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Editorial

Smart Tools for Smart Applications: New Insights into Inorganic Magnetic Systems and Materials

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Abstract: This Special Issue, consisting of four reviews and three research articles, presents some of the recent advances and future perspectives in the field of magnetic materials and systems, which are designed to meet some of our current challenges.

Keywords: magnetic materials; magnetic particle and nanoparticles; single-molecule magnets; molecular magnetism; magnetic separation; magnetic resonance imaging; MRI contrast agents; magnetic domain visualization; paramagnetic properties; magnetically-guided drug delivery systems

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In the recent years, the research in the field of magnetic materials and systems has been very active as documented by the increasing number of contributions (Figure 1). Micro/nanosystems with magnetic properties have been extensively investigated in many fields, ranging from physics and chemistry to mathematics and medicine. The research is consequently very broad and multidisciplinary, from basic studies to more applicative contributions (Figure 2).

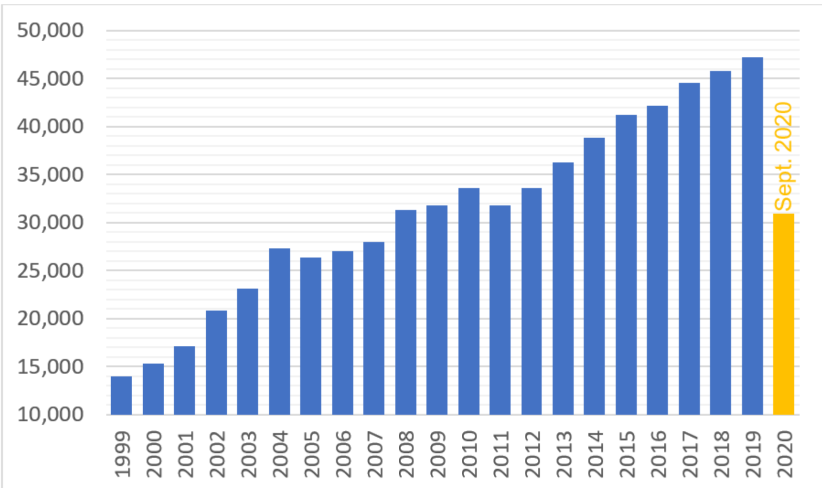

Figure 1. Number of documents published in the last 10 years (source: Scopus).

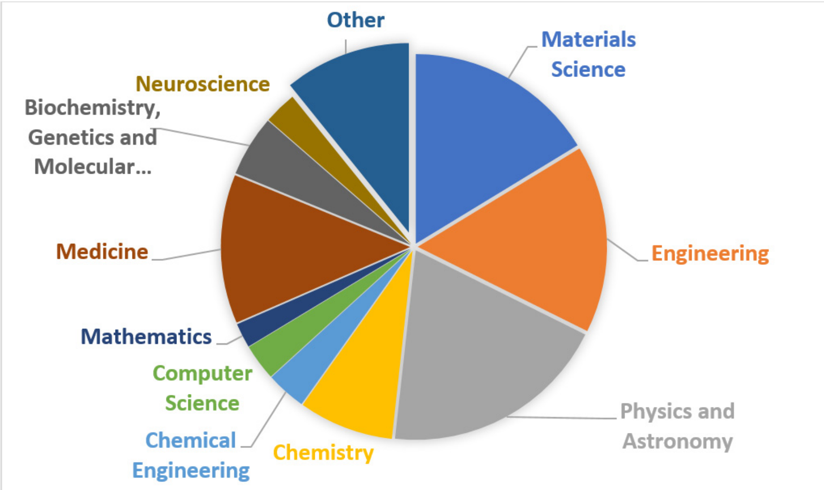

Figure 2. Subject areas of contributions dedicated to magnetic materials and systems (source: Scopus).

The research in these areas has recently shown that if the magnetic compounds are opportunely functionalized and modified with moieties and specific functional groups, a plethora of challenging multidisciplinary applications is available, including the development of magnetically-controlled particles, stimuli-responsive materials, magnetically-guided chemical/drug-delivery systems, sensors, spintronics, separation and purification of contaminated groundwater and soils, ferrofluids and magnetorheological fluids, contrast agents for MRI, and internal sources of heat for the thermo-ablation of cancer. Magnetic compounds have been found to be highly selective and effective in all these application fields, from the molecular to the microscale level. Furthermore, the research on new magnetic systems is very active as documented by recent achievements. Such systems—for example, two-dimensional magnetic materials [1], ferrofluid droplets exhibiting reversible paramagnetic-to-ferromagnetic transformation [2], and oxide heterostructures containing cation defects able to tune magnetism [3]—can be considered materials at the frontiers, which will receive growing attention in the coming years. This Special Issue aims at underlining the latest advances in the field of magnetic compounds, nanosystems, and materials, covering a large variety of topics related to novel synthesis and functionalization methods, properties, applications, and use of magnetic systems in chemistry, materials science, diagnostics, and medical therapy.

The present Special Issue, composed of four reviews and three research articles, showcases some of the latest achievements and future perspectives in the field of the magnetic materials and systems designed to meet some of our present challenges.

Nisticò et al. [4] reviewed the subjects of the domain structure visualization and other characterization techniques to be applied in materials science and biomedicine. In the review, the current understanding of the usage, advances, advantages, and disadvantages of many techniques currently available to investigate magnetic systems are presented with the aim to help the reader in the choice of the most suitable methodology. Due to the multidisciplinary approach characteristic of these studies, in most cases, these very specific characterization techniques are, for a fact, little known (or fully unknown) to most of the users. In the present review, the characterization techniques were classified into three sections and properly discussed with examples from the literature. Section I is dedicated to the definitions of magnetism and magnetization (hysteresis) techniques. Section II is dedicated to the morphological aspects, thus illustrating all the different visualization methods of magnetic domains. Finally, Section III is dedicated to the principal physicochemical characterization methods, with a final section particularly devoted to biomedical applications, including the exploitation of magnetism in imaging for cell tracking/visualization of pathological alterations in living systems (mainly by magnetic resonance imaging, MRI).

Among all fields of magnetism, single-molecule magnets (SMMs) and single-ion magnets (SIM) belong to an extremely interesting and innovative branch of modern magnetism. Perlepe et al. [5] reviewed a few inorganic and organic ligands in the chemistry of 3D-, 4D-, and 5D-metal SMMs and SIMs, through selected examples. Azide ion, cyanido group, tris(trimethylsilyl)methanide, cyclopentanienido group, soft (based on the Hard-Soft Acid-Base model) ligands, metallacrowns combined with click chemistry, deprotonated aliphatic diols, and the family of 2-pyridyl ketoximes including some of its elaborate derivatives are the selected ligands to be discussed with particular emphasis on the rationale behind the selection of the ligands. As underlined by the authors, the contribution is not an exhaustive and comprehensive review of the field, but rather takes a simple approach to the topic without containing large amounts of structural and magnetic information, synthetic discussions and chemical equations. A reader with a good general chemical background will find this material very accessible. Finally, current interests, actual limitations in the field, and perspectives are highlighted.

Fernández-Barahona et al. [6] reviewed the use of iron oxide nanoparticles (IONPs) as positive contrast agents for MRI. The authors highlighted the increasing interest in the development of innovative positive MRI contrast agents, due to the toxicity and retention issues associated with routinely administered Gd-based contrast agents [7]. After an overview of the mechanism of T_1 (longitudinal or spin lattice relaxation time)-based MRI contrast and a critical survey on the most remarkable Gd- and Mn-based nanosystems, the authors discussed the main physicochemical properties that IONPs must possess to act as T_1 agents, i.e., ultrasmall core size with moderate crystallinity (usually maghemite (γ-Fe_2O_3)) and high colloidal stability with hydrodynamic sizes ranging from 5 to 20 nm. The synthetic procedures useful to achieve these properties are then clearly summarized and are thus easily accessible to the readers. Finally, the authors reported the main in vivo applications of T_1-IONPs, not only for MRI but also for multimodal imaging, highlighting that even if longitudinal relaxivity values of IONPs are still far from those of some Gd nanoparticles, there is great potential in the development of these systems, given the status of the area as an emerging research field. Of course, biocompatibility, pharmacokinetics, and delivery pathways must be studied in advance to guarantee their clinical translation.

In this context, Kozlova et al. [8] reported the possibility of modulating the T_1 or T_2 (transversal or spin–spin relaxation time) contrast generated by submicron carriers containing Fe_3O_4 particles, according to their core-shell structure. The authors synthesized three different magnetic submicron core–shells, displaying a single layer of magnetite in the shell and various amounts of Fe_3O_4 particles in the core. They found that all three systems act as dual T_1/T_2 contrast agents. Remarkably, the highest T_1 and T_2 contrast in gradient echo mode can be observed from the core–shell suspension with magnetite nanoparticles contained only in the shell [9]. The addition of magnetite nanoparticles in the core, in fact, seems to impair the contrast properties due to an increase in packing density of magnetite nanoparticles and in the number of interactions between them. However, in the T_1 spin-echo mode, surprisingly the tendency is the inverse, with the greatest T_1 signal enhancement displayed by submicron carriers with one layer of magnetite and four loadings of Fe_3O_4 particles in the core. The authors thus practically proved that different combinations of MRI acquisition modalities and submicron magnetite carrier structures enabled magnetic systems suitable for both T_1 and T_2 MRI that can be also controlled and delivered to the site of interest by an external magnetic field.

Carniato and Gatti [10] contributed to the Special Issue with an interesting research article dealing with Gd_2O_3 nanoparticles doped with various amounts of Yb^{3+}. These mixed oxide nanoparticles were already proposed as a potential dual computed tomography (CT) and positive MRI contrast agent [11]. Carniato and Gatti proposed a cheap and fast co-precipitation synthesis procedure along with functionalization of the particle surface with citrate molecules, in order to confer high hydrophilicity, improve stability, and increase the interaction of the metal ions exposed on the surface with the water molecules. The relaxometric study carried out on the developed nanosystem displayed high relaxivity values at a high magnetic field (with a maximum close to 60 MHz) with respect to the clinically used Gd^{3+}-chelates and comparable to those of similar nanosytems. These features, together with the chemical stability of the nanoparticles in biological fluid and in the presence of a chelating agent, make these nanoparticles suitable for dual MRI-CT diagnostic analyses.

Peralta et al. [12] reviewed the most promising magnet-responsive nanomaterials used in groundwater and wastewater remediation processes. In particular, the authors proposed an overview of the main relevant synthetic methods, surface properties, and clean-up adsorption applications associated with magnetic core–shell nanoparticles and nanocomposites. The discussion is organized into five main sections. Section I is dedicated to silica-based materials, with a specific focus on the incorporation mechanisms of magnetic species (i.e., metallic iron and iron oxides) into silica structures (acting as functional coatings) to produce core-shell systems with freely available functionalities at the surface (namely, silanols and further modifications), as well as on magnetic nanocomposites made of magnetic nanoparticles dispersed in mesoporous silica matrices and hollow particles. Section II is dedicated to clay-based materials, with a specific focus on the incorporation of magnetic nanoparticles within the clays' porous system. Section III is dedicated to carbon-based materials with a particular emphasis on magnetic carbon hybrid nanocomposites. Section IV is dedicated to polymer-based materials, where polymers are chemically anchored or physically adsorbed at the surface of magnetic nanoparticles to form core–shell systems. Lastly, Section V is dedicated to the production of waste-derived magnetic systems produced by means of incorporation processes involving the functionalization of magnetic species (e.g., iron oxides) with waste-derived substances isolated from agricultural residues and biowaste, paving the way for the concept of "waste for cleaning waste", in line with the guide-principles of the circular economy.

In this context, the study reported by de Castro Alves et al. [13] is focused on the production and testing of magnetic alginate activated carbon beads for the removal of heavy metals (i.e., Cd(II), Hg(II), and Ni(II)) from aqueous environments. The study investigated the effect in terms of sorption capacity over different experimental conditions (pH, recycling, and reusability) for mono-metallic systems, as well as the competitive interactions in ternary systems (thus simulating the composition of a real wastewater derived from industrial and mining effluents). Results established a higher affinity of the tested material for Cd(II) ions in both mono-metal and ternary systems, whereas recycling experiments demonstrated that magnetic beads are re-usable for at least five consecutive adsorption/desorption cycles.

We truly hope that the contributions published within this Special Issue can help readers to increase their knowledge in the field of magnetic systems, providing inspiration for novel relevant publications. In this regard, we thank the authors for their valuable contributions; the referees for their insightful and appropriate comments, of paramount importance to enhance the scientific standard of this Special Issue; and the editorial staff, for their constant and unparalleled support.

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References

1. Mak, K.F.; Shan, J.; Ralph, D.C. Probing and controlling magnetic states in 2D layered magnetic materials. *Nat. Rev. Phys.* **2019**, *1*, 646–661. [CrossRef]
2. Liu, X.; Kent, N.; Ceballos, A.; Streubel, R.; Jiang, Y.; Chai, Y.; Kim, P.Y.; Forth, J.; Hellman, F.; Shi, S.; et al. Reconfigurable ferromagnetic liquid droplets. *Science* **2019**, *365*, 264–267. [CrossRef] [PubMed]
3. Park, D.S.; Rata, A.D.; Maznichenko, I.V.; Ostanin, S.; Gan, Y.L.; Agrestini, S.; Rees, G.J.; Walker, M.; Li, J.; Herrero-Martin, J.; et al. The emergence of magnetic ordering at complex oxide interfaces tuned by defects. *Nat. Commun.* **2020**, *11*, 3650. [CrossRef] [PubMed]

4. Nisticò, R.; Cesano, F.; Garello, F. Magnetic materials and systems: Domain structure visualization and other characterization techniques for the application in the materials science and biomedicine. *Inorganics* **2020**, *8*, 6. [CrossRef]
5. Perlepe, P.S.; Maniaki, D.; Pilichos, E.; Katsoulakou, E.; Perlepes, S.P. Smart Ligands for Efficient 3d-, 4d- and 5d-Metal Single-Molecule Magnets and Single-Ion Magnets. *Inorganics* **2020**, *8*, 39. [CrossRef]
6. Fernández-Barahona, I.; Muñoz-Hernando, M.; Ruiz-Cabello, J.; Herranz, F.; Pellico, J. Iron Oxide Nanoparticles: An Alternative for Positive Contrast in Magnetic Resonance Imaging. *Inorganics* **2020**, *8*, 28. [CrossRef]
7. Minaeva, O.; Hua, N.; Franz, E.S.; Lupoli, N.; Mian, A.Z.; Farris, C.W.; Hildebrandt, A.M.; Kiernan, P.T.; Evers, L.E.; Griffin, A.D.; et al. Nonhomogeneous Gadolinium Retention in the Cerebral Cortex after Intravenous Administration of Gadolinium-based Contrast Agent in Rats and Humans. *Radiology* **2020**, *294*, 377–385. [CrossRef] [PubMed]
8. Kozlova, A.A.; German, S.V.; Atkin, V.S.; Zyev, V.V.; Astle, M.A.; Bratashov, D.N.; Svenskaya, Y.I.; Gorin, D.A. Magnetic Composite Submicron Carriers with Structure-Dependent MRI Contrast. *Inorganics* **2020**, *8*, 11. [CrossRef]
9. German, S.V.; Bratashov, D.N.; Navolokin, N.A.; Kozlova, A.A.; Lomova, M.V.; Novoselova, M.V.; Burilova, E.A.; Zyev, V.V.; Khlebtsov, B.N.; Bucharskaya, A.B.; et al. In vitro and in vivo MRI visualization of nanocomposite biodegradable microcapsules with tunable contrast. *PCCP* **2016**, *18*, 32238–32246. [CrossRef] [PubMed]
10. Carniato, F.; Gatti, G. 1H NMR Relaxometric Analysis of Paramagnetic Gd_2O_3:Yb Nanoparticles Functionalized with Citrate Groups. *Inorganics* **2019**, *7*, 34. [CrossRef]
11. Liu, Z.; Pu, F.; Liu, J.; Jiang, L.; Yuan, Q.; Li, Z.; Ren, J.; Qu, X. PEGylated hybrid ytterbia nanoparticles as high-performance diagnostic probes for in vivo magnetic resonance and X-ray computed tomography imaging with low systemic toxicity. *Nanoscale* **2013**, *5*, 4252–4261. [CrossRef] [PubMed]
12. Peralta, M.E.; Ocampo, S.; Funes, I.G.; Onaga Medina, F.; Parolo, M.E.; Carlos, L. Nanomaterials with Tailored Magnetic Properties as Adsorbents of Organic Pollutants from Wastewaters. *Inorganics* **2020**, *8*, 24. [CrossRef]
13. De Castro Alves, L.; Yáñez-Vilar, S.; Piñeiro-Redondo, Y.; Rivas, J. Efficient Separation of Heavy Metals by Magnetic Nanostructured Beads. *Inorganics* **2020**, *8*, 40. [CrossRef]