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ARTICLE

Toward understanding of structure-catalyst activity relationship of new Indium MOFs as catalysts for the solvent-free ketones cyanosilylation

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Four new indium metal-organic frameworks, MOFs, namely [$In_2(hfipbb)_3(1,10\text{-phen})_2]\cdot 2H_2O$ (**InPF-12**), [$In_2(hfipbb)_3(2,2'\text{-bipy})_2]\cdot 2H_2O$ (**InPF-13**), [$In_2(hfipbb)_3(4,4'\text{-bipy})$] (**InPF-14**) and [$In_4(OH)_4(hfipbb)_4(4,4'\text{-bipy})$] (**InPF-15**), (InPF = indium polymeric framework, hfipbb = hexafluoroisopropylidene bisbenzoate, phen = phenantroline, bipy = bipyridine), have been hydrothermally obtained and result efficient Lewis acid catalysts in solvent-free cyanosilylation of carbonyl compounds. For acetophenone: i) the coordination number and μ-OH groups presence seem to be decisive factors to get a better catalytic behavior and ii) the presence of Lewis base moieties (C=O groups not coordinated to indium cation), besides the Lewis acid sites, creates a two-component catalytic system, based on the "dual activation" phenomenon that makes **InPF-15** the best catalyst in this type of reactions. It was also found that the use of this highly reactive, recyclable and environmentally benign catalyst allows the efficient synthesis of various trimethylsilyl cyanohydrins from a wide range of cyclic, aliphatic and aromatic ketones.

Introduction

The development of green materials and processes with easy handling and of low cost has become one of the main goals of synthetic chemistry. The manufacture of economic, easily produced and non toxic materials that can then be used as heterogeneous catalysts becomes very important in the development of processes with less environmental impact. These materials will increase efficiency, and could avoid using of contaminants - toxic solvents, release agents, etc. - and reduce waste.[1] For this purpose, several Metal-Organic Frameworks (MOFs) have attracted great interest during the past years and a large amount of compounds have been designed and synthesized for various energy and environmentally relevant applications, such as heterogeneous catalysis as well as luminescence, magnetism, gas storage and separation, adsorption, conductivity and molecular recognition.[2]

The catalytic interest in MOFs materials arises from the high versatility that they offer. This versatility is due to the wide range of possibilities of combining a variety of polyatomic organic linkers and inorganic units, which act as coordination centers. The control of the bond angles and restricting the number of coordination sites that can be made during the synthesis of MOFs, results in tailored solid robust materials with high thermal and mechanical stability with a wide range of morphologies and geometries, which exhibit particular properties.

Most of the MOFs materials are obtained by slow evaporation method or solvothermal methods. In solvothermal methodology, the use of high-boiling organic solvents (DMF, DEF, acetonitrile, acetone, ethanol, methanol etc.) is preferred; however, most of these solvents are toxic and expensive. On the other hand, when water is chosen as solvent (hydrothermal synthesis), a cleaner, environmentally friendly and easy to handle methodology for MOF material producing can be used.[3] Thousands of reported MOF structures contain divalent cations and carboxylate, sulfonate, phosphonate or N donor linkers. MOFs built up from higher valence cations are less abundant (except lanthanide cations). The use of trivalent metals like the *p* elements in group 13 (Al^{III}, Ga^{III}, In^{III}) for the preparation of MOFs are even less common, in contrast to their use in other

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inorganic materials, such as aluminosilicates, gallium-phosphates and phosphate zeolites.[4]

However, *p* elements based MOFs have proved to be very effective in various catalytic processes.[5] Generally, in terms of catalytic applications, MOFs are relatively new materials within the domain of heterogeneous catalysis. Despite the first report on MOF dealing with a catalytic application appeared in 1994, in which a 2D cadmium network was used as heterogeneous catalyst in the cyanosilylation of aldehydes,[6] very few studies had been performed until ~2000-2005 years. Since then, research in this field has been devoted to probing the concept of heterogeneous catalysis in a variety of reactions, supported by the gradual progress in maturation of crystal engineering.[7] Nowadays, MOF materials are moving towards the discovery of specific and distinctive catalytic applications of these materials that are not matched by their conventional analogues.[8]

On the other hand, cyanohydrins are useful starting materials for the synthesis of several biological active compounds due to the presence of hydroxyl and nitrile functionalities, which can be transformed into a wide range of building blocks.[9] Generally, a common reaction to prepare cyanohydrins is through the cyanosilylation of carbonyl compounds in the presence of trimethylsilyl cyanide (TMSCN) promoted by moderately strong Lewis acid catalysts.[10-11]

The fact that TMSCN is used instead of other cyanide sources which are highly toxic like HCN or alkali metal salts (NaCN or KCN),[12] reduces the safety issues and the handling problems that these classical cyanation reagents usually presented, without losing the efficiency in the reaction process.

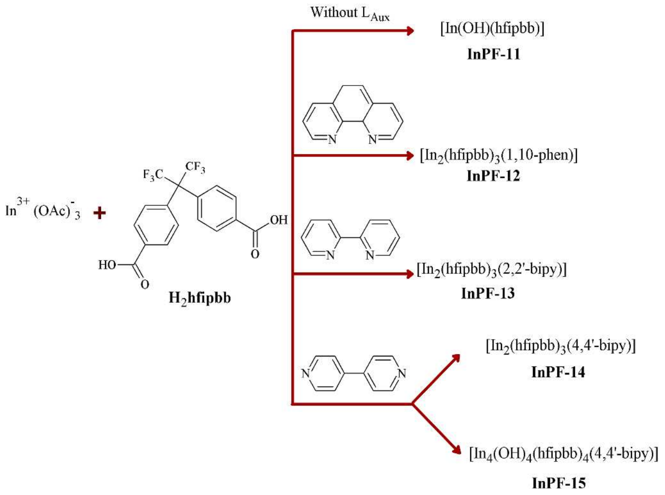
Several different indium (III) compounds have been reported as catalyst in different organic transformations, resulting in high chemical yields under mild conditions. Furthermore, indium-MOFs are typically air and water stable, so that they can be used as catalyst in water based reactions.[13]

During the past years, our research group has synthesized several indium MOFs highlighting their high stability and evaluating their interesting properties as heterogeneous catalysts due to their easy separation (which facilitates product isolation) and elevated recyclability.[14] Among them it is included In(OH)(hfipbb),[14c] hereafter **InPF-11** [**InPF** = indium polymeric framework, H_2hfipbb = 4,4'-(hexafluoroisopropylidene) bis(benzoic acid)]. This MOF, constructed with the linker H_2hfipbb that contains perfluorinated moieties, demonstrated to be an efficient catalyst in the acetalization of benzaldehyde.

In the present work, we have prepared hydrothermally four new indium MOFs with the use of H_2hfipbb in combination with some additional, neutral aromatic nitrogen-contained heterocyclic linkers: $[In_2(hfipbb)_3(1,10\text{-}phen)_2]\cdot 2H_2O$ **(InPF-12)**, $[In_2(hfipbb)_3(2,2'\text{-}bipy)_2]\cdot 2H_2O$ **(InPF-13)**, $[In_2(hfipbb)_3(4,4'\text{-}bipy)]$ **(InPF-14)** and $[In_4(OH)_4(hfipbb)_4(4,4'\text{-}bipy)]$ **(InPF-15)** (phen = phenantroline, bipy = bipyridine) (Scheme 1).

We have first tested the catalytic activity of **InPF-11**, **InPF-12**, **InPF-13**, **InPF-14**, and **InPF-15** in the cyanosilylation of aldehydes, and then focused our catalytic studies on reactions with ketones, which typically show extremely low reactivity, due to their steric hindrance.

We have found that **InPF-15** being the best of the five catalysts in this type of reactions, allows the efficient synthesis of various trimethylsilyl cyanohydrins from a wide range of cyclic, aliphatic and aromatic ketones.



Scheme 1 Indium MOFs obtained with the use of indium salt in combination with H2hfipbb and additional linkers

Results and Discussion

Crystal structures

The details of data collection, refinement, and crystallographic data and the asymmetric units for compounds **InPF-12** to **InPF-15** are found in the **ESI**, Table S1 and Fig. S1†.

InPF-11 with formula **[In(OH)(hfipbb)]** has been synthesized according to the procedure reported in reference 14c. Fig. 1 shows the asymmetric unit and two different views of the structure. A complete structural depiction of the structure can be found in the same reference.

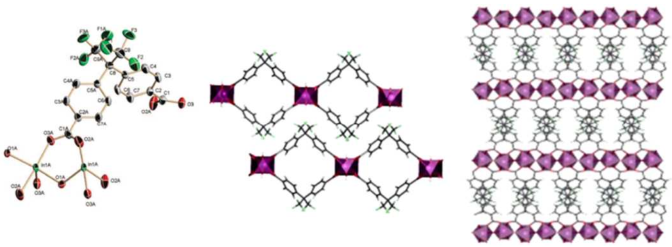


Fig. 1 Atomic and polyhedral representation of InPF-11 2D structure, showing the asymmetric unit (left), a view of the layers forming square shaped channels (middle), and a perpendicular view of one of the layers, showing In(OH) chains connected by the organic linkers.

For ***InPF-12*** and ***InPF-13*** with formulas $\mathbf{[In_2(C_{17}H_8F_6O_4)_3(1,10\text{-}phen)_2]\cdot xH_2O}$ and $\mathbf{[In_2(C_{17}H_8F_6O_4)_3(2,2\text{-}bipy)_2].xH_2O}$ respectively crystallize in the monoclinic *C2/c* space group. In both cases, the asymmetric unit consists of one In^{+3} ion, one phenantroline or 2,2'-bipy molecule, one and a half molecules of the hfipbb^{-2} linker, and one hydration water molecule . The In(III) cation is heptacoordinated in a -[InO_5N_2]- monocapped octahedron OCF-7, where the two In-N bonds come from the chelating ancillary ligand and the five In-O bonds from the fully deprotonated hfipbb^{-2} ligand.

The linker acts in two different ways, one of them (L_2 from now on) in a $\eta^2\mu$- $\eta^2\mu$ mode, and the other (L_1) in a η^1-η^1 manner (Fig.2). As a result, the In cations are bonded to one monodentate L_1 and to two chelating L_2 carboxylate groups, giving rise to ladder shaped chains that run along the [101] direction.

After topological simplification of the chains (TOPOS program[15]) a network of three-connected nodes is described. This uninodal net exhibits a **SP1** topology (point symbol (4^2.6)).

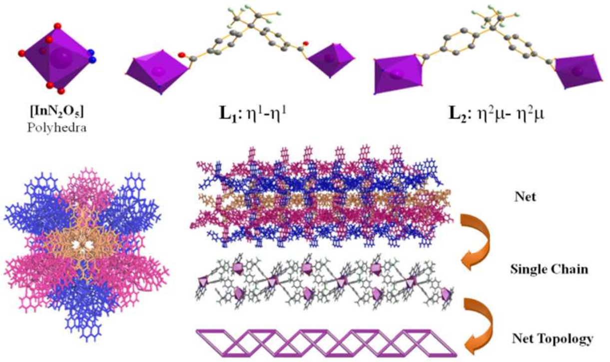


Fig. 2 Above: Representation of **-[InN_2O_5]-** PBU and L_1 and L_2 coordination modes of hfipbb^{-2} organic linker in **InPF-12** and **InPF-13.** Below: Perspective view of **InPF-12** and **InPF-13** along (101) and (001) direction, and topological representation of the 1D covalent chain.

WEAK INTERACTIONS

The highly polar C-F bond and the associated interaction involving organic fluorine is a matter of relevance. It is worth remarking that although single C-H···F-C or C-F···F-C bonds are energetically weak, the total interaction energy may become significant because of the co-operative effect of many interactions providing stability to the crystalline lattice. The stronger hydrogen bonds usually govern the crystal packing but the eventual formation of a supramolecular assembly is a result of a delicate balance of all type of interactions, both weak and strong, that play an important role. [16]

In **InPF-12** and **InPF-13**, several weak interactions contribute to shift from a 1D covalent structure to the 3D supramolecular one; layers are formed through π···π stacking contacts, but interlayer joints are made via halogen interactions (Fig. 3). The first interaction corresponds to a π···π stacking between 1,10-phenantroline or 2,2'-bypiridine rings from parallel chains; the second one corresponds to F···F and F···H-C interactions for **InPF-12** and **InPF-13,** respectively (See **ESI**, Fig. S2 and Fig. S3†).

Hydration water molecules are located inside the supramolecular channels forming hydrogen bonds with carboxylate oxygen atoms and C-H groups from phenantroline ligand. These interactions do not participate in the connectivity of the supramolecular structure.

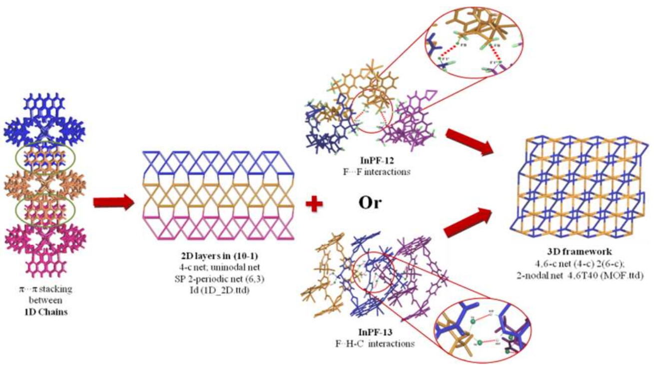


Fig. 3 View of the 2D and 3D supramolecular frameworks of compound **InPF-12** and **InPF-13.**

InPF-14 with formula **[$In_2(C_{17}H_8F_6O_4)_3$(4,4'-bipy)]** crystallizes in the monoclinic *C2/c* space group (Table S1, in the **ESI**). The In^{+3} ion is hepta-coordinated to six oxygen atoms coming from three chelate carboxylate groups and one 4,4'-bipy nitrogen atom, in a monocapped octahedra **[$InNO_6$],** with an average In-O distance of ~2.235 Å and In-N distance of 2.282(6) Å. The linker, acting thus in a $\eta^2\mu$- $\eta^2\mu$ mode, gives rise to a 3D structure. The 3D framework of **InPF-14** consists of three interpenetrated **dia** networks. The main simplification points, as well as the final simplified net are shown in Fig. 4.

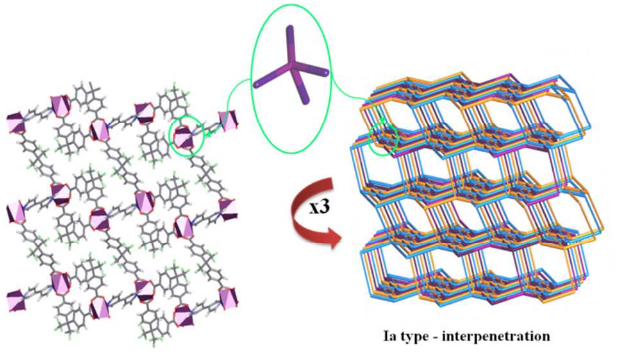


Fig. 4 Perspective view of compound **InPF-14** along (100) and the **dia** topological representation of the 4-connected net and its interpenetration.

InPF-15 with formula **[$In_4(OH)_4(C_{17}H_8F_6O_4)_4$(4,4'-bipy)]** crystallizes in the monoclinic system, *P2/n* space group. The asymmetric unit consist of four crystallographically different In^{+3} ions, one 4,4'-bipyridine molecule, four fully deprotonated hfipbb^{-2} linkers and four hydroxyl groups.

The linker acts, as in **InPF-12** and **InPF-13**, in two different ways, one of them L_2 in a $\eta^2\mu$- $\eta^2\mu$ mode, and the other L_1 in a η^1-η^1 manner. There are two different octahedral coordination environments for the metal centers: for In1 and In2, each cation presents three In-O bonds coming from chelating carboxylate groups, two In-O from the μ-OH hydroxyl bridge and one In-N bond, due to the 4,4'-bipyridine, in a -[**$InNO_5$**]- octahedral PBUs. In case of In3 and In4 polyhedra there are only In-O bonds for each cation, one In-O of L_1 type coordination of hfipbb^{-2} linker, three In-O bonds coming from carboxylate L_2

type groups, and finally two In-O bonds of the hydroxyl bridge forming -[InO_6]- octahedra (Fig. 5).

The SBUs are formed by sharing vertex octahedron chains, that run along the [010] direction, these chains are connected through the complete hfipbb^{-2} linkers along [001] direction, while connection in the [100] direction is made via 4,4'-bipyridine. The result is a 3D structure with **hex** topology of an 8-connected uninodal net (Fig. 5).

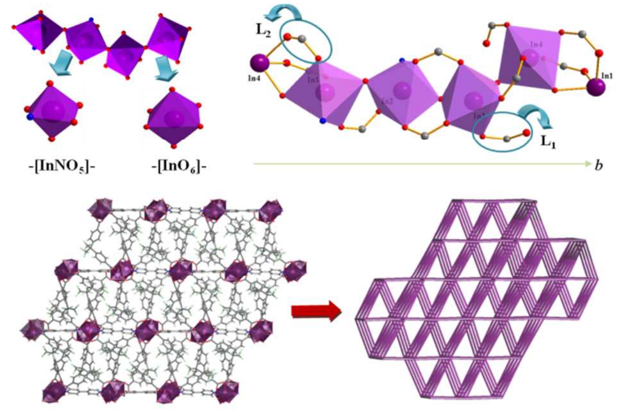
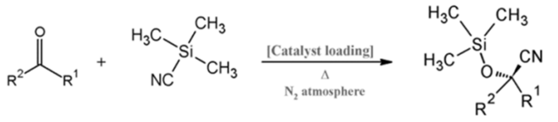


Fig. 5 Above: **-[$InNO_5$]-** and **-[InO_6]-** polyhedra, chain SBU with Representation of L_1 and L_2 coordination modes of hfipbb^{-2} organic linker in **InPF-15**. Below: view of In-O-In chains connected through 4,4'-bipyridine auxiliary ligand and hfipbb^{-2} organic linker generating a **hex** topology of the 8-connected net.

Catalytic Study

A fundamental Lewis acid-catalyzed carbon-carbon bond forming reaction, known as cyanosilylation of carbonyl compounds (C^3), was chosen in order to evaluate the utility, stability and capacity of these five indium MOFs materials as heterogeneous catalysts, **InPF-n** (**n = 11-15**) (Scheme 2). Although several outstanding catalysts have been developed for the cyanosilylation of aldehydes, only a few catalysts have shown good conversions when ketones are employed;[10-11] this is partially due to the extremely low reactivity associated with ketone's steric and electronic constrains towards nucleophiles. Previous studies made with indium MOFs allowed us to determine the best cyanosilylation reaction conditions using different temperatures, solvents and catalyst loadings.[15d] Reactions were performed with 2.5% mol of catalyst loading, without solvent at 50ºC temperature. The initial tests showed that all compounds exhibit good catalytic behaviour in the benzaldehyde cyanosilylation (see Table 1).



Scheme 2. Catalyst mediated cyanosilylation of carbonyl compounds (C3).

InPF-n (n = 11-15) were tested for the cyanosilylation of benzaldehyde and acetophenone (Table 1) and we have found that the reactivity changes as a function of the carbonyl compound nature. The PXRD patterns of the recovered **InPF-11**, **InPF-14** and **InPF-15** after the catalytic reactions indicate that these materials do not suffer any structural change. However, **InPF-12** and **InPF-13** do not maintain structural integrity after the catalytic reaction, as shown in their PXRD patterns (see ESI, Fig. S2 and Fig. S3†).

Table 1. Screening of In(III)-MOFs as catalysts for C^3 reaction[a]

Entry	Catalyst (In_{CN}, Dimensionality)	Benzaldehyde		Acetophenone	
		Yield (%)[b] (h)	TOF (h^{-1})	Yield (%)[b] (h)	TOF (h^{-1})[d]
1	InPF-11[15c] (6, 2D)	99 (0.67)	105	65 (4)	109
2	InPF-12 (7, 1D)	99 (2)	284	24 (4)	1
3	InPF-13 (7, 1D)	93 (2)	298	41 (2)	38
4	**InPF-14** (7, 3D)	**99 (0.75)**	**332**	45 (1)	50
5	**InPF-15** (6, 3D)	80 (1.5)	265	**77 (4)**	**140**

[a] Without solvent, 2.5 mol% of catalyst under N_2 atmosphere and 50ºC (benzaldehyde) or 80ºC (acetophenone). [b] Yields (GC-MS). [c] At 7h all reactions using acetophenone were completed. [d] TOF: mmol subst./mmol Cat. h

The different catalysts behaviour observed when carbonyl source changes from benzaldehyde to acetophenone, is due to the steric hindrance introduced by the $-CH_3$ group present in the acetophenone molecule, which makes difficult its access to the active site in the metallic center in those catalysts with higher coordination number: 7 (entries 2 - 4 in Table 1).

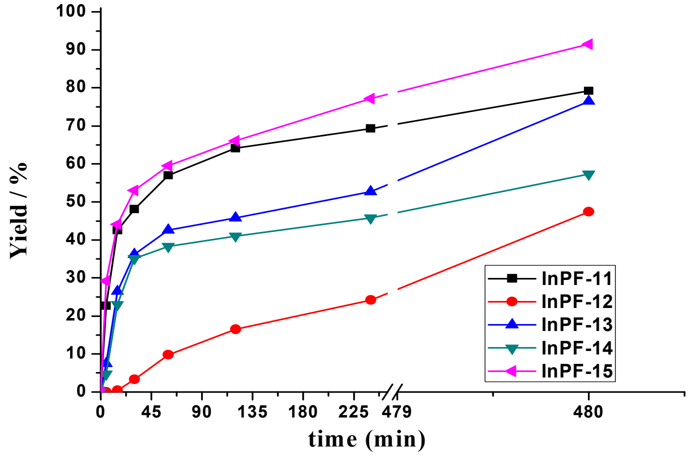


Fig. 6 Kinetic profiles for the cyanosilylation of acetophenone using all In-materials as catalysts.

CYANOSILYLATION OF ACETOPHENONE

From the data of the Table 1 and Fig. 6 it is evident that exits a structure/catalytic ability relationship. In-MOFs with blocking chelate ligands (1,10-phen and 2,2'-bipy) show lower conversion and higher reaction times than those without any auxiliary ligand or with a non-chelate second linker (4,4'-bipy) in their structure. **InPF-11** and **InPF-15**, those with coordination number 6, and μ-OH groups, shows the best catalytic performance, since they own more available active sites around the metallic center. Besides the Lewis acid sites of the indium cation, **InPF-15** possesses in its structure two Lewis base moieties (μ-OH and C=O groups not coordinated to indium cation); due to the presence of this feature, the catalytic system is of a two-component type; a mechanism based on the "dual activation" phenomenon[14d] is proposed (Fig. 7), in which the carbonyl compound is activated by the interaction with the Lewis acid site on the metallic center of our catalyst and the silyl group is activated simultaneously by the Lewis base moieties being **InPF-15** the best catalyst, even for the most sterically hindered substrates. In case of catalyst **InPF-11**, which also is a two-component catalytic system, its structure shows that all linkers are coordinated in a $\eta^2\mu_2$–$\eta^2\mu_2$ mode, leaving only one hindered Lewis base moiety (μ-OH) to activate the silyl group; this moiety is difficult to access due to its metal – metal bridge condition, which results in lower catalysis conversion.

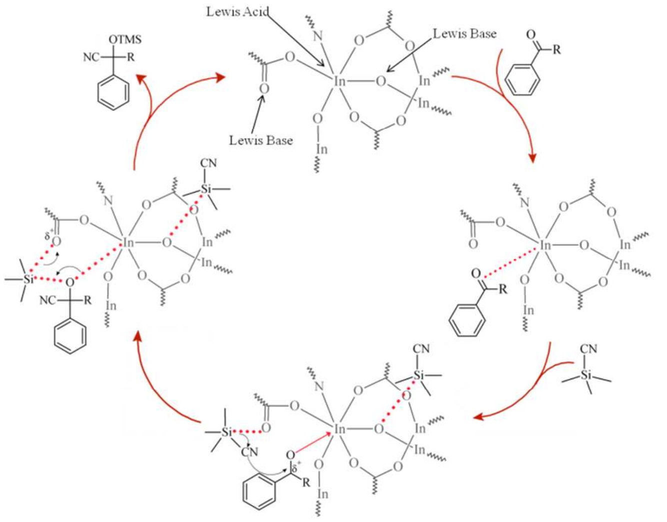


Fig. 7 Mechanism proposed for the Indium mediated cyanosilylation of carbonyl compounds for **InPF-15** catalyst.

Since **InPF-15** is the best catalyst in the cyanosilylation of acetophenone with excellent yield (Table 1, entry 5), it was chosen for the further studies.

Another important point was the influence of the catalyst loading (Table 2). As mentioned before, several indium salts have been tested for the ketone cyanosilylation. Among them, $InBr_3$ (TON: 90, using 1mol %)[13] and $InCl_3$ (TON: 9, using 10mol %)[13] salts showed good yields at mild conditions. When **InPF-15** material was used, we were able to reach higher yields (TON: 990, using 0.1mol %) with the advantage of a solvent free reaction, without side products and an easy recovery and reuse of the catalyst.

Table 2. C^3 reaction using acetophenone as substrate in the presence of different **InPF-15** loadings and temperatures.[a]

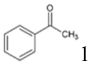
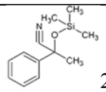
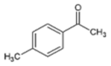
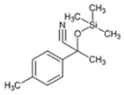
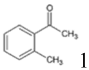
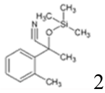
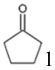
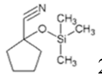
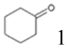
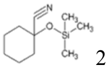
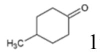
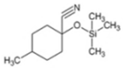
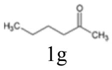
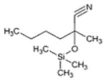
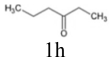
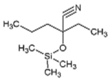
Cat. loading [mol%]	Temperature [ºC]	%Yield (h)	TON[b]	TOF (h^{-1})[c]
2.5	80	>99 (48)	40	140
1.0	80	89 (18)	89	172
0.1	80	>99 (7)	990	2158
0.1	50	90 (96)	900	-
0.1	25	79 (120)	790	-

[a]Without solvent, under N_2 atmosphere. [b]TON: mmol subst./mmol Cat. [c]TOF: mmol subst./mmol Cat. h

The C^3 reaction was also performed at different temperatures using 0.1mol% of **InPF-15** as catalyst; the results in Table 2 show that faster reaction times and higher yields can be obtained when temperature rises. Thus, we decided to use 0.1% mol as catalyst loading and 80ºC for the subsequent reactions.

Table 3 presents the scope of the cyanosilylation of ketones using **InPF-15** as catalyst; the results reveal that higher yields are obtained in case of non-aromatic ketones compared to the aromatic ones. Linear aliphatic ketones proceeded efficiently and gave the corresponding product in yields higher than 96% (entries 12-13). Yields were even higher in case of the cyclic ketones (>99%, entries 9-11). Less reactive but still with good yields, aromatic ketones gave the corresponding cyanohydrin trimethylsilyl ethers yields between 87-95% (entries 6-8). The results of the reactions carried out with acetophenone derivatives with electron-donating substituents show that in case of the *o*-methylacetophenone higher yields are reached (95%) than for the *p*-methylacetophenone which only reaches 89%.

Table 3. Scope of the **InPF-15**-catalyzed cyanosilylation of ketones.[a]

Entry	Ketone **1**	Product **2**	time (min)	Yield (%)[b]	TOF (h^{-1})
6	 1a	 2a	180	87	2158
7	 1b	 2b	180	89	2406
8	 1c	 2c	180	95	5424
9	 1d	 2d	120	98	10951
10	 1e	 2e	120	>99	12048
11	 1f	 2f	240	>99	11686
12	 1g	 2g	120	>99	11400
13	 1h	 2h	120	96	10560

[a]Solvent free reaction at 80ºC and 0.1 mol% of catalyst under N_2 atmosphere.
[b] Yields (GC-MS, **ESI** Fig.S4 – S12†).

The recyclability of the **InPF-15** material was also tested; the catalyst was recovered after centrifugation and washed several times with acetone, then dried at 130ºC and reused. This experiment showed that material maintains its crystallinity even after seven catalytic cycles, with only a small decrease of its catalytic activity, probably due to the losses during the recovery of the catalyst (Fig. 8). Hot filtration experiments reveal that **InPF-15** is a truly heterogeneous catalyst.

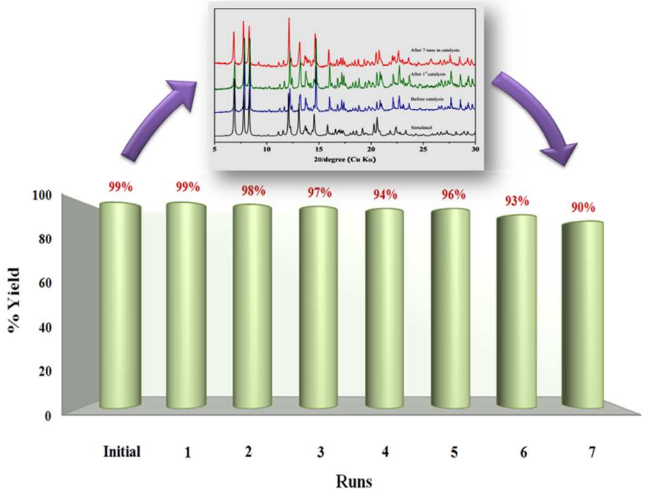


Fig. 8 Above: Powder X-ray pattern before and after seven catalytic cycles of **InPF-15**. Below: Recycling experiments.

Conclusions

Indium-organic framework materials have been solvothermally obtained and used as acid Lewis catalysts in cyanosilylation of carbonyl compounds, showing that i) those catalysts without any auxiliary ligands or with a non-chelate second linker (4,4'-bipy) in their structure exhibit excellent catalytic activity, ii) among the latter, the coordination number and μ-OH groups presence seem to be decisive factors to get a better catalytic behaviour, and iii) the presence of additional Lewis base moieties (μ-OH and C=O not coordinated to indium cation), besides the Lewis acid sites, create a two-component catalytic system, based on the "dual activation" phenomenon that makes **InPF-15** the best catalyst in this type of reactions. It was also found that the use of this highly reactive, recyclable and environmentally benign catalyst allows the synthesis of various trimethylsilyl cyanohydrins from a wide range of cyclic, aliphatic and aromatic ketones.

Experimental

General information

All reagents and solvents employed were commercially available and were used as received without further purification: 4,4'-(hexafluoroisopropylidene)*bis*(benzoic acid), **H_2hfipbb** (98% ABCR); 1,10-phenantroline monohydrate, **1,10-phen** (99+% Acros Organics); 2,2'-bipyridine, **2,2'-bipy** (99+% Sigma-Aldrich); 4,4'-bipyridine, **4,4'-bipy** (98% Acros Organics); indium (III) acetate, **In(OAc)$_3$** (99.99% Strem Chemicals).

X-Ray structure determination

The single-crystal X-ray data for compounds **InPF-12** to **InPF-15** were obtained in a Bruker four circle kappa-diffractometer equipped with a Cu INCOATED microsource, operated at 30 W power (45kV, 0.60mA) to generate Cu Kα radiation (λ = 1.54178 Å), and a Bruker VANTEC 500 area detector (microgap technology). The details of data collection, refinement, and crystallographic data are found in the **ESI**, Table S1†.

Characterization methods

All indium MOFs were characterized by Elemental Analysis (**EA**), FT-IR spectroscopy, Termogravimetric Analysis and Powder X-Ray Diffraction, which confirmed the nature and purity for **InPF-12** – **InPF-15** materials. Equipment specifications and spectroscopy results are shown in the **ESI**, Fig.S13 – S23†.

Synthesis of Indium MOFs

All compounds were hydrothermally synthesized.

InPF-12 was synthesized by addition of 0.201 g (0.513mmol) of H_2hfipbb and 0.067 g (0.342 mmol) of 1,10-phen to a stirred solution of In(OAc)$_3$ (0.100 g, 0.342 mmol) in 8 mL of water. The resultant reaction mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 170 ºC for 18 hours. After cooling to room temperature, colourless crystals formed were collected and washed with distilled water, ethanol and acetone. Yield: 0.223g, 73%. **EA**, % found (calcd): C, 49.69 (49.64); H, 2.65 (2.55); N, 3.04(3.09). **IR** (KBr, cm^{-1}): 3543ν(OH), 3432 ν(C-H) phen, 3079 ν(C-H)L, 1720 ν(C=O)L, 1600 ν(OCO)as, 1549 ν(C=N)phen, 1432 ν(OCO)s, 1421 ν(C-C)as, 1254 and 1212 ν(C-C)s, 1176 ν(C-F), 872, 857 δoop(C-H)phen, 785, 750 and 724 δoop(C-H)L.

InPF-13 was obtained by a similar procedure to the above described but using a mixture of H_2hfipbb (0.201 g, 0.513mmol), 2,2'-bipy (0.047 g, 0.342 mmol) and In(OAc)$_3$ (0.100 g, 0.342 mmol) in 8 mL of distilled water. The mixture was heated in a Teflon-lined stainless steel autoclave at 170 ºC for 72 hours. After cooling to room temperature, colourless crystals formed were collected and washed with distilled water, ethanol and acetone. Yield: 0.230g, 77%. **EA**, % found (calcd): C, 48.36 (48.76); H, 2.17 (2.54); N, 3.11 (3.20). **IR** (KBr, cm^{-1}): 3593ν(OH), 3532 ν(C-H)2,2'-bipy, 3120 and 3064 ν(C-H)L, 1717 ν(C=O)L, 1604 ν(OCO)as, 1541 ν(C=N)2,2'-bipy, 1445 and 1424 ν(OCO)s, 1375 ν(C-C)as, 1250 and 1212 ν(C-C)s, 1176 ν(C-F), 874, 860 δoop(C-H)2,2'-bipy, 781, 775 and 724 δoop(C-H)L.

The synthesis procedure to obtain **InPF-14** is similar to that described for **InPF-12** and **InPF-13** but in this case, a mixture of H_2hfipbb (0.201 g, 0.513mmol), 4,4'-bipy (0.024 g, 0.171 mmol) and In(OAc)$_3$ (0.100 g, 0.342 mmol) in 8 mL of distilled water was heated in a Teflon-lined stainless steel autoclave at 170 ºC for 72 hours. Yield: 0.210g, 79%. **EA**, % found (calcd): C, 46.68 (47.07); H, 2.2(2.07); N, 1.61(1.80). **IR** (KBr, cm^{-1}): 3421 ν(C-H)4,4'-bipy, 3246 and 3117 ν(C-H)L, 1614 ν(OCO)as, 1597 and 1543 ν(C=N)4,4'-bipy, 1426 ν(OCO)s, 1298 ν(C-C)as, 1255 and 1242 ν(C-C)s, 1177 ν(C-F), 878, 859 δoop(C-H)4,4'-bipy, 781, 752 and 726 δoop(C-H)L.

For **InPF-15** a mixture of H_2hfipbb (0.132 g, 0.336 mmol), 4,4'-bipy (0.048 g, 0.307 mmol) and In(OAc)$_3$ (0.100 g, 0.342 mmol) in 6 mL of distilled water was heated in a Teflon-lined stainless steel autoclave at 200 ºC for 72 hours. Colourless crystals formed were collected and washed with distilled water, ethanol and acetone. Yield: 0.568g, 82% **EA,** % found (calcd): C, 41.22 (41.82); H, 1.91(1.80); N, 1.23(1.25). **IR** (KBr, cm^{-1}): 3632ν(OH), 3430 ν(C-H)4,4'-bipy, 1700 ν(C=O)L, 1619 ν(OCO)as, 1588 and 1531 ν(C=N)4,4'-bipy, 1406 ν(OCO)s, 1269 ν(C-C)as, 1255 and 1238 ν(C-C)s, 1173 ν(C-F), 863, 846 δoop(C-H)4,4'-bipy, 769, 736 and 711 δoop(C-H)L.

Catalytic activity

In order to be used as catalysts, all materials were previously treated at 130ºC during 12 h to guarantee the absence of adsorbed solvent molecules. Their purity and crystallinity were confirmed comparing PXRD patterns before and after each catalytic reaction.

PROCEDURE FOR THE CATALYTIC CYANOSILYLATION OF BENZALDEHYDE. Catalytic amounts of **InPF-11** to **InPF-15** (10 mg, 2.5 mol %) were placed in a Schlenk tube under nitrogen atmosphere without solvents, together with the corresponding carbonyl compound (1 equivalent); trimethylsilyl cyanide (1.5 equivalent) was then added dropwise. The mixture was stirred and heated at 50ºC until disappearance of the aldehydes (0.25-2h, checked by GC-MS).

PROCEDURE FOR THE CATALYTIC CYANOSILYLATION OF KETONES. Catalytic amounts of **InPF-11** to **InPF-15** (10 mg, 2.5 mmol %) were placed in a Schlenk tube under nitrogen atmosphere, together with the corresponding ketone (1 equivalent, 0.3 mmol); trimethylsilyl cyanide (1.1 equivalent, 0.33 mmol) was then added dropwise. The mixture was stirred and heated at 80ºC until disappearance of the ketones (1-48 h, checked by GC-MS).

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