



## Novel paramagnetic-luminescent building blocks containing manganese(II) and anthracene-based curcuminoids

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### ABSTRACT

In an effort to study innovative multifunctional molecular materials, two new coordination compounds have been designed containing Mn<sup>II</sup> as a metallic source and a specific curcuminoid called 9Accm as a chelating ligand. Synthetic reactions were carried out between Mn(O<sub>2</sub>CMe)<sub>2</sub>·4H<sub>2</sub>O and 1,7-di-9-anthracene-1,6-heptadiene-3,5-dione (9Accm), leading to [Mn(9Accm)<sub>2</sub>(py)<sub>2</sub>] (1) and [Mn(9Accm)<sub>2</sub>(4,4'-bpy)]<sub>n</sub> (2), respectively. In particular, compound 1 was characterized by analytical, spectroscopic techniques (UV–Vis, fluorescence in the solid state and in solution and EPR), magnetic susceptibility measurements and X-ray crystallography. Compound 2 was characterized by a number of techniques as elemental analysis, UV–Vis, fluorescence (in the solid state and in solution), SQUID magnetic susceptibility studies and EPR. The structure of 1 reveals mononuclear octahedral Mn<sup>II</sup> species incorporating 9Accm and pyridine while analyses of 2 implies the formation of 1D chain in which Mn<sup>II</sup> centers bound to 9Accm and link with each other by 4,4'-bipyridine molecules. Compound 1 is a mononuclear compound that can act as a potential building block for the design of novel Mn<sup>II</sup>-curcuminoid species (e.g. compound 2). Both systems exhibit magnetic properties due to the nature of the metallic source and display fluorescence in the visible region in the solid state and in solution due to the nature of the ligand 9Accm. Therefore, 1 and 2 are excellent examples of multifunctional systems at the molecular scale. Even though both systems are very similar this work depicts the magnetic/fluorescent differences between each other.

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### 1. Introduction

The design of molecular materials with tailored structures and properties is one of the primary goals in nanoscience and nanotechnology [1]. Hence, great efforts are led at the moment toward the formulation of new strategies to create compounds with appealing features at the nanoscale. Such systems will be designed to have electrical, magnetic and optical among others, integrating some of them, the combination of these treats. Related to the latest, in recent years, inspiring materials have been published, showing applications ranging from sensing, catalysis, optoelectronics, etc. [2]. At this point interesting species have been achieved, although most of them by serendipitous methods, lacking on the control of the design and therefore of the final features. At the same time, specialized devices are built for the fabrication of practical systems at the nano-scale, providing further inside on unique

molecules and therefore allowing development of useful multifunctional systems.

Related to applications, organic  $\pi$  conjugated molecular systems display appealing properties and are good candidates for optoelectronic nanodevices along with other purposes [3]. Concerning this matter, curcumin (CCM) and its derivatives, known as curcuminoids (CCMoids), are promising molecules rather unexplored in the lines of research named above. In general, CCM and CCMoids are described as diarylheptanoid chains that contain  $\beta$ -diketone moieties and aromatic groups on the sides of the chains (Fig. 1). This family of molecules are well-known in biomedicine and exhibit many therapeutic properties being applied as antioxidant, anticancer preventive and anti-inflammatory agents [4,5]. Nowadays, great efforts are devoted to the synthesis of new CCMoids with enhanced biological properties existing, for that matter, several publications in bio-oriented journals [6,4,7,8]. Therefore, there is a library of conjugated systems ready to be investigated. From a designing point of view, CCMoids are versatile molecules: aromatic groups can be tuned, the  $\pi$  conjugation skeleton can also be functionalized and the  $\beta$ -diketone group allows coordination to metal centers. In the case of metal-CCM/CCMoids systems, some

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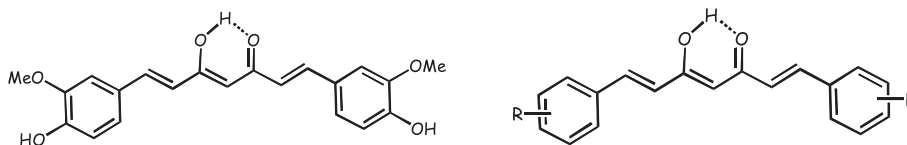


Fig. 1. Representation of curcumin (CCM, left) and general scheme of a curcuminoid. (CCMoid, right). R = various.

complexes have been published during the last decades, [9] with few examples containing complete crystallographic data, with only one example with Ru<sup>III</sup> [10] previous to Cu<sup>II</sup>, Zn<sup>II</sup>, Dy<sup>III</sup> and Yb<sup>III</sup> compounds published recently by our group [11,12].

In this respect since 2010, a family of compounds containing the CCMoid 9Accm (1,7-(di-9-anthracene-1,6-heptadiene-3,5-dione)) has been achieved and published by us [11]. 9Accm by itself, is a symmetric CCMoid containing anthracene groups that shows interesting fluorescent properties in the visible together with solvatochromic effects [11]. At the nanoscale, the conjugated skeleton of the molecule behaves as a nanowire allowing electronic transport at room temperature between nanoelectrodes (graphite surfaces) [13]. On the other hand, once it coordinates, the nature of the metal provides the possibility of new treats. In this regard, Cu<sup>II</sup>-9Accm compounds have been studied for bioinorganic purposes and therefore the potential *in vitro* activity was tested [11]. Moreover, Zn<sup>II</sup>- and Cd<sup>II</sup>-9Accm species, respectively, have been attained as fluorescent enhancers (while Cu<sup>II</sup>-9Accm acts as a quencher) and deposition of the Zn<sup>II</sup>-9Accm species was also carried out [11]. New lanthanides-9Accm species using Dy<sup>III</sup> and Yb<sup>III</sup> salts, respectively, have been isolated too, being the first ones of the aforementioned family; a luminescent single-ion magnet and a paramagnetic system which emits in the visible and near-IR regions, respectively [12]. Therefore, the natures of both, ligand and metal, are fundamental in the formation of multifunctional systems and search of applications. Herein, we present the latest studies targeting the Mn<sup>II</sup>/9Accm system and merging magnetic and luminescent properties together.

## 2. Experimental

Starting materials were purchased from Aldrich and all manipulations were performed using materials as received. Ligand 9Accm was synthesized as reported elsewhere [11].

### 2.1. Preparation of [Mn(9Accm)<sub>2</sub>(py)<sub>2</sub>] (1)

#### 2.1.1. Method A

The ligand, 9Accm, (40 mg, 0.084 mmol) was dissolved in DMF (20 ml) and deprotonated with an aqueous solution (5 mL) of LiOH (4 mg, 0.16 mmol). The resulting orange solution was kept under stirring and then, a solution of Mn(O<sub>2</sub>CMe)<sub>2</sub>·4(H<sub>2</sub>O) (10.3 mg, 0.042 mmol) in DMF (5 ml) was added dropwise. The final solution was warmed up to 90 °C for three hours and the color of the solution change to dark red. The solution was left under stirring overnight at room temperature. An orange precipitate was formed by concentrating the sample using rotary evaporation. The dry solid was washed with water, methanol and ether and dried in the air. Crystals of **1** were achieved by dissolving the solid in pyridine and layering the solution with ether. Yield: 20%. 1635w, 1550 m, 1505 m, 1440s, 1351w, 1166w, 966w, 781w, 735 m, 699w, 440w. Anal. Calc. for **1**·py·H<sub>2</sub>O (C<sub>80</sub>H<sub>56</sub>O<sub>4</sub>N<sub>2</sub>Mn): C, 80.94; H, 5.03; N, 3.33. Found: C, 80.91; H, 5.09; N, 3.31%. MALDI-TOF (CHCl<sub>3</sub>/MeCN): m/z: 1006.3 [Mn(9Accm)<sub>2</sub>+H]<sup>+</sup>, 1028.3 [Mn(9Accm)<sub>2</sub> + Na]<sup>+</sup>, 1192.5 [Mn(9Accm)<sub>2</sub> + Na + 4MeCN]<sup>+</sup>.

#### 2.1.2. Method B

200 mg of 9Accm (0.42 mmol) were added to 5 mL of pyridine in a microwave tube along with 51 mg (0.21 mmol) of Mn(O<sub>2</sub>CMe)<sub>2</sub>·4(H<sub>2</sub>O). The reaction mixture was under continuous stirring while applying a power of 250 microwave energy for 2 min. The temperature was allowed to reach 140 °C and then left to drop to room temperature. Finally, a yellow microcrystalline material was obtained. The compound was washed with water, MeOH and ether. Yield: 67%. The IR of the compound was identical to the crystals achieved by Method A after layering.

### 2.2. Synthesis of [Mn(9Accm)<sub>2</sub>(4,4'-bpy)]<sub>n</sub> (2)

100 mg of 9Accm (0.21 mmol) were added to 5 mL of DMF in a microwave tube together with 25 mg (0.11 mmol) of Mn(O<sub>2</sub>CMe)<sub>2</sub>·4(H<sub>2</sub>O) and 17 mg (0.11 mmol) of 4,4'-bpy. The microwave reaction was performed following the same methodology described above. A dark red solution was obtained and left undisturbed overnight. This way, a dark orange precipitate was attained; the solid was filtered and washed with water, MeOH, and Ether. Yield: 63%. IR (ν/cm<sup>-1</sup>) 1663 m, 1627w, 1549w, 1505 m, 1440 m, 1157w, 983w, 881w, 734w, 604w, 541w, 448w. Anal. Calc. for **2**·4.5H<sub>2</sub>O·0.25DMF (C<sub>90</sub>H<sub>62</sub>O<sub>4</sub>N<sub>4</sub>Mn): C, 76.76; H, 5.32; N, 2.49. Found: C, 76.78; H, 5.11; N, 2.18%. MALDI-TOF (CHCl<sub>3</sub>/MeCN): m/z: 1006.3 [M(9Accm)<sub>2</sub>+H]<sup>+</sup>, 1028.3 [Mn(9Accm)<sub>2</sub>+Na]<sup>+</sup>, 1161.3 (Mn(9Accm)<sub>2</sub>(4,4'-bpy)-1e<sup>-</sup>), 1192.5 [Mn(9Accm)<sub>2</sub>+Na+4MeCN]<sup>+</sup>.

### 2.3. Physical measurements

C, H and N analyses were performed with a Perkin-Elmer 2400 series II analyzer. MALDI-TOF spectra of **1** and **2** were recorded in CHCl<sub>3</sub>/MeCN in a 4800 plus MALDI TOF/TOF (ABSciex-2010) spectrometer. Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded from KBr pellets on a Bruker IFS-125 FT-IR spectrophotometer. Absorption spectra were recorded with 1 nm resolution for all cases on a Cary 100 Bio UV-spectrophotometer. Microwave experiments were performed with the CEM Focused Microwave Synthesis System, Model Discover.

### 2.4. Structure determination

Data for compound **1** were collected on a pinkish red plate on a Bruker Kappa-Mach3/APEXII-CCD diffractometer equipped with a Mo-target rotating anode setup and an Incoatec-Helios-Mirror monochromator. Final cell constants were obtained from a least squares fit of several thousand strong reflections. The structure was readily solved with the Patterson method and subsequent difference Fourier techniques. Refinement on F<sup>2</sup> was performed with the SHELXTL suite [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and isotropically refined as riding atoms.

### 2.5. Fluorescence data

Fluorescence emission spectra in the solid state and in solution were carried out on a Horiba-Jobin-Yvon SPEX Nanolog-TM and a

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