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► **To cite this version:**

Victor Roullier, Valérie Marchi-Artzner, Olivier Cador, F. Dorson, T. Aubert, et al.. Synthesis and characterisation of magnetic-luminescent composite colloidal nanostructures. *International Journal of Nanotechnology*, 2010, 7 (1), pp.46-57. 10.1504/IJNT.2010.029547 . hal-00442819

**HAL Id: hal-00442819**

**<https://hal.science/hal-00442819>**

Submitted on 8 Mar 2024

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## Synthesis and characterisation of magnetic-luminescent composite colloidal nanostructures

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**Abstract:** In this communication, we report a review of our works on luminescent and magnetic bifunctional structures in the nanoscale range. The synthesis and characterisation of various colloidal nanostructures such as  $Y_3Fe_{5-x}Al_xO_{12}$ -TRITC,  $\gamma-Fe_2O_3-Cs_2Mo_6Br_{14}@SiO_2$  and  $\gamma-Fe_2O_3$ -QDs will be presented. At the outset, the first synthesis of aluminium substituted garnet  $Y_3Fe_{5-x}Al_xO_{12}$  by the citrate gel process and its surface modification by TRITC through grafting of 3-aminopropyltrimethoxysilane (g-APS) for hyperthermia application will be reported. Secondly, the synthesis of nanoparticles under restricted environments offered by water-in-oil microemulsions provides excellent control over particle size and shape and interparticle spacing.

These environments have been used in the synthesis of silica nanoparticles (50 nm) with a magnetic nanocrystalline core surrounded by optically active molybdenum atoms clusters. Finally, we will resume the preparation of composite magnetic-QD bioconjugable micelles by simultaneous encapsulation of hydrophobic CdSe/ZnS QDs (2–4 nm) and magnetic  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles (3–4 nm) into water soluble micelles of synthetic functional PEG amphiphiles bearing a bioactivable terminal group.

**Keywords:** silica; ferrites; clusters; quantum dots; magnetic; luminescence; multifunctional nanoparticles; biotechnology.

**Reference** to this paper should be made as follows: Roullier, V., Marchi-Artzner, V., Cador, O., Dorson, F., Aubert, T., Cordier, S., Molard, Y., Grasset, F., Mornet, S. and Haneda, H. (2010) 'Synthesis and characterisation of magnetic-luminescent composite colloidal nanostructures', *Int. J. Nanotechnol.*, Vol. 7, No. 1, pp.46–57.

**Biographical notes:** Victor Roullier moved to Toulouse (France) and obtained a chemical engineer diploma at the Chemistry school of Toulouse (ENSIACET) and also a Master in Biology and Chemistry at Paul Sabatier University, the same year. Now he is a third year PhD student in V. Marchi Artzner's team: Self-organisation and Functional Targeting (UMR 6226, Rennes, France). His research focuses on water soluble micellised fluorescent and magnetic nanoparticles as bioactive nanoprobe for life sciences.

Valérie Marchi-Artzner spent for years at the High Engineer School of Physics and Chemistry in Paris (ESPCI). From 1994 to 1997, she led her PhD with Professor Jean-Marie Lehn at College de France in Paris working on the molecular recognition between lipidic membranes, including six months on the "bilateral Supermolecules project" in the laboratory of Professor T. Kunitake in Fukuoka. After her thesis, she joined the Erick Sackmann's laboratory of Biophysik at the TU of Munich to develop a model system of membrane adhesion based on the molecular recognition between RGD tripeptide and integrin proteins. She combined her interest in the molecular recognition at the interface and the physical tools to visualise and understanding the adhesion process between membranes or/and cell. After four years she moved to the University of Rennes where she initiated a research program at the interface of Chemistry Biology and Biophysik, focused on the development of new chemical tools for studying protein function and trafficking and for the design of nanostructured hybrid materials starting from inorganic nanocrystals and amphiphilic organised phases.

Olivier Cador first studied Mathematics and Physics at the University of Rennes then studied molecular chemistry in the group of the late Professor Olivier Kahn at University of Bordeaux (PhD in 1998). After military service he moved for two years to Japan at RIKEN Institute in the Physics Department to study the magnetism of nanoparticles assembly. Then in 2001 he joined the laboratory of molecular magnetism at University of Florence (Italy) under the supervisions of Professor Dante Gatteschi and Professor Roberta Sessoli where he has examined the magnetic properties of polynuclear molecular magnetic complexes. Since 2003, he is Assistant Professor at University of Rennes. Its research is now focusing on the physical properties (conducting and magnetic) of hybrid organic-inorganic molecular-based materials.

Frédéric Dorson was graduated in 2006 in Master of Inorganic Chemistry from Paris XI University. Now, he is a third year PhD student in the Solid State Chemistry and Material Team (UMR 6226, University of Rennes 1) under the supervision of S. Cordier and Y. Molard. His research focuses on elaboration of hybrid materials by functionalisation of octahedral transition metal clusters with organic ligands by soft solution chemistry routes.

Tangi Aubert obtained in 2008 a Chemical Engineer Diploma at the Graduate School of Chemistry and Physic of Bordeaux (ENSCP) in France and a Master in Structure and Properties of Inorganic Materials at the University of Bordeaux 1. He is now a first year PhD student in the Solid State Chemistry and Material Team (UMR 6226, University of Rennes 1), under the supervision of F. Grasset and S. Cordier. His research project is focusing on the preparation of new bifunctional silica nanoparticles based on metal atom clusters.

Stéphane Cordier received his PhD Degree in Solid State Chemistry from the University of Rennes in 1996 in the group of Marcel Sergent. He undertook a post-doctoral fellowship at the Max Planck Institute for Solid State Research of Stuttgart for the year 1997 in the group of Professor Dr. Arndt Simon. He is currently researcher at CNRS in the team "Solid State Chemistry and Materials" of the "Unité Sciences Chimiques de Rennes". His fields of research are: solid state chemistry, nanomaterials and hybrids based on transition metal clusters and niobiumfluorides and oxyfluorides.

Yann Molard studied Chemistry at the University of Lyon, France, where he received a PhD Degree in 2000 in the field of calixarene and coordination chemistry. After postdoctoral periods in the groups of Professors J.M. Basset (CPE Lyon), J.F. Gerard (INSA Lyon) and J.H.R. Tucker (Exeter University, UK) he joined the Solid State Chemistry and Material Team of the University Rennes 1 as an Associate Professor in September 2005. His research focuses now in the design of building blocks for the synthesis of hybrid nanomaterials based on functionalised metallic cluster.

In 1998, Fabien Grasset received his PhD Degree in Solid State Chemistry from the University of Science and Technology of Bordeaux and the Institute of Condensed Matter Chemistry of Bordeaux (ICMCB) in the group of J. Darriet. After a post-doctoral stay at ICMCB on magnetic nanoparticles for biotechnology (Professor E. Duguet's group), he undertook a post-doctoral fellowship at the National Institute for Materials Science in Japan from 1999 to 2001 in collaboration with Professor H. Haneda on magnetic core@SiO<sub>2</sub> shell nanoparticles. He is currently an Associate Professor at the University of Rennes and his area of research interest at the Solid State Chemistry and Materials Group focuses on the synthesis of new colloids (M@ZnO, M@SiO<sub>2</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and functional thin films. In 2007, he was invited as short term fellow under ICYS program three months.

Stéphane Mornet received his PhD in physico-chemistry of condensed matter at the University of Bordeaux in 2002. After a four years post-doctoral fellowship at the European Institute of Chemistry and Biology of Bordeaux, he undertook a post-doctoral stay from 2006 to 2007 in Italy at the Institute for Health and Consumer Protection (Ispra) where he worked for the European Commission in the field of nanoparticles health risk. He is currently researcher at the French National Center for Scientific Research (CNRS) at the Institute of Condensed Matter Chemistry of Bordeaux and his research, at the interface of chemistry and biology, focuses on the synthesis of magnetic, metallic and

luminescent nanoparticles, their surface functionalisation and conjugation with biomolecules for imaging and therapy purposes.

Hajime Haneda is a Senior Researcher in National Institute for Materials Science in Japan from 1975. He received the PhD Degree in Materials Science from Tokyo Institute of Technology. At the present time, he is Visiting Professor of Kyushu University, Visiting Professor of Shizuoka University and managing-director of Sensor Materials Center at NIMS. His research area is material science, defect chemistry and diffusion. He received award of the Ceramic Society of Japan (2001) and of the Japan Society of Powder and Powder Metallurgy (2003).

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## 1 Introduction

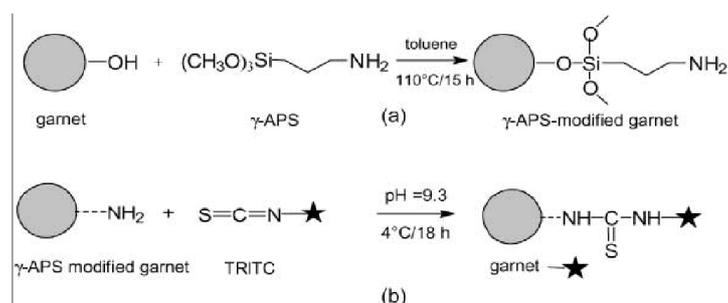
The number of application fields of optical or magnetic inorganic nanoparticles is continuously increasing. Inorganic luminescent materials have practical applications in a variety of devices from conventional TV to electroluminescent, plasma or field emission displays [1] and nowadays luminescent labelling is currently important in biotechnology [2,3]. At the time, magnetic nanoparticles are of great interest for researchers from a wide range of disciplines, including magnetic fluids, catalysis, biotechnology/biomedicine, magnetic resonance imaging, data storage, and environmental remediation [4,5].

Recently, magnetic/luminescent nanocomposite materials provide the possibility for enhanced multifunctional properties [6–27]. One advantage is that this type of bifunctional nanoparticles can be manipulated with magnets and detected by fluorescence. Specially, nanometre sized particles, such as quantum dots (QDs), metal atoms clusters or superparamagnetic oxides have interesting intrinsic physical properties such as optical, electronic and magnetic properties that are not available for either molecules or bulk counter part solids.

In this communication, we report our work on luminescent and magnetic nanoparticles. The synthesis and characterisation of various bifunctional colloidal nanostructures as  $Y_3Fe_{5-x}Al_xO_{12}$ -rhodamine,  $\gamma$ - $Fe_2O_3$ - $Cs_2Mo_6Br_{14}@SiO_2$  and  $\gamma$ - $Fe_2O_3$ -QDs are presented.

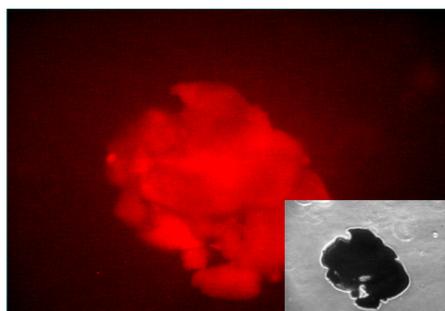
The methods used for preparing multifunctional nanoparticles could be divided into three techniques:

- 1 Direct grafting of organic dyes onto magnetic nanoparticles via reactive functional silane groups [28] (Scheme 1)
- 2 Covering nanoparticles with silica using microemulsion process [27]
- 3 Simultaneous encapsulation of hydrophobic CdSe/ZnS QDs (2–4 nm) and magnetic  $\gamma$ - $Fe_2O_3$  nanoparticles (3–4 nm) into micelles of synthetic functional amphiphilic PEG bearing a reactive terminal group [29].

**Scheme 1** Schematic grafting of functional organic silane molecules g-APS onto garnet nanoparticles via surface hydroxyl groups

### 1 YAIG-TRITC

Since 2001, the first synthesis of aluminium substituted  $\text{Y}_3\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$  (YAIG) (average diameter was ca. 100 nm) by the citrate gel process and its surface modification through grafting of 3-aminopropyltrimethoxysilane (g-APS) for biology-related labelling has been reported [28]. The YAIG-TRITC showed a strong photoluminescence under UV excitation (Figure 1). Cytotoxicity assays were carried during a period of 13 days using two cell lines: human microglia and rat glioblastoma cells. The presence of the amine-functionalised YAIG particles did not affect either the cell viability or the culture growth rate. Hyperthermia application was the motivation of using this complex magnetic oxide. Indeed, for some in vivo applications as localised magnetic hyperthermia using induction heating, ferromagnetic or ferrimagnetic compounds generate heat in AC magnetic fields.

**Figure 1** Image showing the TRITC labelling visualisation of YAIG particles (inset: same particle in phase contrast) (see online version for colours)

For a defined magnetic field, the maximum temperature of the particles could be limited by a correctly adjusted Curie temperature ( $T_C$ ) [4]. In order to understand the role of aluminium in the magnetic properties of our substituted garnet a complete study from 5 K to 900 K was undertaken. The relation between site preference of cations and the structural variation was studied by DC magnetic measurements and the variation of magnetic moment of the compound with  $x < 0.7$  indicates that aluminium cations replace iron cations in tetrahedral sites. The Curie temperature ( $T_C$ ) ranged from  $-40^\circ\text{C}$  (for  $x \sim 2$ ) to  $280^\circ\text{C}$  (for  $x \sim 0$ ). Therefore it was possible to adjust  $T_C$  at the temperature

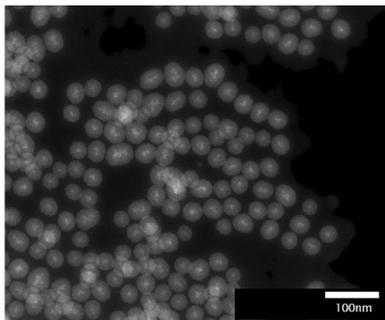
necessary for hyperthermia experiments. By interpolation, it was found that the aluminium content corresponds to value for  $x$  of about 1.5. Nevertheless, at body temperature, the magnetisation of this compound (which decreases with increasing  $x$  value) is not high enough for efficient heating. Nevertheless, recently, Duguet and coworkers demonstrated that during hyperthermia process the increase of temperature induced by magnetic field could be controlled for manganese type-perovskite nanoparticles [30].

## 2 $\gamma\text{-Fe}_2\text{O}_3\text{-Cs}_2\text{Mo}_6\text{Br}_{14}@SiO_2$

Encapsulation of fluorescent dyes, quantum dots, magnetic nanoparticles in silica shells is useful for bio-labelling application, thanks to the easy functionalisation of silica surface, the high colloidal stability of silica-like particles and their non-toxicity [31,32]. Additionally, silica can protect the surface of the core from oxidation or photobleaching. For the preparation of monodispersed silica nanoparticles (with diameter  $< 100$  nm) these methods can be roughly divided into techniques based on so-called Stöber method [33] and microemulsion process [34–36]. For imaging applications, the current probes (fluorescent dye, QD, lanthanides) encounter several challenges, such as poor photostability, limited tissue penetration and potential toxicity. To address these needs, it is important to develop near-infrared emission in order to improve tissue penetration depth [37] coupled with silica coating. During the last decade, we demonstrated that microemulsion process could be a simple and straightforward method for the encapsulation of a large variety of oxide nanoparticles ( $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CeO}_2$ ) within monodisperse silica nanospheres [38–42]. More recently,  $\text{Cs}_2\text{Mo}_6\text{X}_{14}@SiO_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) luminescent nanoparticles (diameter of 45 nm) were synthesised by water in oil microemulsion technique from  $\text{Cs}_2\text{Mo}_6\text{X}_{14}$  inorganic solids [43]. The present work described the preparation of magnetic/luminescent silica nanoparticles by mixing magnetic core  $\gamma\text{-Fe}_2\text{O}_3$  and optically active  $\text{Cs}_2\text{Mo}_6\text{Br}_{14}$  metal atoms clusters. Recently, we propose to use molybdenum metal atom clusters as new probe. They emit in the near infra-red window (600–900 nm), a region of interest for bio-imaging, and are based on  $[\text{Mo}_6\text{X}_{14}]^{2-}$  transition metal cluster units. Many research works have been devoted to molybdenum octahedral  $\text{Mo}_6$  clusters since the discovery of the  $\text{A}_x\text{Mo}_6\text{Y}_8$  solid-state series ( $Y = \text{S}, \text{Se}, \text{Te}$ ) in the early 1970s [43 and reference therein, 44]. They are based on  $[(\text{Mo}_6\text{L}^i_8)\text{L}^a_6]$  units ( $\text{L}^a = \text{apical ligand}$ ,  $\text{L}^i = \text{inner ligand}$ ) that constitute the basic building blocks in molybdenum octahedral cluster chemistry. The  $\text{Mo}_6$  cluster is face-capped by eight inner ligands ( $\text{L}^i$ ) and is additionally bounded to six apical or terminal ligands ( $\text{L}^a$ ). The physical properties of  $\text{Mo}_6$  solid state compounds are related to the number of electrons available for metal-metal bonding within the cluster (VEC) and to the strength of interaction between the units. Metallic electrons are located on 12 metal-metal bonding molecular orbitals of the molecular orbital diagram. Their full occupation leads to a close-shell configuration with a VEC of 24. In the  $\text{A}_x\text{Mo}_6\text{Y}_8$  series, the units are strongly interconnected by double  $\text{L}^{i-a}/\text{L}^{a-i}$  chalcogen bridges leading to band structures and transport properties with the possibility of VEC values lower than 24. Halogen ligands (Cl, Br, I) favour the formation of molecular compounds based on  $[\text{Mo}_6\text{X}^i_8\text{X}^a_6]^{2-}$  units with VEC values of 24 with 1 nm in size. A previous study using HAADF-STEM mode image presented in Grasset et al. [43] constitutes a remarkable result since it is possible to clearly distinguish the  $\text{Mo}_6\text{Br}_{14}$  units inside the silica based hybrids nanoparticles. The morphology studies of these new bifunctional nanoparticles were performed by combined SEM (Scanning Electron

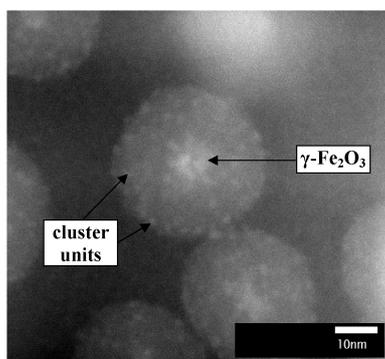
Microscopy), EELS-TEM (Electron Energy Loss Spectroscopy-Transmission Electron Microscopy) and HAADF-STEM (High Angular Annular Dark Field-Scanning Transmission Electron Microscopy) analysis. Figure 2 show STEM micrographs of  $\gamma\text{-Fe}_2\text{O}_3\text{-Cs}_2\text{Mo}_6\text{Br}_{14}\text{@SiO}_2$  sample. The silica nanoparticles consisted of an arrangement of relatively uniform particles with a particle average diameter of 50 nm.

**Figure 2** STEM image  $\gamma\text{-Fe}_2\text{O}_3\text{-Cs}_2\text{Mo}_6\text{Br}_{14}\text{@SiO}_2$  nanoparticles

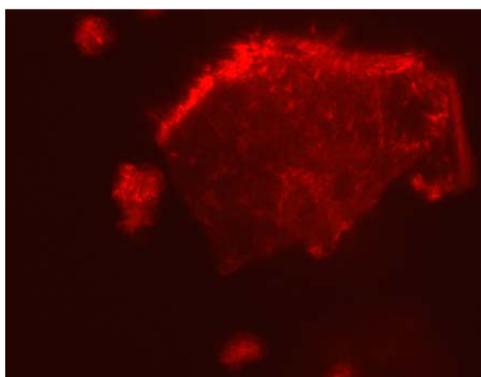


It is possible to observe that the  $\gamma\text{-Fe}_2\text{O}_3$  occupied almost always the centre of the silica nanoparticles whereas the metal atoms clusters are placed around in order to maximise the photoluminescence emission (Figure 3). Indeed, irradiation at 546 nm of the modified silica particles induces the red phosphorescence of the embedded molybdenum clusters, as depicted in Figure 4. Magnetic characterisation was performed using a superconducting quantum interference device (SQUID). Zero-field-cooled (ZFC) and field-cooled (FC) magnetisation curves were obtained under an applied field of 100 Oe between 5–300 K. They exhibited the typical behaviour of ferrite nanocrystals well dispersed in silica matrix [5,34–36]. To conclude with this second part, regarding the optical properties of tissues, it turns out that, owing to their phosphorescence in the near infrared region (580–900 nm),  $\gamma\text{-Fe}_2\text{O}_3\text{-Cs}_2\text{Mo}_6\text{Br}_{14}\text{@SiO}_2$  nanoparticles could constitute relevant candidates in bio-imaging strategies coupling with magnetic resonance imaging [27]. The  $\gamma\text{-Fe}_2\text{O}_3$  could be used for their significant capacity to produce predominantly  $T_2$ -relaxation effects, which result in signal reduction on  $T_2$ -weighted images ('negative' contrast) [45].

**Figure 3** HAADF-STEM image  $\gamma\text{-Fe}_2\text{O}_3\text{-Cs}_2\text{Mo}_6\text{Br}_{14}\text{@SiO}_2$  nanoparticles



**Figure 4** Optical microscopy image of  $\gamma\text{-Fe}_2\text{O}_3\text{-Cs}_2\text{Mo}_6\text{Br}_{14}\text{@SiO}_2$  nanoparticles between two plates of glass under irradiation at  $\lambda_{\text{ex}} = 546 \text{ nm}$  (zoom  $\times 25$ ) (see online version for colours)



### 3 $\gamma\text{Fe}_2\text{O}_3\text{-QD}$ -water dispersible micelles

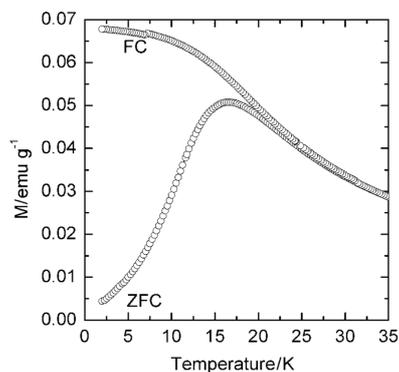
The last part of this paper is regarding the simultaneous encapsulation of hydrophobic CdSe/ZnS QDs (2–4 nm) and magnetic  $\gamma\text{-Fe}_2\text{O}_3$  nanocrystals (3–4 nm) into micelles of synthetic functional amphiphilic PEG bearing a reactive terminal group. This work is based on the recent method proposed by Dr. Marchi-Artzner's group [46]. This method used the dispersion of fluorescent quantum dots (QD) into a liquid crystal phase that provides either nanostructured material or isolated QD micelles depending on water concentration. In this work, the liquid crystal phase was obtained by using a mixture of pegylated gallate amphiphile composed of three undecanoyl aliphatic chains and a polyethylene glycol (34 units) bearing various terminal group such as OH,  $\text{NH}_2$ , COOH, or recognition functions. The hydration of  $\gamma\text{Fe}_2\text{O}_3\text{-QD}$ /amphiphile mixtures resulted in the formation of different composite phase identified by small-angle X-ray scattering. This composite mesophase can be converted into isolated  $\gamma\text{Fe}_2\text{O}_3\text{-QD-I}$  micelles by dilution in water. The fluorescent  $\gamma\text{Fe}_2\text{O}_3\text{-QD-I}$  micelles, purified by size exclusion chromatography, are monodisperse with a hydrodynamic diameter of 30 nm. The temperature dependence of the magnetisation of solution has been measured in Zero-Field Cooled (ZFC) and Field Cooled (FC) modes within an applied field of 20 Oe (Figure 5). In ZFC mode the magnetisation passes through a broad maximum at  $T_{\text{max}} = 16.5 \text{ K}$  characteristic of the freezing of superparamagnetic nanoparticles due to magnetic anisotropy. On cooling the FC magnetisation coincides with the ZFC magnetisation at higher temperatures than 22 K then they split confirming the good monodispersity and dispersion of magnetic nanocrystals.

The synergy between magnetic and luminescent properties was observed under an optical microscope. As observed on Figure 6, when a magnet is close to the aqueous solution containing the mixed micelles, the magnet attracts the quantum dots.

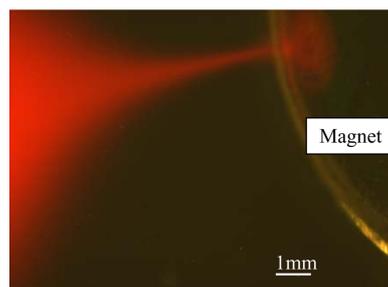
The presence of PEG at the surface of  $\gamma\text{-Fe}_2\text{O}_3\text{-QD-I}$  micelles efficiently prevents the non-specific adsorption of nanocrystals onto lipidic and cellular membranes. In addition, the pegylated amphiphile was chemically modified to introduce a specific targeting recognition group at the polar headgroup. Therefore, the present method offers the

possibility to prepare either functional fluorescent nanoprobe or composite mesophases opening the route to the fabrication of new bioactive functional materials [29,47].

**Figure 5** Zero-field-cooled (ZFC) and field-cooled (FC) magnetisation curves of a suspension of  $\gamma\text{-Fe}_2\text{O}_3\text{-QD-I}$



**Figure 6** Optical microscopy image of  $\gamma\text{-Fe}_2\text{O}_3\text{-QD-I}$  micelles between two plates of glass under irradiation at  $\lambda_{\text{exc}} = 400 \text{ nm}$  (see online version for colours)



In summary, we have reported different strategies to develop bifunctional structures in the nanoscale range. These nanostructures are expected to serve as luminescent markers when attached to bioligands and are capable of being driven in a magnetic field gradient.

### Acknowledgements

The work was supported by Région Bretagne, the University of Rennes, the University of Bordeaux, NIMS-ICYS, the fondation Langlois and the CNRS.

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