.[3] Since the synthesis of polynuclear complexes does not follow a predictable synthetic method, we have to consider the design inside of the serendipitous assembly process.[4] In order to attain multifunctional materials, coordination chemistry molecular systems offer the advantage of the possibility of tailoring ligands to carry desired specific functions, like fluorescence, additional to the magnetic properties provided by transition metal. Additionally, functionalization of the ligands with characteristic chemical groups can also facilitate deposition and organization on surfaces. Thus, different properties can coexist in one same material and be activated by different inputs or there can be synergy between them. The use of multifunctional molecular complexes in the assembly of nanodevices is a hot topic in the fast development of molecular electronics. In order to include these materials in devices and prior any possible application, the study of nanostructuration of the prepared systems is of outmost importance. [5] Molecular magnetism is now progressing in this new track, focusing on the organization of nanomagnets in low-dimensional arrays suitable for addressing single-molecules. Many efforts are being devoted with this goal in mind; however the characterization of thin films, monolayers or sub-monolayers of nanomagnets on surfaces is far from trivial: the amount of material is extremely small and the use of surface sensitive techniques is absolutely necessary. Furthermore, the stability and robustness of the molecular complexes in the deposition conditions must be clearly ascertained. Our group has been interested in nanostructuration of molecular magnets [6] and research efforts are especially being devoted to prepare multifunctional magnetic systems based on molecular species. Gatteschi, Sessoli and co-workers have addressed this issue in several of their publications, where deposition methods are surveyed.[7] Winpenny and co-workers have studied the surface deposition of Cr$_2$Ni nanomagnets, [8] with outstanding results. The work on Mn$_2$ and Fe$_2$ single-molecule magnets (SMMs) by Sessoli, Sanctavit and co-workers has pioneered the use of X-ray absorption (XAS) and X-ray magnetic circular dichroism (XMCD) to characterize thin layers of molecular species on a surface. These studies clearly show that for the Mn$_2$ SMMs[9] the molecules do not
remain intact after deposition, usually presenting reduction to Mn(II) and decomposition, with the loss of the SMM property. The reported data are far better for the Fe(II) SMMs, which are robust molecules that can be deposited intact on a surface, maintaining the SMM property.[10] Thus, deposition methods for molecular systems greatly depend on the nature of the molecule and its functional groups. As chemists, the main challenges we face are the design and synthesis of new functional nanomagnets which are robust and can be processed without suffering decomposition. This is the key to being able to use these molecular systems in technological devices in the not-so-far future. In this paper we report our latest results in this direction: The new fluorescent ligand ACRI-1 and its Co(II) complex [Co(ACRI-1)] (1) are presented. The new fluorescent complex 1 has been characterized in bulk and as thin films on a HOPG surface.

Results and Discussion

We have designed and prepared the fluorescent ligand ACRI-1 based on acridine yellow via Schiff base formation with salicylaldehyde.[11] ACRI-1 is a ditopic ligand with two separate coordination pockets which are far enough to avoid quenching of the fluorescence of the central fluorofore by coordination to a metal atom. The fluorescent properties of ACRI-1 and its complexes are derived from the fluorescent group acridine yellow. Reaction of ACRI-1 with Co(II) nitrate hexahydrate afforded a precipitate which was recrystallized in chloroform to afford dark red crystals of complex 1, [Co(ACRI-1)] in 25 % yield.

Description of crystal structures

Table 1 contains the crystallographic data and structural parameters for ACRI-1 and complex 1 (see Supplementary Information for additional crystallographic parameters). The ligand ACRI-1 crystallizes in the Monoclinic space group C2/c and the crystal structure is shown in Figure 1. The crystal structure shows the intramolecular hydrogen bond between the oxygen atom of the phenol group and the iminic nitrogen. Complex 1 crystallizes in the triclinic space group P-1. The crystal structure and packing diagrams are shown in Figure 2. In [Co(ACRI-1)] the Co(II) atoms are tetracoordinated in a distorted tetrahedral environment. The asymmetric unit contains two half molecules (Co1 and Co2) with a torsion angle Co1-Co1''-Co2-Co2' of 112º (Co1 and Co2 are the symmetry related atoms to Co1 and Co2), these are shown in green and blue in the packing diagram of Figure 2. The intramolecular Co-Co' distances are Co1--Co1' 12.015 Å and Co2--Co2' 11.901 Å. Between different molecules the Co(II)-Co(II) distances range between 12.168 Å and 8.069 Å. The acridine core of the ligand ACRI-1 displays parallel-displaced intramolecular π-π stacking. The average distance between the aromatic rings is 3.5 Å. Between molecules with the same symmetry there are several types of interaction: π-π stacking between salicylaldehyde rings with average distance of 3.346 Å, π-π stacking between anthracene and salicylaldehyde rings with average distances of 3.321 Å, and H-bonds between the oxygen of the phenoxy group of one molecule with a C-H of salicylaldehyde ring of the neighbour, O2—C31' C31—O2' at 3.777 Å.

Table 1: Crystal data and structure refinement parameters for ACRI-1 and complex 1.

| Sample          | ACRI-1       | Complex 1   |
|-----------------|--------------|-------------|
| Crystal system  | Monoclinic   | Triclinic   |
| Space group     | C2/c         | P-1         |
| a / Å           | 27.571(3)    | 10.0214(5)  |

Between molecules with different symmetry the interactions are π-π stacking between anthracene rings, and between salicylaldehyde rings with distances between 3.698 Å and 3.309 Å. In addition there are H-bonds between the oxygen of the phenoxy group and a C-H of the salicylaldehyde ring O3—C54 at 3.588 Å, and the nitrogen of the anthracene and a C-H of the salicylaldehyde ring N3—C25 at 3.375 Å. These distances are in agreement with the expected for weak CH-X hydrogen bonds.[12] The interactions repeat over the crystal packing and even though they are weak by themselves cooperatively they are of vital importance for the magnetic properties of complex 1. The intermolecular interactions can be easily visualized calculating the Hirshfield surface,[13] see Additional Information for a figure, which shows that the points of maximum intermolecular interaction, shown in red, are those close to the first coordination sphere of the Co(II) ions.

Figure 1. Crystal structure of the ligand ACRI-1. Intramolecular OH- N hydrogen-bonds are shown as dashed lines

Figure 2. a) Crystal structure of one of the two isostructural dinuclear units that compose the asymmetric unit of complex 1; b) packing diagram where the two crystallographically independent dinuclear units of complex 1 are shown in green and blue (colour online).
Fluorescent properties

Emission spectra of ligand ACRI-1 and complex 1 are shown in Figure 3 at an excitation wavelength of 350 nm. In all cases a peak corresponding to excimer formation of the acridine core is observed at circa 550 nm. Dilution to 10^{-9} M of ACRI-1 is necessary to observe the fluorescence of the ligand, which is blue shifted to 425 nm, as usual for anthracene and pyrene derivatives. The emission spectrum of complex 1 shows the expected intramolecular excimer emission around 550 nm at all concentrations, which should be proofs that the molecule remains stable in solution. The coordination of Co(II) does not suppress the fluorescence of the ACRI-1 ligand. However, a quenching of the fluorescence is observed, resulting in less intense signals. The fluorescence spectrum of complex 1 shows no traces of free ligand, supporting the stability of complex 1 in solution as observed by NMR (see below).

Stability of complex 1 in solution

In order to deposit complex 1 from solution on a substrate, its stability under the treatment conditions must be established without questions. The solution stability of complex 1 can be assessed by means of mass spectroscopy and paramagnetic proton NMR. The ESI mass spectrum of complex 1 shows the molecular ion peak at m/z = 1006. However, under the conditions of the electrospray, complex 1 breaks-up easily and the most important signals are the peaks for ACRI-1 (m/z = 446) and acridine yellow from ligand fragmentation (m/z = 238). A solution of complex 1 in deuterated chloroform was prepared and its proton NMR studied over time. The NMR did not change over long periods of time of up to one day. The proton NMR of solid samples kept at room temperature, open to air, did not change over long periods of time (several months to one year), thus the bulk solid is stable and no oxidation of Co(II) to Co(III) due to atmospheric oxygen occurs. The proton NMR of complex 1 is shown in Figure 4, with the signals assigned to the respective protons as indicated. The simple NMR clearly shows that the complex is stable in solution and that the ligand remains coordinated to the complex. The solution can be driven to dryness by evaporation of the CDCl3 and then the solid re-dissolved in deuterated chloroform again: no changes are observed in the spectrum. The proton NMR of the precipitate, as obtained from the reaction, without further treatment, is that of complex 1, with a small amount of free ligand. A treatment of this precipitate at 200°C for 2 hours in an oven results in the elimination of the free ligand and a residue of pure complex 1, as checked by proton NMR. Thus the NMR and mass spectroscopy, together with the fluorescence analysis of complex 1 in solution show that it is stable and further processing using a solution of the complex can be pursued.

Bulk magnetic properties

The magnetic susceptibility of 1 was investigated in the temperature range 2-300 K at applied fields of 300 and 5000 Oe. The plot of $\chi_T$ vs $T$ is shown in Figure 5. Upon cooling the $\chi_T$ value is nearly constant down to 60 K. Below this temperature the $\chi_T$ product increases to 4.06 cm^3 mol^{-1} K at 15 K. Below 15 K the $\chi_T$ product drops to a value of 1.85 cm^3 mol^{-1} K at 2 K. The $\chi_T$ value 4.31 cm^3 K mol^{-1} at 300 K is in agreement with the calculated value of 3.75 cm^3 K mol^{-1} for two magnetically isolated distorted tetrahedral Co(II) atoms ($S = 3/2, g = 2.0$). Ac magnetic susceptibility data of complex 1 were collected at different frequencies of an oscillating ac field of 4 Oe. A signal is observed in the out-of-phase susceptibility with a maximum at 5 K indicating the onset of ferromagnetic order. This long range interaction is promoted by the intermolecular interactions in the 3D network of complex 1, as discussed before. The peak in the out-of-phase ac magnetic susceptibility has a maximum at 5 K, and the ZFC-FC measurement shows a splitting of the two curves at this same temperature (as shown in the inset of Figure 5) indicating that 5 K is the blocking temperature for the ferromagnetic order of complex 1. Many molecular magnets based on Co(II) are reported in the
The X-ray structure was treated as an initial guess to perform the quantum chemical calculations for both intra and inter molecular interactions in complex 1. The DFT [17] calculations using Gaussian 09 suite programs [18] were carried out to yield the single point energies of all possible electronic states (see ESI for details). Single point computed structure of the tetramer has been shown in Figure 6a. The magnetic exchange interactions were calculated for complex 1 to underpin the mode of coupling between the two tetrahedral Co(II) ions mediated via extended aromatic ring system. DFT calculations reveals that both the intra and inter dimer exchange interactions are ferromagnetic in nature with $J$ value of 0.15 cm$^{-1}$ and 0.03 cm$^{-1}$ respectively. The computed values are in good agreement to the experimental observation. The magnitude of intramolecular exchange is relatively weak, essentially due to the long distance between the two Co(II) centres. The interdimer exchange is much weaker as the exchange interactions are mediated via H-bonding interactions. The spin density plots are shown in Figure 6. In all cases the spin density on the Co(II) atom are ca. 2.7 suggesting significant delocalization of spin density to other atoms. Particularly the coordinated N- and O- donor atoms have significant positive spin density due to spin delocalization. Particularly on coordination nitrogen spin density of two Co(II) centres. The GIXRD of the spin coated HOPG, some diffraction pattern like that of the pellet was observed in Figure 8a. From the computed Eigen value plot for complex 1. From the coordinating atoms spin polarization propagates as evidence from the alternating spin densities on the spacer atoms. Significant contributions from ACR-I ligand to the HOMO reveals that observed exchange is super-exchange in nature via the aromatic spacer ligands. The ferromagnetic coupling is essentially related to the metal-metal distance and number of the spacer groups/atoms. Earlier prediction of long range coupling on Cu(II) complex suggest that the exchange should be ferromagnetic in this case as there are three aromatic spacer groups.[19]

Surface deposition and characterization

To study the surface deposition, a $10^{-3}$ M solution of complex 1 in acetone was deposited onto freshly cleaved HOPG by spin coating at 500 rpm during 30 seconds. Clean acetone was deposited on HOPG by spin coating in the same conditions as those used to prepare the sample of complex 1 and the AFM showed a pristine HOPG surface. The topography of the samples was characterized by atomic force microscopy (AFM) using peak force mode. Figure 7 shows two AFM images of a thin-layer of complex 1 with an average height of 1.2 nm. The observed 1.2 nm height of the layer fits with the height of the molecule when it is placed with the salicylaldehyde groups interacting by $\pi-\pi$ stacking with the HOPG surface. A ToF-SIMS experiment was performed in order to see of complex 1 was deposited and remained intact under the deposition conditions. The surface used was conductive Si, since the ToF-SIMS technique requires a conductive surface. The samples were prepared under the same spin-coating conditions used to prepare the samples for AFM, one was studied by TOF-SIMS and the other by AFM. The AFM revealed a continuous coverage of the surface with aggregates with heights of around 1 to 2 nm distributed on the surface. The TOF-SIMS spectra (see supplementary information) showed peaks at 446 and 488 m/z which can be associated to the $[(ACRI-I)+H]^+$ and $[Co(ACRI-I)-Me]-$ fragments, and the presence of Cobalt in the deposited layer, confirming that the aggregates observed in the AFM images correspond to molecules of complex 1, which had been deposited intact on the surface. Grazing incidence X-ray diffraction (GIXRD) was performed on a spin coated HOPG sample, prepared in the same conditions as the AFM samples, and compared to that of a pellet of bulk complex 1. Unfortunately, the diffraction features observed were very weak due to the extremely low quantity of material of the monolayer and the very strong diffraction signals of the polycrystalline HOPG substrate. A saturated solution of complex 1 was drop casted on a glass plate and GIXRD of the thin film measured, it showed a weak diffraction pattern like that of the pellet of bulk complex 1, (see the Supplementary Information). Thus, polycrystalline thin layers of complex 1 can be deposited on a surface. In the GIXRD of the spin coated HOPG, some diffraction peaks observed over long acquisition times coincided with those of the bulk sample of 1 and the drop-casted 1 on glass. Bulk complex 1 and thin films of complex 1 on HOPG were studied by X-ray absorption spectroscopy (XAS) at ESRF beamline ID-08. XAS spectra were taken at both Co- and N-edge. The X-ray magnetic circular dichroism (XMCD) spectra is defined by the difference between the absorption spectra collected with left and right polarized light. XAS spectra and the dichroic signal at Co-edge for a thin layer of complex 1 on HOPG and a powder sample of complex 1 are shown in Figure 8. A full study was performed varying the field and temperature down to 10 K, both the powder of complex 1 and the thin layer of complex 1 on HOPG displayed a paramagnetic signal. Unfortunately, 10 K is above the
blocking temperature of the ferromagnetic order of complex 1, thus we have been unable to establish whether the thin layer of complex 1 displays long-range magnetic order as the bulk sample does. Clearly the spectra of complex 1 on HOPG is very similar to that of bulk complex 1, proving that complex 1 is intact after deposition on HOPG by spin coating. A simulation of the spectrum with the software CTM4XAS [20] is also shown in Figure 8. The software performs atomic multiplet calculations and allows the crystal field parameters to be adjusted. The spectral features observed both for complex 1 and complex 1 on HOPG can be simulated with crystal field parameters in agreement with those expected for distorted tetrahedral Co(II) in a coordination environment like that found in complex 1. It has been found that in both cases the spectra are well simulated for Co(II) in a distorted tetrahedral environment. The crystal field parameters used in the simulation are 10Dq, which is the crystal field splitting of the d-orbitals (in the program a negative value is used for tetrahedral crystal field), Dt and Ds, which reflect the distortion with respect to an ideal environment. The best simulation of XAS and XMCD spectra was obtained for 10Dq = 0.63 eV (5081 cm⁻¹), Dt = 0.025 and Ds = -0.15 for the powder complex 1 sample and 10Dq = 0.70 eV (5645 cm⁻¹), Dt = 0 and Ds = -0.2 for the thin layer of complex 1 on HOPG, and these are shown as dashed lines in Figure 8. The 10Dq values obtained are in agreement with the expected 10Dq values for tetrahedral Co(II) with N and O donors.[21] At N-edge, and XLD signal was measured presenting a maximum at 45 degrees from the plane of the surface, in agreement with the DFT calculations that suggest that there is unpaired electron density on the N atoms of the ACRI-1 ligand.

![Figure 8. X-ray absorption (XAS) and X-ray magnetic circular dichroism plots for a thin layer on complex 1 deposited on HOPG by spin coating (Complex 1 on HOPG) and a bulk sample of complex 1 (Complex 1 powder). The dashed lines are simulations calculated using CTM4XAS (see text for the simulation parameters).](image)

**Conclusion**

We have presented here the new multifunctional material [Co3(ACRI-1)2] (I) with fluorescent and magnetic properties. The stability of the complex has been established and surface deposition studies performed. The fluorescent complex 1 can be deposited intact on a surface, as shown by XAS. The XAS and XMCD spectra of complex 1 can be modeled with crystal field parameters in agreement with the crystal structure of the molecule. The N-edge measurements suggest a preferential orientation of the molecules on the HOPG surface. For possible applications of nanomagnets in devices, this is a key point that still needs to be carefully assessed, especially when the nanomagnets in question are polynuclear coordination complexes.

**Experimental Section**

All chemicals were purchased from commercial sources and used as received.

**CoH2N2O2 (ACRI-I).** To a mixture of acridine yellow hydrochloride (C15H12N2Cl) (1.215 g, 4.45 mmol) and triethylamine (3.10 mL, 22.33 mmol) in ethanol (100 mL) was added salicylaldehyde (931 µL, 8.89 mmol) The resulting solution was stirred and heated up to 79 °C. Reflux was maintained during eight hours. After standing overnight, a precipitate was filtered, washed with ethanol and dried with diethyl ether. The yield of the reaction is 73% (1.45 g obtained). Suitable crystals for single-crystal X-ray diffraction were grown from concentrated acetonitrile solution by slow evaporation. Elemental Analyses: calculated for CoH2N2O2.12H2O: C, 76.62%; H, 5.32; N, 9.24%. Experimental: C, 76.6; H, 5.06; N, 9.14%. Selected IR data in cm⁻¹ (KBr): 3310.72 (m), 3196.04 (s), 1645.65 (s), 1569.05 (m), 1504.37 (s), 1460.63 (m), 1388.36 (m), 1353.19 (m), 1185.98 (m), 1130.18 (m), 847.79 (m), 759.94 (w), 615.00 (w).

Single crystal diffraction data were collected on a Bruker APEXII SMART diffractometer at the Facultad de Quimica, Universitat de Barcelona, using a microfocus Molybdenum kα radiation source. The structures were solved by direct methods (SHELXS) and refined on F² (SHELX). CIF files for the reported complexes have been deposited at the Cambridge Crystallographic Data Centre and allocated with deposition numbers CCDC 917646 (ACRI-1) and 917647 (Complex 1) and are available upon request at the website: http://www.ccdc.cam.ac.uk/. IR, UV-vis and fluorescence spectra were recorded at the in-house facilities. Elemental analyses, magnetic measurements (SQUID magnetometer equipped with a 5T magnet on crushed crystals) and 1H-NMR (Varian Unity 300 MHz) were performed at the CCGT-UB. Surface characterization was done at the CCIT-UB by using an AFM Multi mode. The electronics of the system are Nanoscope V from Bruker. Topographic mode: peak force. Each image has a resolution of 512x512 pixels, taken at a velocity of 1 row/s. Tip used: silicon oxide with a nominal radius of 5 nm. The X-ray diffraction experiment at grazing incidence angle was carried out at a fixed wavelength of 0.826 Å on a six-circle diffractometer, using a 2D-charge coupled device (Photonic Science CCD) detector, at SPring beamline (BM23B), ESRF, Grenoble, France. The detector has an active area of 250x125 mm² and 60 3825 x 1913 (2x2 binned) pixels, with a 6.56 micron pixel size. The sample-detector distance during the experiment varied from 180 up to 630 mm. The X-ray magnetic circular dichroism (XMCD) measurements have been performed at the beamline ID08 at ESRF, which is based on Apple II undulator source allowing a full control of linear and circular polarization and a high scanning speed spherical grating monochromator Dragon type. The absorption signal has been measured in total electron yield at 10 K. A magnetic field parallel to the incident beam was provided by a superconducting electromagnet. **Computational details:** Magnetic exchange coupling constant (J) was evaluated by employing the Noolde's broken symmetry approach, as developed by Ginesberg and Noolde.[22] The hybrid B3LYP functional [23] which is known to better reproduce the numerical estimates of magnetic exchange especially for transition metal complexes have been used for our calculations. Ahrleichs triple-Q valence basis set (TZV[24]) employed over all the elements in order to have better understanding in terms of the energies and spin densities. Molekel version 4.3 has been used to generate the spin density plots and Chemcraft version 1.6 has been used to visualize and represent the geometry of the complexes for this article.[25] For calculating magnetic susceptibility along with the relative spin state energies we have employed the MAGPACK software.[26]
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Entry for the Table of Contents (Please choose one layout only)

Layout 2:

**Molecules intact on surfaces**

Maria José Heras Ojea, Daniel Reta Mañeru, Lidia Rosado, Juan Rubio Zuazo, German R. Castro, Subrata Tewary, Gopalan Rajaraman, Guillem Aromí, Erika Jiménez and E. Carolina Sañudo*

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**Characterization of a robust Co(II) fluorescent complex deposited intact on HOPG**

The new fluorescent ligand ACRI-1 is reported along with its coordination complex [Co(ACRI-1)]$_2$ (1), a fluorescent weak ferromagnet. Complex (1) has been deposited on highly ordered pyrolitic graphite (HOGP) from solution. The thin films prepared have been characterized. The data show that the complex is robust and remains intact on the surface of graphite.