

The National IOR Centre of Norway

Development of nanoparticle tracers based on C-dots for interwell applications & Single-Well Chemical Tracer Technology

Projects 2.5.4 and 2.5.3

Project manager: Tor Bjørnstad (IFE)

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Project duration: 2014-2016

Final Project Report

Task 5.4. Development of nanoparticle tracers based on C-dots for interwell applications

Task 5.3. Single-Well Chemical Tracer Technology, SWCTT

Project number and location (UiS, IRIS, IFE):

Project duration: 2 years

Project manager: Tor Bjørnstad

Postdoc: Thomas Brichart

Other key personnel: Alexander Krivokapic / Laura Ferrando-Climent / Sissel Opsahl Viig

Executive summary

Tracer technology for well experiments is one of very few applicable technologies for collection of unique dynamic data of reservoir flows (other technologies being collection and evaluation of “normal” production data, well pressure test analysis and 4D seismics). Two main tracer tests are commonly used for reservoir characterization: (i) the Single-Well Chemical Tracer Test (SWCTT) and (ii) the Inter-Well Tracer Test (IWTT) which includes Partitioning Inter-Well Tracer Tests (PITT). SWCTT and PITT give access to the residual oil saturation (SOR) respectively in the near-well and interwell regions. Non-partitioning IWTT allows assessing qualitatively and quantitatively interwell flow connections, swept volumes between wells and conducting fractures or barriers to flow, etc., resulting in a better reservoir description and an improved reservoir model.

This project aims to study the potential use of two novel classes of tracer which can constitute a breakthrough for Single-Well and Interwell (non-partitioning) testing. The studied tracers are respectively: (i) phase-partitioning lanthanide-chelates and (ii) C-Dots nanoparticles.

1. Introduction and background

(Project initiation, tasks involved, collaboration (national and international), user partner involvement if relevant)

(i) Partitioning lanthanide-chelates for SWCTT (at the time of execution: Task 5.4., Theme 2)

The traditional method for single-well push-and-pull determination of SOR applies simple esters as primary tracers coupled with GC-MS analysis. The high detection limit of those tracers involves the injection/handling of big amount of chemicals. Recent findings inspired from PITT technologies enabled to reduce the tracer concentration by several orders of magnitude (from 10^{-6} [L/L] to 10^{-10} - 10^{-12} [L/L]) using current analysis methods (GC-MS). The team of Professor Olivier Tillement has patented in 2013, in collaboration with TOTAL SA, the use of lanthanide complexes, as tracers for labeling of oilfield injection water. The main asset is their unique fluorescent properties [1]. The patent claims that those tracers can be used to monitor flow between wells and, if the metal complex is partitioning, to assess the volumes of oil reserves [1].

Based on the idea of using such tracers for SOR determination, this project aims to develop new lanthanide-based tracers that can be detected at low concentrations using time-resolved fluorescence and specifically designed for creating phase-partitioning compounds able to measure the oil saturation in the near-wellbore zone through push-and-pull operations. In this case, small volumes of chemicals are required and this would considerably reduce the physical footprint, environmental pollution

concerns, the operational time and the worries about locally increased acid concentration during primary tracer hydrolysis. The operation costs of the test will therefore be reduced correspondingly, allowing for onsite or online detection of the tracers, which would lead to more rapid results.

(ii) C-Dots nanoparticles for IWTT (at the time of execution: Task 5.3., Theme 2)

Traditionally, reservoir tracers have been, and still are, suitable atoms, ions or molecules which survive reservoir conditions and have a well-described dynamic behavior at various reservoir conditions (temperature, pH, pressure, water salinity, formation rock type and mineralogy etc.). A new option has recently opened up by introduction and development of various nano-sized particles which may function as both passive and so-called active tracers for description of fluid flow in porous media. We have started to examine this possibility experimentally of using such particles. The C-Dots nanoparticles had been the only type of nanotracer which have been tested with some success in a real formation (Saudia Arabia, Ghawar field) both in single-well tracer test (push-hold-pull) [2] and in interwell tracer test [2, 3].

In this area we have established an active co-operation with Cornell University (Professor Larry M. Cathles) who initiated the synthesis of the C-Dots tested in the Ghawar field [4]. The main objective of the collaboration aims at joining the efforts to, at some stage, carry out a small-size field pilot test in Colorado in cooperation with Colorado State University. The purpose is to study the penetration of C-dots in a porous medium with larger dimensions than can be created in a laboratory test and examine the possibility to use such particles as interwell reservoir tracers. This constitutes a key step for a thorough understanding of the mechanisms governing their transport in the porous media.

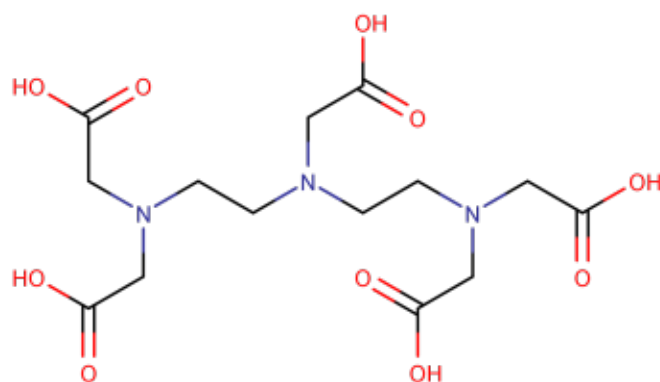
The work done at IFE within the Post-Doc period was focused on the flooding behavior of the C-Dots in Berea and Clashach packed-columns and evaluated the influence of temperature, pH and salinity.

2. Results

(Description and discussion, research-/user partner involvement)

Partitioning lanthanide-chelates for SWCTT (Task 5.4., Theme 2)

Work in 2015 was focused on establishing a proof of concept for our tracers and the way they



should be detected. Multi-ester lanthanide chelates were synthesized from DTPA (Figure1), mass spectroscopy revealed the presence of mono-, di-, tri-, tetra- and penta-ester in the different batches with a large prevalence of penta-ester and di-esters where esters were located on opposite sides of the molecule.

Figure 1: Molecule of DTPA

DTPA possesses five acid groups. In order to synthesize mono-ester derivatives, one needs to provide protection to four of the five acid groups. This can be achieved by forming anhydride on both sides of the molecule, thus deactivating four acids, leaving the center acid to be reacted upon. The reaction is described in Figure 2.

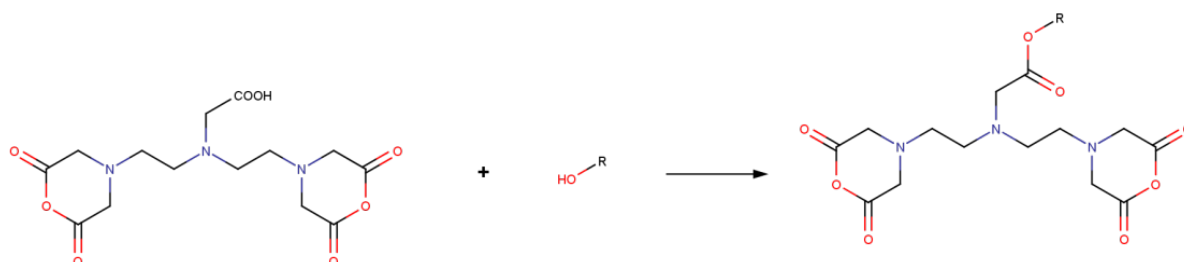


Figure 2. Mono-ester synthesis of DTPA

The monoester chelate was obtained in a minor ratio together with the unreacted DTPA and the poly-esterified chelates. After the esterification of the DTPA, europium was added in a molar ratio (1:1) to the mixture and complexed by the chelates.

Measuring the fluorescence during hydrolysis of the multi-esters at 70°C revealed a progressive change in the intensity of the different emission peaks as the various ester functions hydrolyse over time. As can be seen in Figure 3, a general increase in the luminescence intensity was revealed by the evolution of the intensity of the peaks centered around 595 nm ($^5D_0 \rightarrow ^7F_1$) and 700 nm ($^5D_0 \rightarrow ^7F_4$) as compared to the intensity measured at 565 nm (no signal expected at that wavelength). The approximately 30% increase in signal can be attributed to a better chelation of the europium ion by the surrounding chelate former; this well-known phenomenon better shields the europium against undesired vibration relaxation pathways.

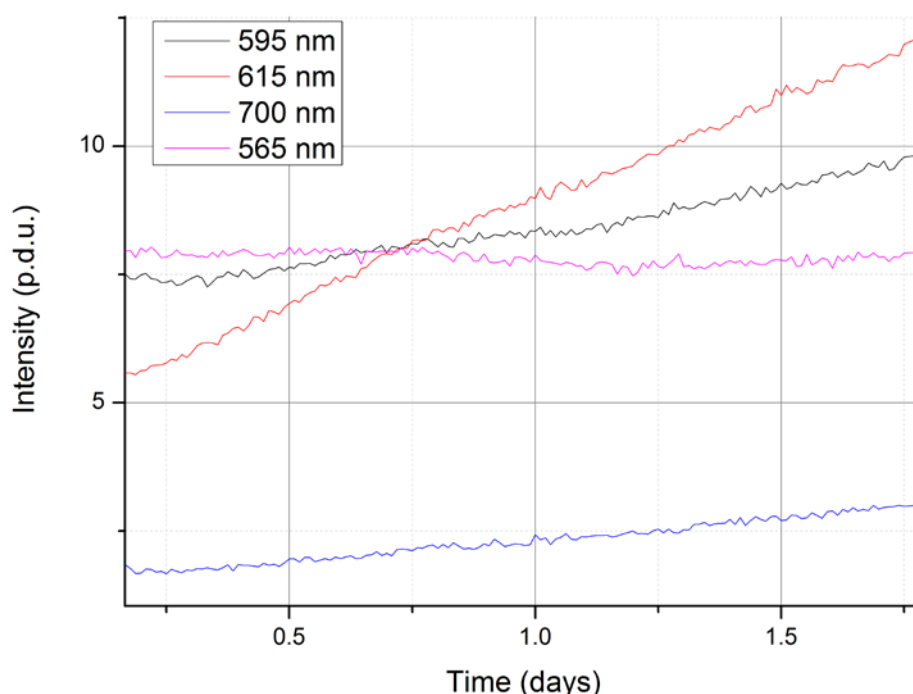


Figure 3. Intensity of fluorescence at 565, 595, 615 and 700 nm during hydrolysis of a penta-ester DTPA chelate of europium [5]

A more than 100% increase can be observed for the intensity of the peak centered around 615 nm ($^5D_0 \rightarrow ^7F_2$). This increase results in a change in the peak ratio after approx. 18 hours where the

peak at 615 nm becomes greater than the one at 595 nm. The europium emission peak at 615 nm is well known in the literature for its sensitivity to the immediate europium surroundings. This is a direct consequence of the hydrolysis performed. As the various esters are hydrolyzed, the acids formed during hydrolysis provide a better chelation of the europium by creating coordination bonds. This phenomenon results in a progressive removal of water molecules in the coordination spheres close to the lanthanide atom; this in turn increases the luminescence quantum yield and the lifetime of the complex.

As each complex (ester and acid version) displays a unique lifetime, it becomes possible to separate the signal from each of the complex forms enabling detection and quantification of both forms during the same analysis (time-resolved fluorescence analysis).

Mono-ester tracer synthesis

Multi-ester molecules are not desirable as the interpretation of results will be more difficult. Therefore, numerous syntheses were performed to produce mono-ester chelates in reasonable quantities. Mono-esters are preferable to multi-ester chelates as only two compounds would be recovered, one partitioning (the ester) and one passive (the acid produced by the hydrolysis of the ester). New synthesis routes were found using “milder” methods based on the use of DTPA-BA (describes previously) and DOTAGA anhydride. The cyclic nature of DOTA derivatives provides more stability to the complex they form with lanthanides as compared to DTPA derivatives. However, their low solubility in solvents other than water could prove a hindrance for this specific application.

In order to synthesize mono-ester derivatives of DOTA compounds, DOTAGA was used. DOTAGA incorporates one more acid group than DOTA. This additional group is also situated farther from the metallic center and thus participates less in the chelation process. In order to esterify only one of the acids, a metallic protection was chosen. In this method, a lanthanide is first chelated; this chelation renders unavailable the four acids closest to the lanthanide as they are now bound to the metal. The farther acid however displays a weaker bond to the lanthanide and can be reacted upon.

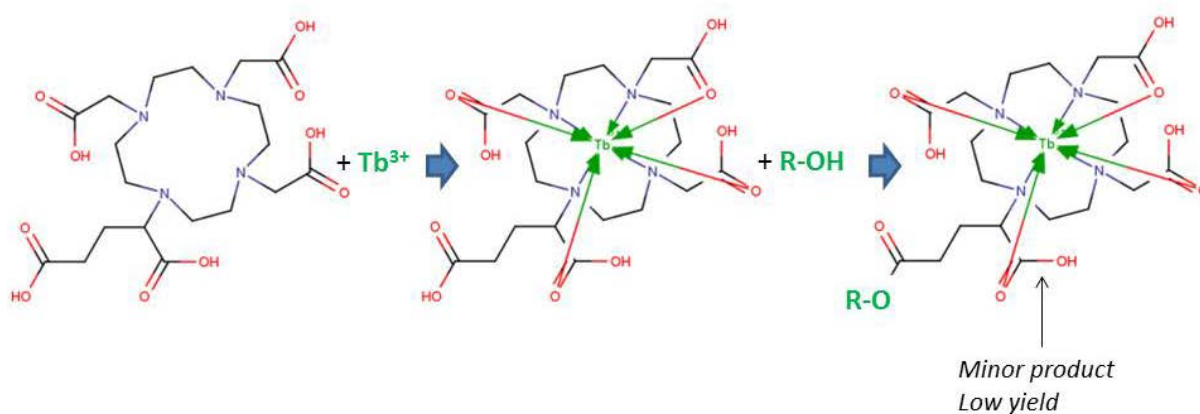


Figure 4. Mono-ester of DOTAGA synthesized via metal protection

The synthesis route is described in Figure 4.

Analysis on LC-MS and HPLC confirmed the synthesis of several new lanthanide mono-ester chelates with different chain length. The structure of these new chelates is described in Figure 5.

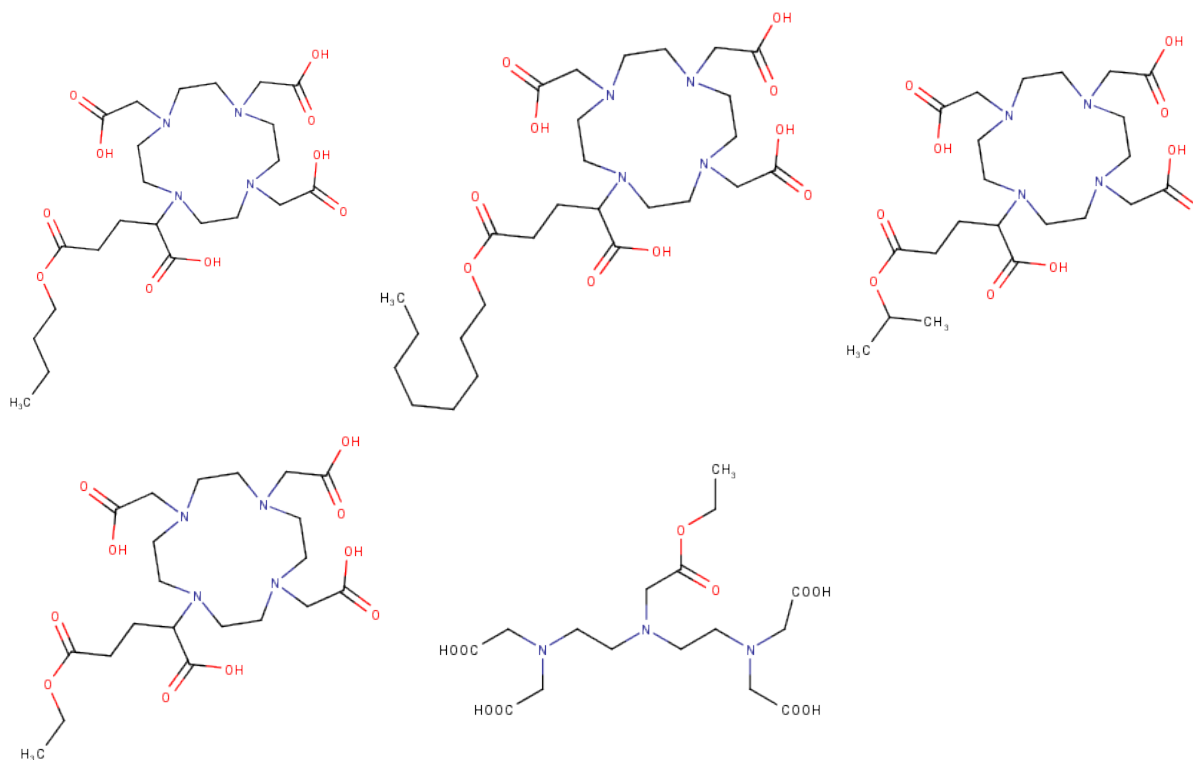


Figure 5. Chemical structure of new lanthanide chelate formers

However, all the synthesized lanthanide mono-esters were minor in the obtained mixtures with many others poly-esters. The synthesis route established for the DOTA-ester derivatives appear as non-specific and provides a low yield.

Several difficulties have been encountered for the separation of those compounds in large quantities making it more difficult to determine some of their properties accurately and thus increasing uncertainties. A preparative separation column setup was build but suffered from limitations by only allowing small quantities to be separated.

C-Dots nanoparticles for IWTT (Task 5.3., Theme 2)

C-Dots NPs exhibit unique physical-chemical properties (inert, non-volatile, chemically stable and non-reactive) that make them adaptable to the harsh conditions encountered in reservoirs including salinity, high-pressure/high-temperature (HP/HT) and rocks composition. Moreover, they constitute the only type of nanotracer which has been tested in a real formation (Saudi Aramco) both in single-well tracer tests (push-hold-pull), and in inter-well tracer tests. The C-dots provided by the team of Professor Cathles (Cornell University), were obtained through a bottom-up chemical route synthesis approach. More precisely, the C-dots are synthesized by one-step thermal decomposition of citric acid-based molecular precursors in presence of ethanol amine (Figure 6).

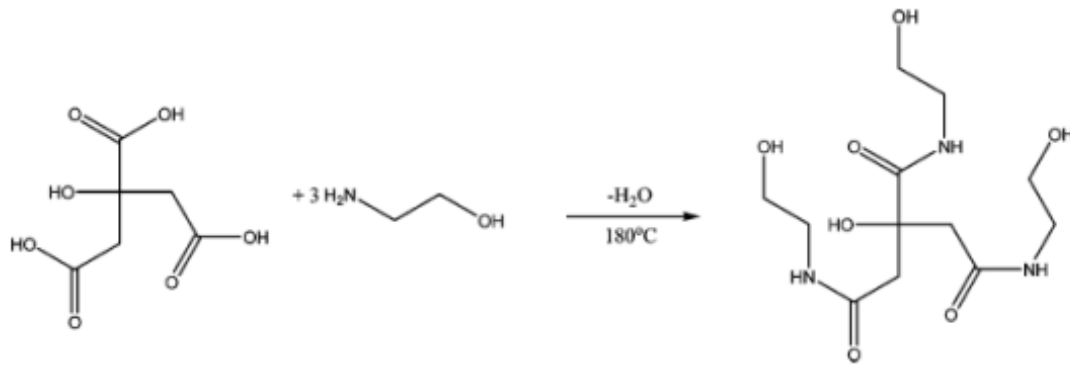


Figure 6 : Reaction scheme of ethanolamine and citric acid

Physical Characteristics

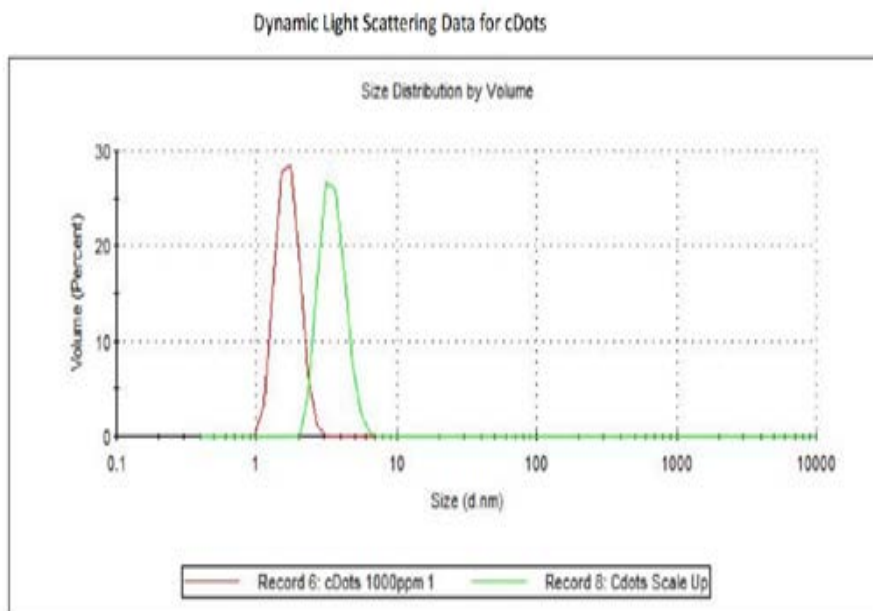


Fig.7. Size distribution (DLS) of produced C-dots

Dynamic Light Scattering (DLS) measurements reveal a low polydispersity with a size centred on 3.5 nm (see C-Dots Scale Up, Figure 7). The *Size Distribution By Volume* shows a very low polydispersity not in agreement with the *Size Distribution By Intensity* which reveal aggregates in the micrometer range.



Fig.8. TEM images of C-dots

However, Transmission Electron Microscopy (TEM) imaging reveals a single population of $\sim 2\text{-}3$ nm (size distribution by volume) particles observed (Figure 8). It should be noticed that the TEM pictures are not representative of the colloidal stability and that it depends on the deposition method.

Luminescence

The C-Dots provided by Cornell University were analyzed using fluorescence spectroscopy. The study revealed a high intensity luminescent signal with a large absorption peak centered on 376 nm and a large emission peak centered on 463 nm (Figure 9).

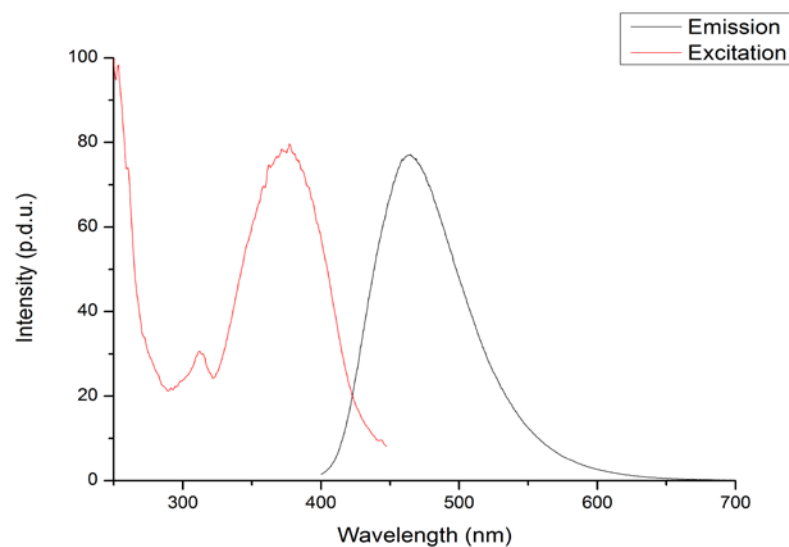


Fig.9. Emission and excitation spectrum of C-dots in water

It should be notice that the batch provided by Cornell wasn't purified and contains both NPs and a fluorescent by-product which have similar emission and excitation properties [3]. The presence of those by-products has an important influence on the fluorescent properties as well as on the flooding behavior characterizations.

The life-time of the C-dot luminescence is short ($< 5 \mu\text{s}$). This fast luminescence could be problematic when measuring the C-dots in highly polluted samples where other compounds may interfere. However, the large Stokes shift displayed by the particles (~ 90 nm) and the important brightness may counteract this limitation and allow the detection nonetheless.

Flooding behavior

C-dots have been injected in a Berea sand-packed column, 25 cm long and 4.6 mm in diameter simultaneously with a passive water tracer I⁻ (as dissolved KI), with a porosity measured at 32%. 20 µL of tracer solution have been injected at a flow rate of 0.2 mL/min. Data points were acquired by both fluorescence and absorption on collected samples of the produced fluid.

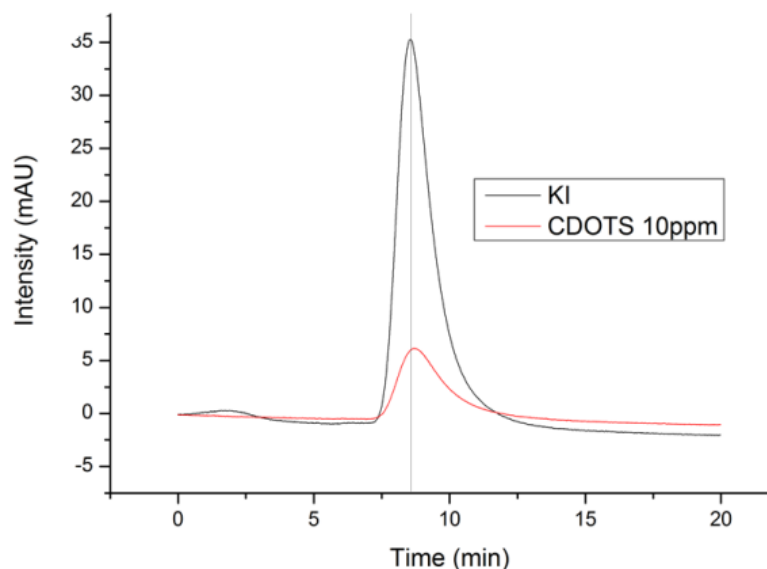


Fig.10. Production curves of C-dots in pure water

Results from using pure distilled water are given in Figure 10. C-dots present no retardation in distilled water compared to the reference used (KI). In 0.1% H₃PO₄ however, the C-dots seem to arrive with a significant delay and in formation water they seem to reach their maximum somewhat before the reference.

The C-Dots have been tested in packed columns of Clashach sandstone using different temperatures, salinity and pH.

Table 1: C-dots recovery (%) in flooding experiments on a Clashach-packed column with various elution liquids at two temperatures.

	Solvent	Deionized Water	Deionized Water	0.1 % H ₃ PO ₄	0.1 % H ₃ PO ₄	Formation water pH7	Formation water pH7
	Temp. (°C)	20	99	20	99	20	99
C-Dots concentration	1 ppm	71 %	72 %	14 %	69 %	62 %	70 %
	10 ppm	70 %	73 %	14 %	66 %	62 %	69 %

As can be seen in the Table 1, recovery rates rarely exceed 70 % in the best-case scenarios. The C-Dots batch provided by Cornell was not purified. As explained before (see *Luminescence*), the particles come together with a fluorescent by-product which interferes and influences the recovery rates determination. The tracer signal is generated by first injecting the C-dots in the HPLC without percolation through the sandstone column to obtain the initial concentration (intensity) by UV and/or

fluorescence. The tracer is afterward injected in the column and the difference between the integrated area with and without tracer gives the relative amount of tracer retained and/or delayed by the rock.

Further experiments will focus on the C-Dots synthesis and purification in close collaboration with Cornell and the related size distribution obtained by DLS. In the second effort, C-Dots will be carefully purified using a dialysis membrane, before injection onto the columns.

Conclusion(s)

Partitioning lanthanide-chelates for SWCTT (Task 5.4., Theme 2)

The sensitivity of the lanthanide chelates toward temperature combined with water has been shown using a complex of DTPA monoethyl ester-europium. In contact with water at 70°C the hydrolysis of the ester into an acid (DTPA-europium) has a quantifiable impact on the luminescence of the europium complex which can be used to estimate the residual oil saturation in the near-well zone. Considering that the ester form of the complex has a higher affinity to the oil phase than the acid hydrolysis product, this new class of tracers can be used as partitioning molecules, like the ethylacetate which, at present, is the most used tracer for SOR estimation.

Moreover, cyclic lanthanide complexes derived from DOTA chelates have been studied and more specifically the chemical routes to obtain the desired chelates (DOTA ethyl ester, DOTA propyl ester, etc.). It has been shown that the synthesis route was unspecific leading to the formation of a polyester mixture unsuitable for the application, and this has to be improved in further experiments.

C-Dots nanoparticles for IWTT (Task 5.3., Theme 2)

The present results confirm the behavior observed by Cornell University and seem to indicate that the solvent influences somewhat the way the C-dots behave during transport. Thus, their use as passive water tracers may not be advisable for all environments. More tests will be run in the future to eventually confirm those results and determine more exactly under which conditions their passive behavior is affected and how and why.

3. Future work/plans

(Work in progress, journal papers in particular)

Partitioning lanthanide-chelates for SWCTT (Task 5.4., Theme 2)

The main challenge highlighted in the study is the ability to synthesize the desired monoethyl ester chelates in a high specific ratio. Present results are not satisfactory. New synthesis routes will be implemented in the next steps of the project to meet the requirements cited previously. Also, the partitioning behavior or affinity with oil has to be evaluated in order to design the best series of ester tracers to determine the SOR at different depths of the well. The partition coefficients will be experimentally determined using both synthetic and crude oil.

C-Dots nanoparticles for IWTT (Task 5.3., Theme 2)

The main plan in the next steps of the project will focus on the study of the surface properties of the nanoparticles to explain the very low recovery rates obtained (up to 70%). The possibility to encode the C-Dots by chemical doping will be studied in order to get a more specific fingerprinting together with a higher sensitivity to allow a better quantification/detection.

4. Dissemination of results

(Include testing/implementation by research-/user partners if relevant)

Partitioning lanthanide-chelates for SWCTT (Task 5.4., Theme 2)

A proceedings paper was published in 2017 and the results have been presented in the 19th edition of the IOR conference co-organized with EAGE [5]. No journal publication has yet been produced with IFE-authors. This is planned for 2018.

C-Dots nanoparticles for IWTT (Task 5.3., Theme 2)

No journal publication has yet been written with IFE-authors. A few oral ppt-presentations have been given in conferences, seminars and technical meetings. Dr Thomas Brichart has presented an overview of the work done in this task at the 13th edition of *Nanohybrid* conference in Porquerolles (France) co-organized by ENS Cachan (Paris) and University of Lyon.

References

1. AGENET, N., et al., *FLUORESCENT TRACERS FOR MARKING OILFIELD INJECTION WATERS*. 2013.
2. Kanj, M.Y., M.H. Rashid, and E. Giannelis, *Industry First Field Trial of Reservoir Nanoagents*, in *SPE Middle East Oil and Gas Show and Conference*. 2011, Society of Petroleum Engineers: Manama, Bahrain.
3. Alaskar, M. and D. Kosynkin, *Successful crosswell field test of fluorescent carbogenic nanoparticles*. *Journal of Petroleum Science and Engineering*, 2017. **159**: p. 443-450.
4. Krysmann, M.J., et al., *Formation Mechanism of Carbogenic Nanoparticles with Dual Photoluminescence Emission*. *Journal of the American Chemical Society*, 2012. **134**(2): p. 747-750.
5. Brichart, T.B., et al., *New Fluorescent Tracers for SWCTT*, in *IOR 2017 - 19th European Symposium on Improved Oil Recovery*, EAGE, Editor. 2017, EAGE: Stavanger, Norway.