



Reprint of “Using single-molecule magnets as analyte-recognition compounds in photo-electric chemical sensors: Recent results from $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 2\text{CH}_3\text{COOH}\cdot 4\text{H}_2\text{O}$, and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$ ”[☆]

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ABSTRACT

Single-molecule magnets (SMMs) were tested for their chemical sensing properties on photo-electric chemical sensors. Photo-electric chemical sensors or PECS are contact sensors for the detection of various chemical analytes, with a wide range of possible applications, using different analyte-recognition compounds (ARCs). The ARC-analyte interaction on the surface of the sensor generates photovoltages (PVs), due to the Becquerel effect, as in photovoltaics. Detection of analyte is documented as modified PVs upon excitation of both the analyte and the ARC using an optical source providing fast light flashes (<10 μs). Single crystals of the SMMs were grown, and were applied mechanically on the PECS electrodes. The background-corrected data revealed significant ARC activity for the two SMMs considered, namely $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 2\text{CH}_3\text{COOH}\cdot 4\text{H}_2\text{O}$, and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$, for vapor and liquid analytes, respectively.

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1. Introduction

Modern technology, and our quality of life largely depend on various types of sensors and detectors. A sensor's function is the conversion of a physical quantity into a measurable signal. The latter, triggers a response and produces a visual, audio, or other feedback indicating what was detected. A simple detector is a thermometer connected to a thermocouple, which converts the temperature to an output voltage, which is read by a voltmeter [1]. There is a vast range of applications of sensing devices; i.e. sensors have been protecting us from fires (thermal and CO sensors), from having an accident with our car (proximity sensors), and from toxic gasses produced by modern machinery and factories

(chemical sensors), to name a few. The latter type of detectors has been attracting progressively more attention in recent years, for reasons that include high demands for energy (more coal-, natural gas-, or petroleum-burning power stations), demands for defense and national security against chemical/biological weapons, as well as demands for detection of contaminants in the water supply, or other public-serving major infrastructure. It is thus understandable that due to the complexity of the analytes, the demand for new sensing technologies is high. Along these lines, we have been developing sensing technologies for various analytes, and recently we extended our investigations to the use molecular clusters and single-molecule magnets as analyte-recognition compounds (ARCs) in our platform photo-electric chemical sensors (PECS) (Fig. 1), [2–4].

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2. The PECS technology

PECS technology is based on the Becquerel effect [5]. The Becquerel effect, the basis of photovoltaic energy, refers to the phenomenon in which illumination of conducting surfaces generates charge movements at that surface, which are readily observed as photo-voltages (PVs), and which can be easily detected, digitized, and quantified. Sensors made using these methods are direct-con-



Fig. 1. Photograph of the handheld-type of PECS sensor, illuminated by a light-emitting diode. The experiments reported herein were performed on a larger scale of this setup, using a xenon strobe light as the light source, and the duration of the flash was $t < 10 \mu\text{s}$.

tact sensors, meaning the analytes must come into contact with the sensors. Target analytes interact with PECS sensing layers containing the ARCs. Such interactions cause transitions of ARCs to alternate states that in colorimetric sensors would be of a different color, but in PECS produce modified PVs. This modification is in general quantized molecule by molecule, and is progressive with increasing analyte concentrations. The latter allows for different analyte concentrations to be measured, meaning that the signal increases with increasing analyte concentration; the sensitivity of PECS reaches parts-per-trillion (ppt) in many cases.

The ARC-analyte interactions may or may not be reversible. Both cases have advantages in different applications: (a) Electrodes with reversible ARC-analyte interactions can monitor the change in concentration of the analyte (both positive or negative), making them candidates for flow and control applications as well as long term monitoring. (b) Irreversible ARC-analyte interactions find applications in remote detection, providing readings of the maximum analyte concentration detected. ARCs for more than 150 analytes are known, varying from amalgam-forming reagents, antibodies for microbes, aptamers, chelating organics for the detection of metals, preformed coordination complexes, colorimetric reagents, dyes, materials capable of ion-exchange reactions, organic acids and bases, reagents for forming host-guest compounds, and others [2–4,18].

The Sensors Group at the University of North Florida has also developed multiple analyte sensors, by using multiple electrodes with each having a different ARC. Such composite sensing devices can be particularly useful, provided high specificity for each analyte-ARC pair. The utility of comparable composite arrays that use colorimetric dyes rather than PECS has been demonstrated by Suslick et al. [6].

The electrodes used for the acquisition of the data presented herein had $\sim 3 \text{ mm}^2$ surface area, using 3 ml of aqueous electrolyte volume, or the vapor of different analytes (*vide infra*). Smaller surface area electrodes typically exhibit higher sensitivities, and are used for the detection of analytes at particularly low concentrations. However, the purpose of the present work was to discover additional analyte-ARC pairs, and furthermore investigate the ability of molecular clusters to be used as ARCs, and thus the standard 3 mm^2 electrodes were used for the reported experiments.

3. Single-molecule magnets

Single-molecule magnets (SMMs) are molecular clusters of transition metal ions, which exhibit superparamagnetic properties below a blocking temperature (T_B) [7]. The properties are intrinsic to the molecules, and SMMs exhibit a combination of classical and quantum properties [8]. These property combinations include the classical property of any magnet, namely hysteresis loops in magnetization versus field studies, together with quantum properties, such as quantum tunneling of the magnetization [9], spin parity effects [10], quantum-phase interference [11], magnetic deflagration [12], among others [13]. They are thus mesoscopic particles, and as such they have been used as models for a variety of complex quantum phenomena, such as the ones mentioned (*vide supra*). Potential applications of SMMs include their use in spintronics and quantum computation [14].

The inorganic core of SMM clusters is constructed by several metal ions at various oxidation states (or oxidation state combinations) usually bridged by oxides. These metal-oxide cores are enveloped in an organic shell, which can be varied at will using soft chemistry methods. Thus, the cores of SMMs can be considered as a small piece of a metal oxide network, protected by organic groups in the periphery. The first cluster to be identified as an SMM was $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$, (Fig. 2) often abbreviated as Mn_{12}Ac [8a], and since this discovery in 1993 the SMM family of Mn_{12} complexes has grown substantially [15]. The latter family has included Mn_{12} complexes with bulky carboxylates, different terminal ligation, as well as different electronic characteristics [15]. The family of Mn_{12} SMMs still remains the most well-studied series, even though other SMM-types have sur-

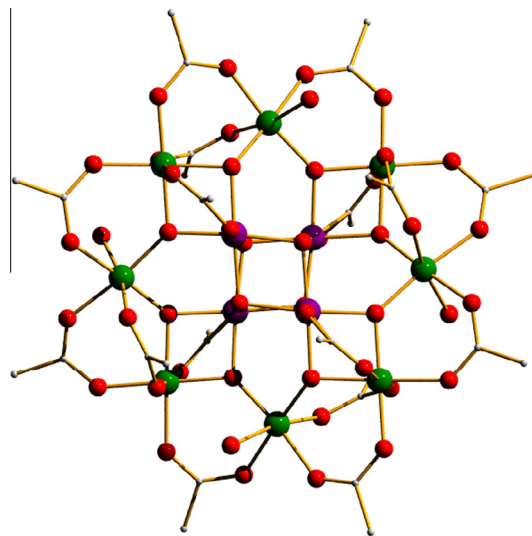


Fig. 2. X-ray crystal structure of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ (Mn_{12}Ac). Hydrogen atoms have been omitted for clarity. Color code: Mn^{IV} purple, Mn^{III} green, O red, C gray. Mn_{12}Ph is nearly isostructural, with the only difference being the organic shell, which in Mn_{12}Ph consists of sixteen benzoate groups, in place of the sixteen acetate ones in Mn_{12}Ac . (Colour online)

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