

Communication

Luminescent Lanthanide Metal Organic Frameworks for *cis*-Selective Isoprene Polymerization Catalysis

Samantha Russell ¹, Thierry Loiseau ¹, Christophe Volklinger ^{1,2} and Marc Visseaux ^{1,*}

¹ Univ. Lille, CNRS, Ecole Nationale Supérieure de Chimie de Lille, UMR 8181-UCCS—Unité de Catalyse et Chimie du Solide, F-59000 Lille, France; E-Mails: sr90@st-andrews.ac.uk (S.R.); thierry.loiseau@ensc-lille.fr (T.L.); christophe.volklinger@ensc-lille.fr (C.V.)

² Institut Universitaire de France, 75231 Paris, France

* Author to whom correspondence should be addressed; marc.visseaux@ensc-lille.fr; Tel.: +33-320-336-483; Fax: +33-320-436-585.

Academic Editors: Stephen Mansell and Steve Liddle

Received: 18 September 2015 / Accepted: 29 October 2015 / Published: 9 November 2015

Abstract: In this study, we are combining two areas of chemistry; solid-state coordination polymers (or Metal-Organic Framework—MOF) and polymerization catalysis. MOF compounds combining two sets of different lanthanide elements (Nd³⁺, Eu³⁺/Tb³⁺) were used for that purpose: the use of neodymium was required due to its well-known catalytic properties in dienes polymerization. A second lanthanide, europium or terbium, was included in the MOF structure with the aim to provide luminescent properties. Several lanthanides-based MOF meeting these criteria were prepared according to different approaches, and they were further used as catalysts for the polymerization of isoprene. Stereoregular *cis*-polyisoprene was received, which in some cases exhibited luminescent properties in the UV-visible range.

Keywords: MOF; lanthanide; neodymium; isoprene polymerisation; *cis*-selective; luminescence

1. Introduction

Metal-Organic Frameworks (MOFs) are three-dimensional frameworks that are obtained by a reaction between organic O-/N-donor ligands and metallic cationic species [1]. The resulting crystalline

structure consists of inorganic units connected via organic linkers that are often porous; their porosity are exploited in many applications, such as gas storage, separation, controlled drug release and catalysis [2]. Luminescence properties can be observed when MOFs materials are built up from active elements like for example light-emitting rare earths europium or terbium [3,4]. We showed recently that Nd carboxylate based MOFs are efficient pre-catalysts for the stereo-selective polymerization of conjugated dienes [5]. In addition, some unreacted MOF compound residues, that had not been involved in the polymerization, were found disseminated into the polymer matrix, so as the result could be considered as a MOF/polymer composite. However, at this stage, despite the presence of Nd element, the resulting material showed no luminescent properties [6].

Typically, organic luminescent materials, such as polymers, suffer poor stability under harsh conditions and have poor long-term reliability [7]. However, they have a greater ductility and processability than inorganic materials, which allows for polymer films to be produced and the material to be molded and shaped [8]. In comparison, inorganic luminescent materials are known to be a lot more durable and have a greater thermal stability. Therefore, the combination of inorganic and organic materials, such as the MOF and polymer respectively, may allow for the production of a durable luminescent hybrid material with enhanced properties in comparison to organic-only or inorganic-only luminescent materials [9]. Previous work on luminescent polymer composites has been published but current limitations are related to the nature of the polymer matrix, until now rather restricted to thermoplastics [10] or hard to process chitosan [11], and with only scarce examples of synthetic elastomers [12–14].

This contribution considered different lanthanide-based MOF assemblies, obtained by three different synthetic methods, in which were included two elements, neodymium, for its catalytic ability, and europium (or terbium), for luminescence. These compounds were then assessed for isoprene polymerization, with the aim to afford a luminescent diene based-rubber.

2. Results and Discussion

There were two main MOF structures that were intended in the present work. The first one was a lanthanide formate $\text{Ln}(\text{form})_3$, a MOF-like compound that has been previously synthesized and contains the Ln element (typically neodymium) for the inorganic moieties and formic acid to produce formate groups as organic linkers [6]. With neodymium, the three-dimensional structure consists of NdO_9 neodymium-centred tricapped trigonal prisms that are connected to each other via the formate ligands (Figure 1A). Previous work showed that $\text{Nd}(\text{form})_3$ was an efficient pre-catalyst for the polymerization of isoprene when combined with MMAO (modified methylalumoxane), with yields of polyisoprene ranging from 27% to 83% and *cis*-1,4 selectivity ranging from 48% to 88% [6]. The analysis of the synthesized polyisoprene by scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD) revealed that partial fragmentation of the MOF particles had occurred and produced a dispersion of un-activated MOF compound within the polymer matrix. We prepared similarly as their congeners Eu- and Tb-based MOFs having the above-described structures. They were assessed for polymerization catalysis, but no polymer was obtained (*vide supra*), showing that Nd is necessary to catalyze the polymerization. The second MOF structure used was the material MIL-103(Nd) (Figure 1B), a porous

neodymium-based MOF [15], which had already previously been shown to act as a successful pre-catalyst for isoprene polymerization [5].

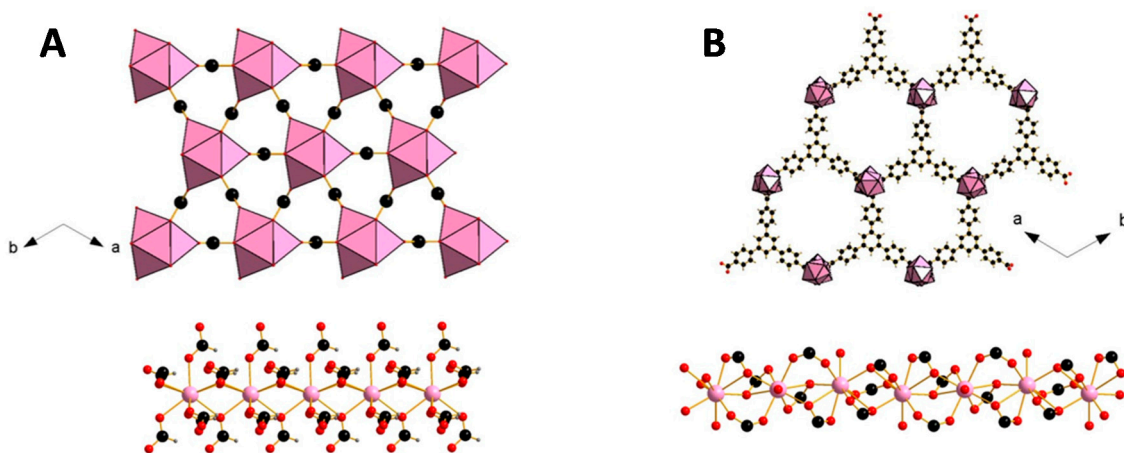


Figure 1. Illustration of the structural organization of $\text{Nd}(\text{form})_3$ (A) and MIL-103(Nd) (B). Pink for Nd, black for C, red for O, grey for H, a and b: crystallographic axes.

Three strategies that are represented in Figure 2 were considered, to have a combination of Nd/Eu(Tb) elements within a MOF structure intended to be further assessed for polymerization: (a) the synthesis of mixed Ln based-MOFs; (b) the use of a mixture of two different pure Ln based-MOF; (c) the inclusion of a second Ln element into a Nd based-MOF.

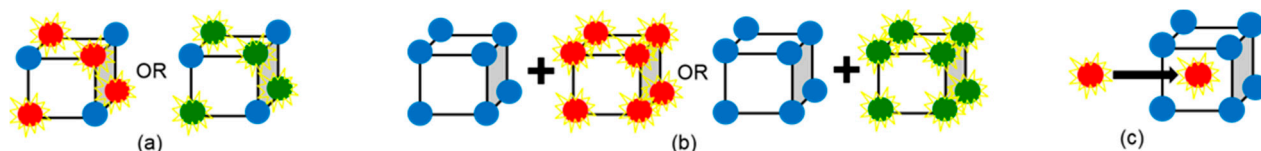


Figure 2. Schematic representations of the expected combined MOF structures: (a) mixed Ln based-MOFs; (b) mixture of two different pure Ln based-MOF; (c) Nd based-MOF including a second Ln element (Nd, blue; Eu, red; Tb, green; yellow circumference represents luminescence).

2.1. Mixed Ln-MOF Synthesis for $\text{Ln}(\text{form})_3$

MOF compounds containing both neodymium and europium (or neodymium and terbium) within the same structure (Figure 2a) were synthesized. The feed molar ratios of the two lanthanides were varied to 1:3, 1:1 and 3:1 in three different MOFs preparations. The true ratios of the two lanthanides within the final MOF structure were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The results (Experimental Section) revealed a difference between the initial feed ratio and the final quantities of the two lanthanides within the MOF, however the major lanthanide element was the one expected (Nd/Eu: 0.49, 1.59, 5.14, respectively). The powder X-ray diffraction (PXRD) of $\text{Ln}(\text{form})_3$ (Ln = Nd/Eu, Figure 3; Ln = Nd/Tb, Figure S1), showed in both cases a single peak with gradual shift in the 2θ value as the quantity of europium (or terbium) within the MOF increased, proving that the two lanthanides are present within the same crystalline MOF structure.

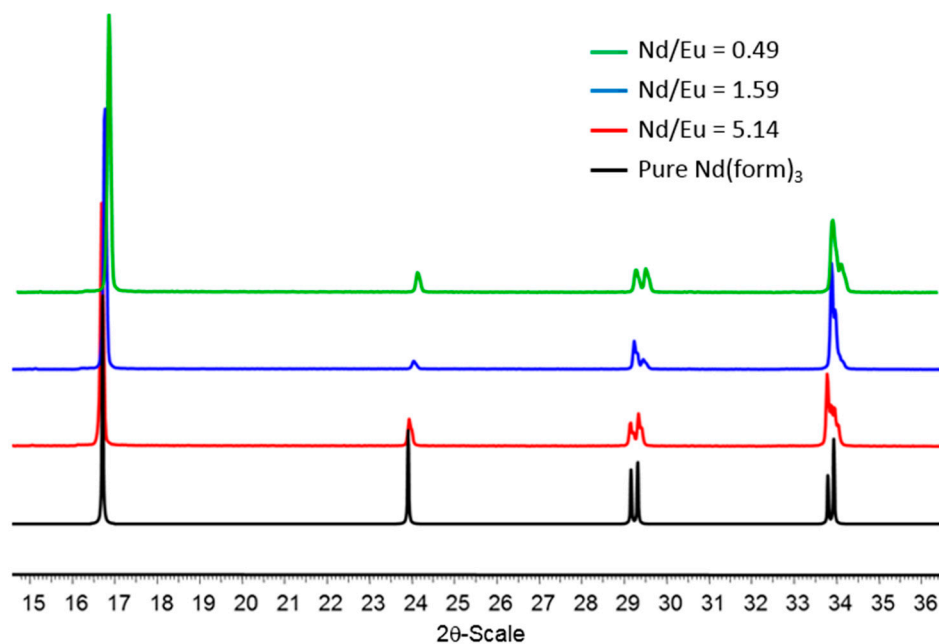


Figure 3. The PXRD pattern of the $\text{Nd}(\text{form})_3$ MOF and the three MOFs with varying Nd/Eu ratios.

Scanning Electron Microscopy (SEM) was used to study the size and shape of the crystals. In pure $\text{Ln}(\text{form})_3$ MOFs, europium-based crystals are smaller than neodymium-based crystals, where the former ones are relatively spherical and the latter ones are longer and more needle shaped (Figure S2). Although the SEM images have shown that there is not a uniform size for all the crystals within one synthesis—some larger needle-shaped crystals due to a slight variation of Nd/Eu ratio are present within every sample—a general trend that smaller crystals are produced when the MOF has a higher europium content may be deduced from observations (Figure 4).

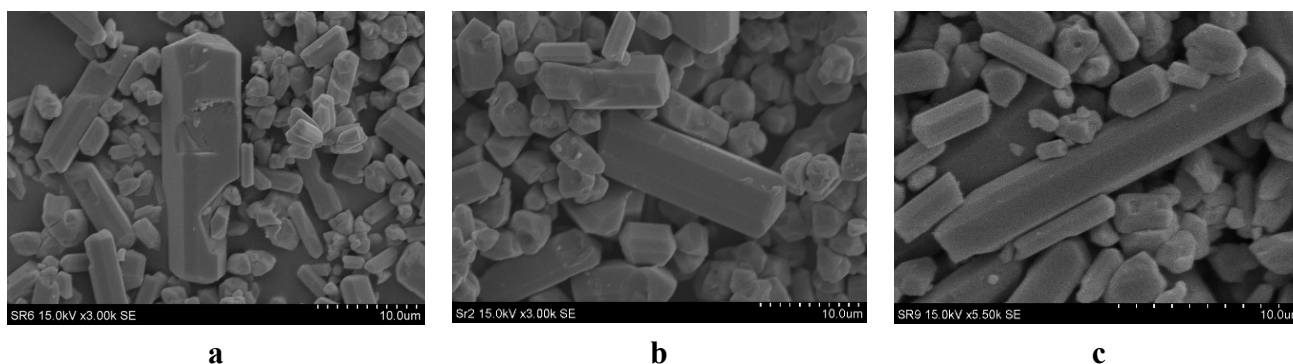


Figure 4. SEM image of $\text{Ln}(\text{form})_3$ MOF compounds with Nd/Eu of 0.49 (**a**, average crystals size $\approx 3 \mu\text{m}$), 1.59 (**b**, av. crystal size $\approx 5 \mu\text{m}$), and 5.14 (**c**, av. crystals size $\approx 6 \mu\text{m}$).

2.2. Pure Lanthanide-Based MOFs

A second approach attempted to mix two lanthanides by combining two distinct MOF solids; this mixing took place further during the polymerization. For that purpose, pure MOF compounds containing only one lanthanide of neodymium, europium or terbium were synthesized. The picture representation of this method can be seen in Figure 2b. Powder X-ray diffraction was used to confirm the purity of the

three distinct MOF solids. (Figure S3) The resulting pattern showed that the three MOF compounds were pure and they had the same peak pattern. Due to the different lanthanides, there was a slight shift of the Bragg peaks in the 2θ scale. This is due to the well-known contraction effect in the lanthanide series, since ionic radius of neodymium is the largest and that of terbium the smallest of the lanthanides investigated here.

2.3. MIL-103(Nd) with Eu-Insertion

The third method used the material MIL-103(Nd) (Figure 1B), with the aim of inserting europium within the pores (Figure 2c). A dried sample of MIL-103(Nd) was impregnated with a solution of Eu^{3+} , then isolated and dried (see Experimental Section). A luminescence spectrum was recorded, showing the characteristic europium peak at 614 nm, which was a positive indication that the europium was within the pores [16]. However, the rest of the spectrum was severely distorted, signifying that the luminescence was limited (Figure S4). This distortion could be due to a slight quenching from the neodymium within the MIL-103 framework, likely related that the europium and neodymium were now too close in space. Since the result was not concluding in terms of luminescence properties, further characterization of this modified MIL-103 MOF were not conducted.

2.4. Elaboration of *cis*-Polyisoprene/MOF Composite Materials

The MOFs were studied as pre-catalysts for isoprene polymerization (Scheme 1) in the presence of MMAO (Modified Methyl AluminOxide) as co-catalyst, by varying the percentage of lanthanide present in each MOF structure, and with the expectation to finally produce a polymer material having luminescent properties.



Scheme 1. The activation of the catalyst by the combination of a MOF pre-catalyst and alkyl-aluminum co-catalyst.

We had previously established that homoleptic $\text{Nd}(\text{form})_3$ and mixed $\text{Nd}(2,6\text{-ndc})(\text{form})_3$ (2,6-naphthalenedicarboxylate ligand) are efficient pre-catalysts towards isoprene polymerization in the presence of an Al co-catalyst [5,6]. This reactivity is connected to the neodymium carboxylate nature of these MOF compounds, which are known to produce efficient catalysts for conjugated dienes [17]. The experimental conditions in the present study were then chosen as adequate to the heterogeneous nature of the catalytic system, *i.e.*, heating (in general $50\text{ }^\circ\text{C}$), long reaction times ($>20\text{ h}$), and large excesses of MMAO (20–50-fold molar compared to the Ln pre-catalyst), in order to produce *cis*-stereoregular polyisoprene, as previously determined [5].

2.4.1. Mixed Nd/Ln(form)₃ MOF Polymerization (Ln = Eu, Tb)

The polymerizations were completed in duplicate and the results are shown in Table 1 below.

Table 1. Isoprene polymerization using mixed Nd/Ln(form)₃ (Ln = Eu or Tb) as pre-catalysts.

Run ^a	Ratio of Nd/Ln	Yield (%)	M_n (Đ) ^b	Selectivity (%) ^c
				<i>cis</i> -/ <i>trans</i> -/3,4-
1 ^d	100% Nd	27	64,900 (2.3)	92/2/6
2 ^d	5.14	46	nd	84/8/8
3 ^d	1.59	29	34,400 (5.0)	95/1/4
4 ^d	0.49	11	nd	79/14/7
5 ^d	100% Eu	5	-	-
6 ^e	3.00	40	77,600 (2.4)	92/2/6
7 ^e	1.00	36	49,700 (3.5)	82/1/17
8 ^e	0.33	35	35,600 (3.8)	85/7/8
9 ^e	100% Tb	1	nd	-

^a Typical conditions: 1 Ln:100 MMAO:500 Isoprene; $V_{\text{toluene}} = V_{\text{isoprene}} = 1$ mL; $V_{\text{MMAO}} = 1$ mL (1.84 mmol); $t = 24$ h; $T = 50$ °C; ^b Determined by SEC with reference to PS standards; $\text{Đ} = M_w/M_n$; ^c From ¹H and ¹³C NMR; ^d The mass of MOF precatalyst was fixed at 6 mg (*ca.* 20 μmol), where Ln = Nd + Eu; ^e All quantities divided by a factor of 2: mass of MOF precatalyst 3 mg (*ca.* 10 μmol), where Ln = Nd + Tb, $V_{\text{isoprene}} = V_{\text{toluene}} = 0.5$ mL. $V_{\text{MMAO}} = 0.5$ mL (0.92 mmol). nd: non determined.

The results of the polymerization show a trend between the ratio of Nd/Eu and the yield, *i.e.*, the larger the quantity of neodymium, the greater the yield (runs 2–4). This result is due to the fact that neodymium is the active species within the polymerization, with the exception of run 1, where the yield of polymer obtained is lower than the yield obtained for the MOF containing lower quantities of neodymium (runs 2,3). A possible reason could be due to insufficient grinding and drying of the MOF prior to the polymerisation as already noticed [6]. Smaller effect of the Nd quantity, though similar, is observed with experiments performed with Nd/Tb(form)₃ (based on the initial ratio of the starting materials for the preparation of the mixed MOFs). MOFs containing no Nd were poorly active (run 5) or inactive (run 9). The NMR analyses of the polymers received show, as expected (*vide infra*) a highly *cis*-1,4-polyisoprene selective polymerization (79%–95%), with a particularly stereoregular polymer produced when the compound with Nd/Eu ratio of 1.59 was used as pre-catalyst (run 3, Figure S5). Molecular weights were found in the range 30,000–80,000, and dispersities were rather broad (2.3–5.0), as already noticed and discussed under similar polymerization conditions [5,6]. SEM images of the polymers in film form were recorded to determine if MOF fragments were dispersed throughout the polymer matrix (run 3, Table 1, Figure S6). The results showed that there were relatively small fragments (\approx 1–50 μm) within the sample, suggesting that some MOF particles remained. Unfortunately, the luminescence tests of all the polymers using the spectrofluorimeter SAFAS FLX-Xenius (equipped with a Xenon lamp) gave spectra that showed no emission. Coming back to the starting mixed MOFs Nd/Ln(form)₃ (Ln = Eu, Tb), we observed that the results were also negative in terms of luminescence. This suggested that quenching process, *i.e.*, the excited energy of a center is not emitted as light, but instead transferred to another unit within the system [18] was present within the MOF structure, and the problem did not lie within the transfer of MOF properties to the hybrid MOF/polymer material.

2.4.2. Pure MOF-[Nd(form)₃ + Ln(form)₃] Polymerization (Ln = Eu, Tb)

A range of molar ratios of [Nd(form)₃ + (Eu or Tb)(form)₃] mixtures was used in an attempt to find out the best conditions for the polymerization, where the three main factors were the yield, selectivity and luminescence. The volumes of MMAO, isoprene and toluene stayed constant at 0.5 mL throughout the experiments while the masses of the two MOFs were changed, affecting the final ratios of all reagents. The mass of Ln(form)₃ was increased to attempt to enhance the luminescence properties within the final polymer. The conditions and results of the polymerizations can be seen in Table 2.

Table 2. Isoprene polymerization using [Nd(form)₃ + Ln(form)₃] as pre-catalysts.

Run ^a	Ratio of Reagents Nd/Ln/MMAO/Isoprene	Time (h)	Yield (%)	Selectivity (%) ^b <i>cis-trans-3,4-</i>	Luminescence
10	1/10Eu/100/500	48	77	87/5/8	yes
11 ^c	10/10Eu/100/500	48	78	93/2/5	yes
12 ^d	50/50Eu/100/500	75	80	92/2/6	yes
13 ^d	50/50Eu/100/500	336	89	86/4/10	yes
14	1/10Tb/100/500	48	77	70/4/26	yes
15 ^d	50/50Tb/100/500	166	64	91/2/7	yes
16 ^d	50/50Tb/100/500	336	85	89/6/5	yes
17 ^e	1/92/500	48	17	88/1/11	no

^a Typical conditions: [Nd] = 10 μmol; $V_{\text{toluene}} = V_{\text{isoprene}}$; $T = 50\text{ }^{\circ}\text{C}$; ^b From ¹H and ¹³C NMR; ^c [Nd] = 100 μmol;

^d [Nd] = 500 μmol; ^e ratio of reagents Nd/MMAO/Isoprene, [Nd] = 10 μmol.

All experiments afforded polyisoprene having high *cis*-content. Remarkably, the excess of non-catalyst-active MOF (Eu or Tb) was a drawback neither with regard to the yield, at the condition to extend the reaction time (runs 11–12 and 15–16) nor with regard to the stereo-selectivity. Selected samples were analyzed by SEC, to verify the high M_n values (124,000 and 302,000, runs 11 and 14, respectively), which was in agreement with the slow kinetics of the initiation step of the polymerization, due to the robust nature of the MOF pre-catalyst, as previously observed [5,6]. When using Tb(form)₃ instead of Eu(form)₃ in association with Nd(form)₃, the yields of polymer were a little lower, as well as the *cis*-1,4-polyisoprene selectivity. A powder XRD diagram of polyisoprene was recorded (Figure 5a, run 11). The diagram showed two peaks, which corresponded to Nd(form)₃ and to Eu(form)₃, indicative of MOF solids still remaining within the final polymer matrix in its original MOF form. SEM images of the polymer materials showed small fragments, most likely the MOF residues detected by PXRD, which were dispersed throughout the polymer matrix (run 11, Table 2, Figure 5b). This result would confirm that the polymerization reaction is most likely occurring on the surface of the MOF.

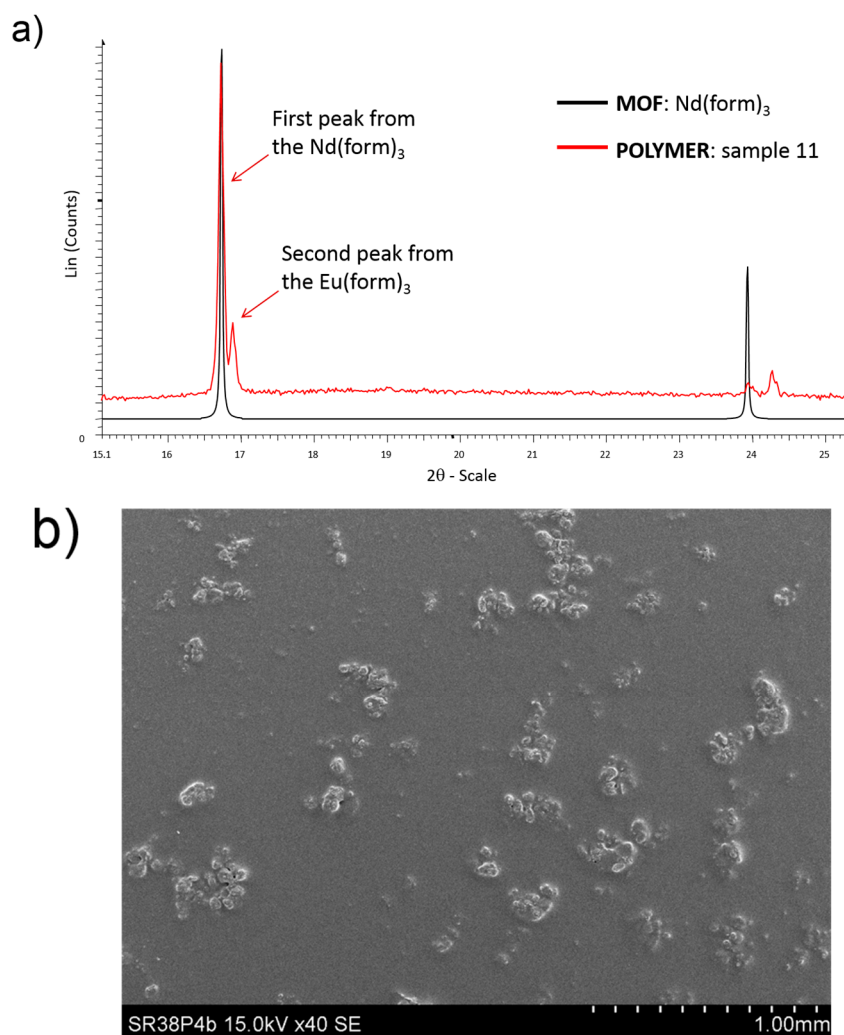


Figure 5. (a) The PXRD diagram of polymer sample 11 showing MOF residues of $\text{Nd}(\text{form})_3$ and $\text{Eu}(\text{form})_3$; (b) The SEM image of sample isolated from run 11 showing dispersed MOF particles.

The luminescence of all hybrid materials thus prepared was this time both visible by eye under the UV lamp, and detected by the spectrophotometer, as shown for selected samples (Figure 6). The luminescence spectrum of pink sample 12 shows three clear peaks, which represent the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions. The two weaker transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ are not as prominent within the spectrum, although both expected transition wavelengths, at 578 and 650 nm respectively, do appear to show very weak broad bands. The green luminescent material received from run 15 has a spectrum showing $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions, which provides the evidence that there are Tb^{3+} particles within the polymer sample, but there is also an extra peak at 466 nm, which remained present within all the luminescence scans of the polymer samples synthesized using $[\text{Nd}(\text{form})_3 + \text{Tb}(\text{form})_3]$ as pre-catalysts.

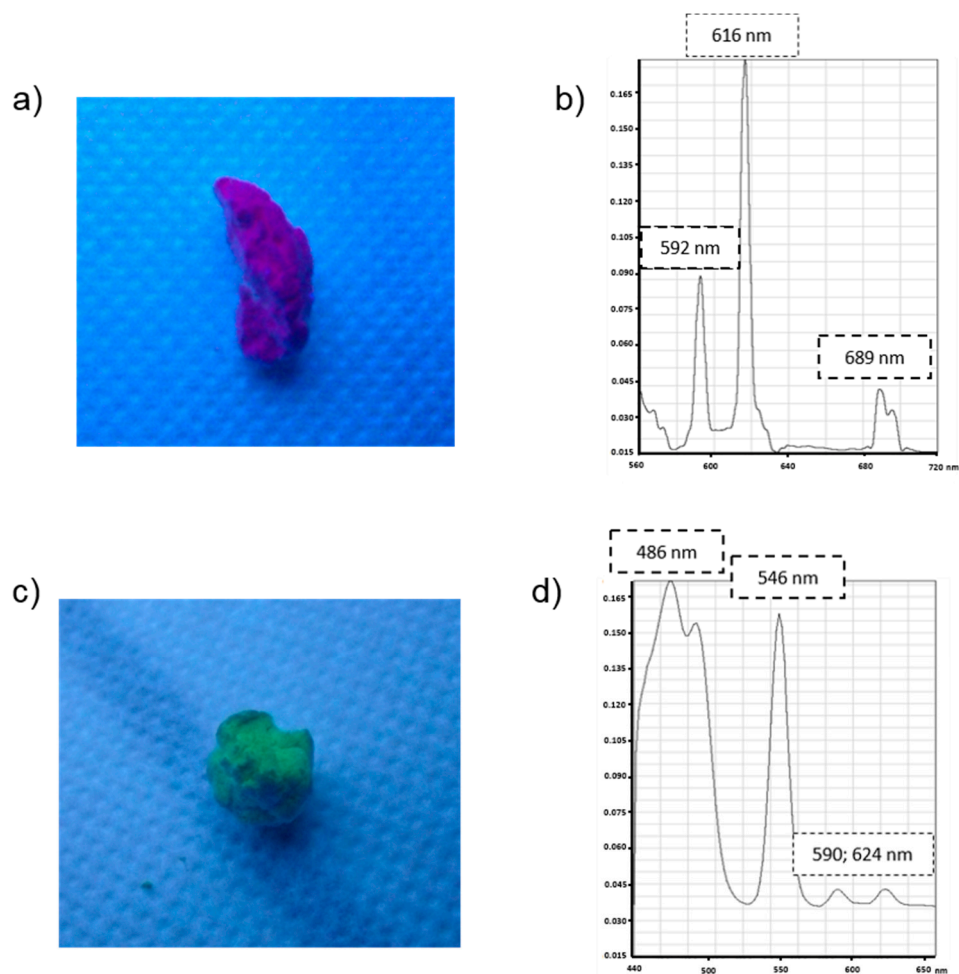


Figure 6. (a) The image of sample material obtained from run 12 as seen under the UV lamp and (b) the luminescence spectrum of the same sample showing the characteristic peaks of Eu^{3+} ; (c) the image of sample material obtained from run 15 as seen under the UV lamp and (d) the luminescence spectrum of the same sample showing the characteristic peaks of Tb^{3+} .

2.4.3. Polymerization with MIL-103(Nd) with Eu-Inserted

The experiment was conducted with 10 μmol of MOF as precatalyst (run 17, Table 2). The resulting polymer showed a highly quenched luminescence spectrum (Figure S7) and no color emission was observed under the UV lamp. Moreover, just regarding the result of this polymerization, *i.e.*, relatively low yield (17% in 48 h) and high percentage of *cis*-1,4-polyisoprene (88%), it can be compared to the previous work [5] done with MIL-103(Nd) as a pre-catalyst for isoprene polymerization. One main difference in experimental is that the authors obtained 33.5% yield in 20 h, when using the porous MIL-103 with empty pores. This would suggest that the filling of the pores of the MOF is detrimental to the activity of the pre-catalyst. This is possibly due to a limitation of active catalytic sites, as filled pores do not allow access to the active metal sites. Previous papers have discussed the advantages of porous material in the use of catalysis and the discussion of a confinement effect due to the controlled polymerization that can take place with porous materials [19].

3. Experimental Section

3.1. MOF Syntheses

3.1.1. Pure MOF Synthesis—Ln(form)₃ (Ln = Nd, Eu, Tb)

The preparation of Nd(form)₃ was recently described in the literature [20]. We used a closely related protocol for its synthesis [6]: A mixture of 0.360 g (1 mmol) of NdCl₃·6H₂O, 3 mL (79 mmol) of formic acid, and 2 mL (2 mmol) of 1 M KOH was placed in a Parr bomb and then heated statically at 180 °C for 24 h. The solution pH was 1.45 at the end of the reaction. The resulting pink product was then filtered off, washed with water, and dried at room temperature. Elemental analysis, observed (calculated): C, 12.6% (12.9%); H, 0.2% (1.1%). The same procedure was also completed using EuCl₃·6H₂O (0.36 g, 1 mmol) and TbCl₃·6H₂O (0.37 g, 1 mmol). The MOF was collected via filtration, washed with water and left to dry under air. The purity was analysed by microscopy, powder X-ray diffraction (PXRD), and eventually ICP-AES.

3.1.2. Mixed Ln-MOF Synthesis

Syntheses were completed using two lanthanides with varying ratios; the equivalents of each lanthanide used in each synthesis are detailed in Table 3. NdCl₃·6H₂O and EuCl₃·6H₂O were weighed on the balance and placed within the Teflon part of an autoclave. Formic acid (3 mL, 25 M, 75 mmol) and sodium hydroxide (2 mL, 4 M, 8 mmol) were then added using syringes. The Teflon part was closed and sealed within the outer steel part. The autoclave reactor was then placed inside the oven for 24 h at 180 °C. The same procedure was also completed using NdCl₃·6H₂O and TbCl₃·6H₂O. Once removed from the oven, the sample was collected via filtration, washed with water and left to dry under air. The purity was determined by two methods, microscopy and powder X-ray diffraction.

Table 3. The reactants used within the combined Nd/Ln(form)₃ MOF syntheses (0.5 mmol Nd initial feed).

Structure	Ln Ratio (Feed)	Ln Ratio (ICP-AES)
Ln(form) ₃	1Nd:1Eu	1.59
Ln(form) ₃	1Nd:3Eu	0.49
Ln(form) ₃	3Nd:1Eu	5.14
Ln(form) ₃	1Nd:1Tb	-
Ln(form) ₃	1Nd:3Tb	-
Ln(form) ₃	3Nd:1Tb	-

MIL-103 Synthesis—Nd(C₂₇H₁₅O₆)(H₂O)·(C₆H₁₁OH): the MIL-103 MOF was synthesized using previous literature [15]. H₃BTB (1,3,5-Benzenetrisbenzoic acid, 500 mg, 1.14 mmol) and Nd(NO₃)₃·6H₂O (500 mg, 1.14 mmol) were placed inside a 125 mL Teflon-lined steel autoclave. Water (12.5 mL) and NaOH (1 mL, 2M, 2 mmol) were added using syringes and the mixture was then stirred for 2 min. Cyclohexanol (12.5 mL, 0.12 mol) was warmed a little to increase the fluidity of the solution, then added to the Teflon part using a syringe. The solution was stirred for a further 10 min. The autoclave was sealed and placed in the oven for 5 days at 100 °C. Once removed from the oven, the

sample was filtered and washed with ethanol (20 mL), water (10 mL), ethanol (10 mL), acetone (10 mL) and then left to dry in the air. The purity was determined using powder X-ray diffraction (PXRD). Procedure for MIL-103 Eu-Insertion: the synthesised MIL-103 (120 mg) was weighed into a vial and dried in the oven at 130 °C for 3 h. Meanwhile, a 1.0 M solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was prepared by placing $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (3.66 g, 1 mmol) in 10 mL of water. The 10 mL solution was added to the dried MIL-103 in the vial and allowed to soak for 24 h. The solution was then removed using centrifugation and the sample washed with 3×10 mL of water, where centrifugation was used to remove the water after each washing. The sample was then placed in the oven at 150 °C for 12 h to dry. To determine if the europium insertion had been successful, a luminescence spectrum was recorded and the sample was examined under the UV lamp.

3.2. Isoprene Polymerisation

The MOF (pre-catalyst) was ground and dried in the oven prior to use to optimize the catalytic activity. The polymerizations were completed in duplicate to ensure reliable results. The polymerization tubes, stirrer bars and MOF were inserted into the Jacomex glove box via the antechamber. The general equivalents of reagents used for the polymerization were as follows: 1 Ln:100 MMAO:500 Isoprene, with $V_{\text{isoprene}} = V_{\text{toluene}}$. The required mass of MOF was weighed using the balance inside the glove box and was then placed within the polymerisation tube. Next, the toluene (1 mL, 9 mmol) was added using a syringe, followed by the MMAO (1 mL, 1.84 mmol). The sample was then left to stir for 20 min. After this the monomer, isoprene (1 mL, 10 mmol) was added. The lid was placed on the tubes using grease to ensure a tight seal and the tubes were removed from the glove box. The tubes were placed in an oil bath, with stirring, set at the correct temperature (50 °C) and left until the solution increased in viscosity. The polymerization was quenched by toluene containing H^+ ions, which came from diluted hydrochloric acid. Toluene was added to the quenched polymer until the solution became fluid enough to pipette. The polymer solution was then pipetted drop-wise into a stirring beaker of methanol to unravel the chains of polymer. The methanol contained the anti-oxidizing agent 2,6-di-tert-butyl-4-methylphenol as a stabilizer which helps prevent oxidative and thermal degradation of the polymer over time. The methanol was decanted and the polymer collected and dried under air.

3.3. MOF Characterization

3.3.1. Powder X-Ray Diffraction (PXRD)

The purity of the MOFs was determined by powder X-ray diffraction (PXRD). X-ray diffraction is an analysis method, which uses Bragg's equation to determine the scattering of radiation from crystals.

A small quantity of MOF was placed onto the center of a sample holder and flattened using a glass slide until securely held in place. The samples were analyzed by a Siemens D5000 diffractometer (Siemens AG, Munich, Germany) working at the $\text{CuK}\alpha$ radiation in the θ - 2θ mode. The selected parameters were a scanning range of 5°–50°, a step of 0.6° and a time of 0.2 s/step. The results were compared with computer-generated references.

3.3.2. Scanning Electron Microscopy (SEM)

SEM images were used to determine the size and shape of the crystals within the MOF powder. A small quantity of crystals were placed on a sample holder and sprayed with gold. Gold is a conductive metal and is used to prevent the collecting of electrons on the non-conductive sample, which could affect the electron beam and result in blurred images. The samples were analyzed using a Hitachi S-3400N scanning electron microscope (Hitachi High-Technologies, Krefeld, Germany).

3.3.3. ICP-AES

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Vista-Pro VARIAN, Agilent tech, Santa Clara, CA, USA) was used to accurately determine the concentrations of the two lanthanides within the final MOF structure.

The ICP-AES samples were prepared by initially creating the oxide of the MOF, this was achieved by heating the sample up to 700 °C. The oxide (3 mg) was then dissolved in concentrated nitric acid (1 mL, 16 M, 16 mmol). The sample was diluted by a factor of 500 by placing 0.2 mL into a 100 mL volumetric flask and filling with water. A small part of the solution was removed for the analysis (*ca.* 10 mL).

3.4. Polymer Material Characterization

3.4.1. Polymer Yield

The final mass of polyisoprene obtained and the volume of isoprene used in the polymer synthesis were used to determine the final yield of polymer. The calculation was completed as follows:

$$\% \text{ YIELD} = (\text{MASS OF POLYMER} \div \text{MASS OF MONOMER}) \times 100 \quad (1)$$

3.4.2. NMR Analysis

The selectivity of the polymer was determined by ¹H NMR recorded on an AC 300 Bruker (Bruker Biospin, Wissembourg, France) at 300 MHz, with assignation as published [21]. Five to ten mg of polymer was placed into an NMR tube and approximately 0.6 mL of the solvent, chloroform-D, was added. When necessary, ¹³C NMR analysis with quantitative Bruker sequences was performed.

3.4.3. Luminescence

There were two methods used for determining the luminescent properties of the polymer. The first was the use of a UV lamp in a dark environment to observe any colour emission. The second used a SAFAS Xenius XC spectrofluorimeter (SAFAS, Monaco) with a xenon lamp to record the emission spectrum of an excited compound. Europium-based compounds were excited at 394 nm and the emission spectrum was recorded between 560 and 720 nm. Terbium based compounds were excited at 283 nm and the emission spectrum recorded between 440 and 660 nm.

3.4.4. Preparation of Polymer Films–Spin Coater

Before examining the polymers by SEM, they were prepared into films using a SPIN150 Wafer Spinner (SPS, Antwerp, Belgium) to provide clearer images of any MOF dispersion within the matrix. A small quantity of polymer (≈ 50 mg) was dissolved in toluene (≈ 5 mL) to produce a viscous solution. Five drops of the sample were placed onto the center of a glass slide, which was placed onto the center of the spin coater. The vacuum was activated to keep the slide in place, the lid closed and the spin coater started. The result was a thin circular polymer film on a glass slide.

4. Conclusions

Lanthanide based-MOF compounds having luminescent properties and polymerization catalysis capability were prepared and assessed to the stereoregular polymerization of isoprene. This was supposed to allow for any properties exhibited from the lanthanide-based MOF, to be transferred to the resulting polymer material, and hence give an elastomer composite having luminescent properties. The results of the polymerizations showed that the combination of the two MOF-like compounds, $\text{Nd}(\text{form})_3 + \text{Ln}(\text{form})_3$, when added together at the beginning of the polymerization, successfully produced luminescent *cis*-1,4 polyisoprenes. Two alternative strategies involving mixed (Nd, Eu) and (Nd, Tb) lanthanide MOFs and porous MIL-103(Nd) with Eu included, as a pre-catalysts for isoprene polymerization, produced polyisoprene with good *cis*-selectivity, but they failed to afford a luminescent material due to quenching phenomena.

Supplementary Materials

Supplementary materials can be found at <http://www.mdpi.com/2304-6740/3/4/0467/s1>.

Acknowledgments

The authors thank the Region Nord-Pas-De-Calais-Picardie and the Fédération Chevreul FR 2638 for financial support (MULTI-NANO-MOF project) and Hao Wu (ISP Master Student) for his participation to this work. Erasmus Program is also acknowledged for funding to Samantha Russell.

Author Contributions

Samantha Russell: MOFs syntheses and polymerizations, SEM, PXRD, luminescence measurements; Thierry Loiseau: discussion of the results; Christophe Volkringer: MOFs syntheses, PXRD measurements, SEM characterization, luminescence, discussion of the results; Marc Visseaux: Writing the manuscript and discussion of the results, NMR measurements.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Ferey, G. Hybrid porous solids: Past, present, future. *Chem. Soc. Rev.* **2008**, *37*, 191–214.
2. Special Issue—Metal-Organic Frameworks. Available online: <http://pubs.acs.org/toc/chrey/112/2> (accessed on 5 August 2015).
3. Binnemans, K. Lanthanide-based luminescent hybrid materials. *Chem. Rev.* **2009**, *109*, 4283–4374.
4. Cui, Y.; Yue, Y.; Qian, G.; Chen, B. Luminescent functional metal-organic frameworks. *Chem. Rev.* **2012**, *112*, 1126–1162.
5. Vitorino, M.; Devic, T.; Tromp, M.; Ferey, G.; Visseaux, M. Lanthanide metal-organic frameworks as Ziegler–Natta catalysts for the selective polymerisation of isoprene. *Macromol. Chem. Phys.* **2009**, *210*, 1923–1932.
6. Rodrigues, I.; Mihalcea, I.; Volkringer, C.; Loiseau, T.; Visseaux, M. Water-free neodymium 2,6-naphthalenedicarboxylates coordination complexes and their application as catalysts for isoprene polymerisation. *Inorg. Chem.* **2012**, *51*, 483–490.
7. Escribano, P.; Julian-Lopez, B.; Planelles-Arago, J.; Cordoncillo, E.; Viana, B.; Sanchez, C. Photonic and nanobiophotonic properties of luminescent lanthanide-doped hybrid organic–inorganic materials. *J. Mater. Chem.* **2008**, *18*, 23–40.
8. Hou, S.; Chan, W.K. Preparation of functionalized polystyrene-block-polyisoprene copolymers and their luminescence properties. *Macromolecules* **2002**, *35*, 850–856.
9. Otsuka, T.; Chujo, Y. Highly stabilized luminescent polymer nanocomposites: Fluorescence emission from metal quinolate complexes with inorganic nanocrystals. *J. Mater. Chem.* **2010**, *20*, 10688–10695.
10. Yang, C.; Sun, Z.; Liu, L.; Zhang, L. Preparation and luminescence performance of rare earth agriculture-used light transformation composites. *J. Mater. Sci.* **2008**, *43*, 1681–1687.
11. Liu, F.; Carlos, L.D.; Ferreira, R.A.S.; Rocha, J.; Ferro, M.C.; Tourrette, A.; Quignard, F.; Robitzer, M. Synthesis, texture, and photoluminescence of lanthanide-containing chitosan-silica hybrids. *J. Phys. Chem. B* **2010**, *114*, 77–83.
12. Agostini, G. Self-luminescent pneumatic tire. U.S. Patent S7234498 B2, 26 June 2004.
13. Zuo, Y.; Lu, H.; Xue, L.; Wang, X.; Wu, L.; Feng, S. Polysiloxane-based luminescent elastomers prepared by thiol-ene “click” chemistry. *Chem. Eur. J.* **2014**, *20*, 12924–12932.
14. Bao, S.; Li, J.; Lee, K.I.; Shao, S.; Hao, J.; Fei, B.; Xin, J.H. Reversible mechanochromism of a luminescent elastomer. *Appl. Mater. Interfaces* **2013**, *5*, 4625–4631.
15. Devic, T.; Wagner, V.; Guillou, N.; Vimont, A.; Haouas, M.; Pascolini, M.; Serre, C.; Marrot, J.; Daturi, M.; Taulelle, F.; *et al.* Synthesis and characterization of a series of porous lanthanide tricarboxylates. *Microporous Mesoporous Mater.* **2011**, *140*, 25–33.
16. An, J.; Shade, C.M.; Chengelis-Czegan, D.A.; Petoud, S.; Rosi, N.L. Zinc-Adeninate metal-organic framework for aqueous encapsulation and sensitization of near-infrared and visible emitting lanthanide cations. *J. Am. Chem. Soc.* **2011**, *133*, 1220–1223.
17. Friebe, L.; Nuyken, O.; Obrecht, W. Neodymium-based Ziegler/Natta catalysts and their application in diene polymerisation. *Adv. Polym. Sci.* **2006**, *204*, 1–154.
18. Kautsky, H. Quenching of luminescence by oxygen. *Trans. Faraday Soc.* **1939**, *35*, 216–219.

19. Uemura, T.; Hiramatsu, D.; Kubota, Y.; Takata, M.; Kitagawa, S. Topotactic linear radical polymerization of divinylbenzenes in porous coordination polymers. *Angew. Chem. Int. Ed.* **2007**, *46*, 4987–4990.
20. Lin, J.M.; Guan, Y.F.; Wang, D.Y.; Dong, W.; Wang, X.T.; Gao, S. Syntheses, structures and properties of seven isomorphous 1D Ln³⁺ complexes Ln(BTA)(HCOO)(H₂O)₃ (H₂BTA = bis(tetrazoly)amine, Ln = Pr, Gd, Eu, Tb, Dy, Er, Yb) and two 3D Ln³⁺ complexes Ln(HCOO)₃ (Ln = Pr, Nd). *Dalton Trans.* **2008**, 6165–6169, doi:10.1039/b808394k.
21. Martins, N.; Bonnet, F.; Visseaux, M. Highly efficient *cis*-1,4 polymerisation of isoprene using simple homoleptic amido rare earth-based catalysts. *Polymer* **2014**, *55*, 5013–5016.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).