

Investigating the Case of Titanium(IV) Carboxyphenolate Photoactive Coordination Polymers

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KEYWORDS coordination polymers, Metal Organic Frameworks, titanium, phenolic ligands, reactivity, crystal structure, photoactivity.

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3 ABSTRACT The reactivity of the 2,5-dihydroxyterephthalic acid (H₄DOBDC) with Ti(IV)
4 precursors was thoroughly investigated for the synthesis of MOFs under solvothermal conditions.
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6 Four crystalline phases were isolated, whose structures were studied by a combination of single-
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8 crystal or powder X-ray diffraction and solid state NMR. The strong coordination ability of the
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10 phenolate moieties was found to favor the formation of isolated TiO₆ octahedra bearing solely
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12 organic ligands in the resulting structures, unless hydrothermal conditions and pre-condensed
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14 inorganic precursors are used. Noteworthy, these solids strongly absorb visible light, as a
15
16 consequence of the ligand to metal charge transfer (LMCT) arising from Ti-phenolate bonds.
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18 Preliminary photocatalytic tests suggest that one compound, namely MIL-167 presents a higher
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20 activity for H₂ evolution than the Ti-carboxylate MIL-125-NH₂, but that such effect can not be
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22 directly correlated with its improved light absorption feature.
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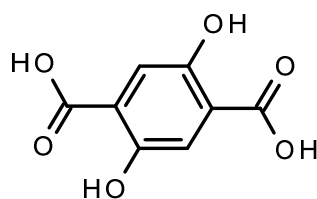
33 **Introduction**

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35 While porous coordination polymers (PCPs) or Metal-Organic Frameworks (MOFs) are
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37 considered as promising candidates in various domains (gas storage, fluids separation, acid or
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39 base catalysis, biomedicine, among others),^{1, 2} their use as heterogeneous photocatalysts has
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41 exploded only very recently.³⁻⁷ Considering the well-established photocatalytic properties of
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43 TiO₂, it seems logical to develop porous Ti-based MOFs for such applications. Precisely,
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45 photocatalytic systems based on MOFs may be beneficial due to the various combinations of
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47 oxo-metal clusters and organic linkers together with their intrinsic porosity that facilitates the
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49 diffusion of the substrates and products to the catalytic centers. Nevertheless, because of the
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51 inherent difficulty in controlling the reactivity of Ti(IV) ions in solution (especially out of the
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3 very acidic conditions),⁸ among the numerous MOFs reported so far, those based on titanium are
4 still very limited.^{4, 9-22} If open framework Ti bisphosphonates¹⁵ such as MIL-22(Ti) or MIL-
5 25(Ti) (MIL stands for Materials Institute Lavoisier) were discovered end of 1990's, the first
6 microporous crystalline Ti(IV) diphosphonate, MIL-91, was reported by some of us only in
7 2006,¹⁴ followed by the Ti(IV) terephthalate MIL-125. If MIL-91(Ti) bears Tancoite type chains
8 of corner sharing metal octahedra bridged by bisphosphonate moieties delimiting a narrow 1D
9 pore system, MIL-125(Ti) is a cubic network built up from $Ti_8O_8(OH)_4$ oxo-clusters related
10 together via terephthalate linkers to define a 3D microporous system with a high surface area
11 ($S_{BET} \sim 1500 \text{ m}^2 \text{ g}^{-1}$) and a photocatalytic activity.¹⁰ Since then, few photoactive porous Ti(IV)
12 carboxylates such as the functionalized MIL-125-NH₂,^{4, 17, 23} the porphyrinetetracarboxylate
13 derivative PCN-22¹⁶ and the flexible 1,4-cyclohexanedicarboxylate COK-69⁹ were described, as
14 well as a Ti(III) terephthalate MIL-101.¹¹ Note that these MOFs bear each of them different
15 inorganic sub-units, highlighting the poor degree of control of the Ti polymerization in solution
16 even in the presence of strongly complexing ligands. As an alternative to direct synthesis, post-
17 synthetic cation exchange was also reported.^{18, 24, 25} Absorption of light in the visible range is a
18 prerequisite for many photo-driven applications. In the case of Ti(IV) carboxylates, such feature
19 is obtained through the use of an organic ligand presenting a low HOMO-LUMO gap,^{4, 5, 16, 26, 27}
20 with the light absorption thus only governed by 'organic-like' electronic levels. Alternatively,
21 Ti(IV)-phenolate bonds are known to lead to ligand to metal charge transfer (LMCT) giving rise
22 to a strong absorption in the visible range.²⁸⁻³¹ Indeed, both amorphous³² and crystalline³³⁻³⁸
23 Ti(IV) phenolates open frameworks were described since the 1990's, all presenting a deep red
24 color. More recently, α -hydroxycarboxylate³⁹ and catecholate¹² ligands were also considered to
25 build up both pure Ti(IV) and bimetallic Ti(IV)/Zn(II)^{40, 41} open frameworks.

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3 The 2,5-dihydroxyterephthalic acid (H₄DOBDC, scheme 1) is a typical linker to built up MOFs
4 comprising both carboxylate-cation and phenolate-cation bonds, such as the archetypical
5 M₂(DOBDC) CPO-27 or MOF-74 (M = Ni, Co, Mg, Zn, Mn, Fe,...) porous solids.^{42, 43} Upon
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10 reacting H₄DOBDC with Ti(IV) isopropoxide in acetic acid, Gao *et al.* isolated a layered solid
11 formulated Ti₂(HDOBDC)₂(HDOBDC) (labelled NTU-9, NTU stands for Nanyang
12 Technological University),³⁹ built up from isolated TiO₆ octahedra connected through the organic
13 units acting as ditopic ligands to afford a 2-D honeycomb-like network with a (6,3) topology.⁴⁴
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Very recently Zou *et al.* also prepared the almost pure Ti version of the CPO-27/MOF-74 by post-synthetic cation exchange.¹⁸ We here systematically investigated the reactivity of this specific ligand with Ti(IV) precursors under solvothermal conditions, in order to not only obtain new open photoactive frameworks but also to expand our understanding of the chemistry of titanium. We report the in-depth characterization of few of the resulting solids, including structure determination by either single crystal or powder X-ray diffraction (XRD), solid state NMR analysis, gas sorption properties as well as preliminary photocatalytic activity tests.



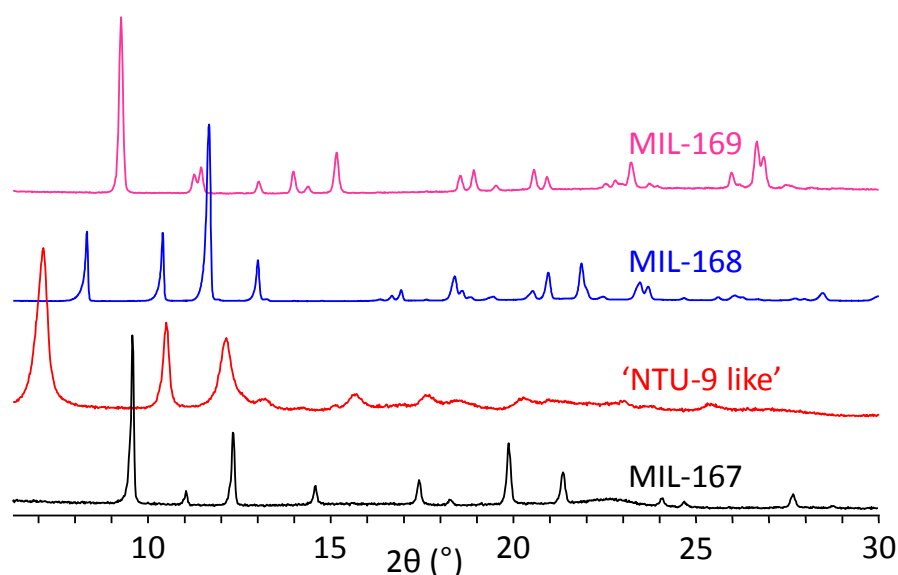
Scheme 1. The 2,5-dihydroxyterephthalic acid (H₄DOBDC) used in the present study.

Experimental section

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3 Details about the synthesis, structure determination by XRD analysis and further
4 characterizations (solid state NMR, TGA, IR, thermodiffraction, porosimetry, SEM imaging) as
5 well as catalytic tests can be found in Supporting Information.
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14 Synthesis and structure determination

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17 The reactivity of H₄DOBDC with Ti(IV) sources under solvothermal conditions was first
18 evaluated using a miniaturized high throughput setup developed by Stock *et al.*,⁴⁵ allowing the
19 rapid screening of a broad range of synthetic conditions in series of small reactors (< 2 mL). The
20 nature of the Ti(IV) precursor and the solvent, as well as the addition of catechol, possibly acting
21 as a growth modulator,⁴⁶⁻⁴⁸ were found to be the key experimental parameters. Upon
22 systematically varying such parameters, four crystalline phases were identified, whose X-ray
23 powder diffraction (XRPD) patterns are shown in Figure 1 and unit-cell parameters summarized
24 in Table 1. The syntheses were then up-scaled in 25 mL reactors for full characterization.
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56 **Figure 1.** XRPD patterns of MIL-167, MIL-168, MIL-169 and 'NTU-9 like' ($\lambda = 1.5418 \text{ \AA}$).
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Solid	Formula	Space group	Cell parameters
MIL-167	Ti(DOBDC) _{1.5} (Et ₂ MeNH) ₂ · <i>n</i> H ₂ O	<i>I</i> -43 <i>d</i>	<i>a</i> = 22.9118(4) Å <i>V</i> = 12027.6(6) Å ³
MIL-168	Ti(DOBDC)(cat)(DEAH) ₂	<i>Pbcn</i>	<i>a</i> = 16.863(1) Å <i>b</i> = 13.3677(8) Å <i>c</i> = 10.7622(6) Å <i>V</i> = 2426.1(3) Å ³
MIL-169	TiO _{0.5} (DOBDC)(H ₂ O)(pipH ₂) _{0.5} ·H ₂ O	<i>P</i> -1	<i>a</i> = 8.10511(5) Å <i>b</i> = 8.15098(5) Å <i>c</i> = 9.90029(6) Å <i>α</i> = 75.8518(4)° <i>β</i> = 82.3596(4)° <i>γ</i> = 76.9343(6)° <i>V</i> = 615.707(7) Å ³
'NTU-9' like	Ti(H _x DOBDC) _{1.5} (DEAH) _{2-1.5x} · <i>n</i> solv	<i>P</i> -31 <i>c</i>	<i>a</i> = 14.69(1) Å <i>c</i> = 11.47(1) Å <i>V</i> = 2144(3) Å ³

Table 1. Crystallographic parameters of the title solids.

First, when using N,N-diethylformamide (DEF) as a solvent and Ti(IV) isopropoxide as a precursor, three phases were isolated, whose structures will be described below. In pure DEF and using a ligand to Ti(IV) ratio equal to 4, a first solid exhibiting a XRPD pattern very similar to the one of NTU-9 and further labelled 'NTU-9 like' (see Figure S2) was isolated. Upon addition of catechol (3eq. per Ti(IV)), a new crystalline phase (labelled MIL-168) was obtained. Addition

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3 of methanol to the reaction medium in the absence of catechol ultimately leads to the formation
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5 of a third solid, MIL-167 (detailed synthetic conditions can be found in Supporting Information).
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7 Note that the use of dimethylformamide as a solvent led to different crystalline phases whose
8
9 crystal structures could not be solved yet. Crystallites of MIL-168 suitable for single crystal
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11 XRD analysis using synchrotron radiation (beamline Cristal, Soleil, France) could be produced.
12
13 MIL-167 was obtained as large, but intergrown crystallites (see [Figure S13](#)) preventing any
14
15 structure determination by single crystal analysis. Additionally, 'NTU-9 like' was isolated as
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17 micrometer-sized platelets (see [Figure S15](#)). Both MIL-167 and 'NTU-9 like' were hence studied
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19 by XRPD analysis, in combination with solid state NMR spectroscopy to extract information
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21 about the content of the unit-cell and the local environment (see Supporting Information and
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23 below).
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29 MIL-167 crystallizes in a cubic setting, space group $I-43d$ (see Table 1), with one Ti(IV) ion
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31 on a 3-fold axis and half of a ligand in general position (see [Figure S5](#) for the final Rietveld
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33 refinement), hence leading to the stoichiometry of three ligands for two Ti(IV) ions. The
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35 structure consists of isolated TiO_6 octahedra, with the oxygen atoms arising solely from DOBDC
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37 ligands (Figure 2a), connected to each other by the ditopic linkers through chelating 6-member
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39 rings involving both phenolic and carboxylic oxygens (see Figure 2a) to afford a 3-D chiral
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41 network exhibiting the (10,3)-*a* topology (Figure 2b).⁴⁴ Two enantiomeric networks are then
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43 interpenetrated to afford the final MIL-167 solid (Figure 2b), which hold cavities of about 6-7 Å
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45 free diameter.
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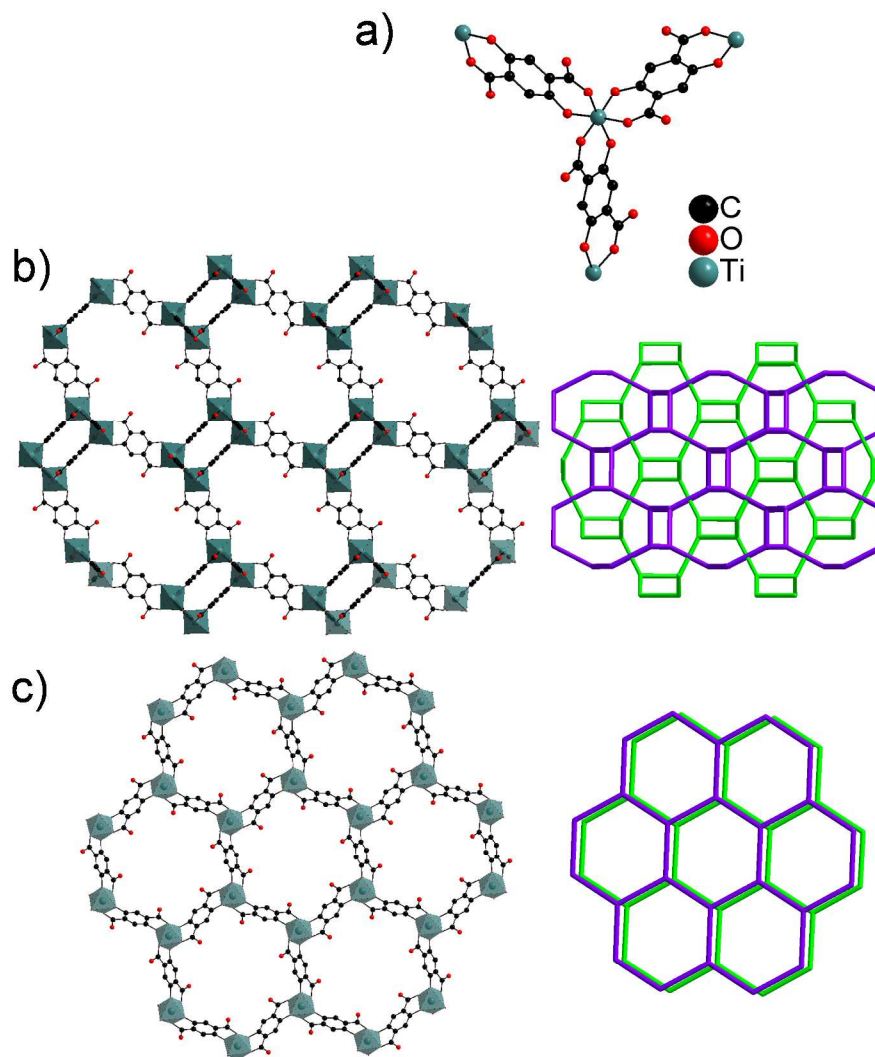
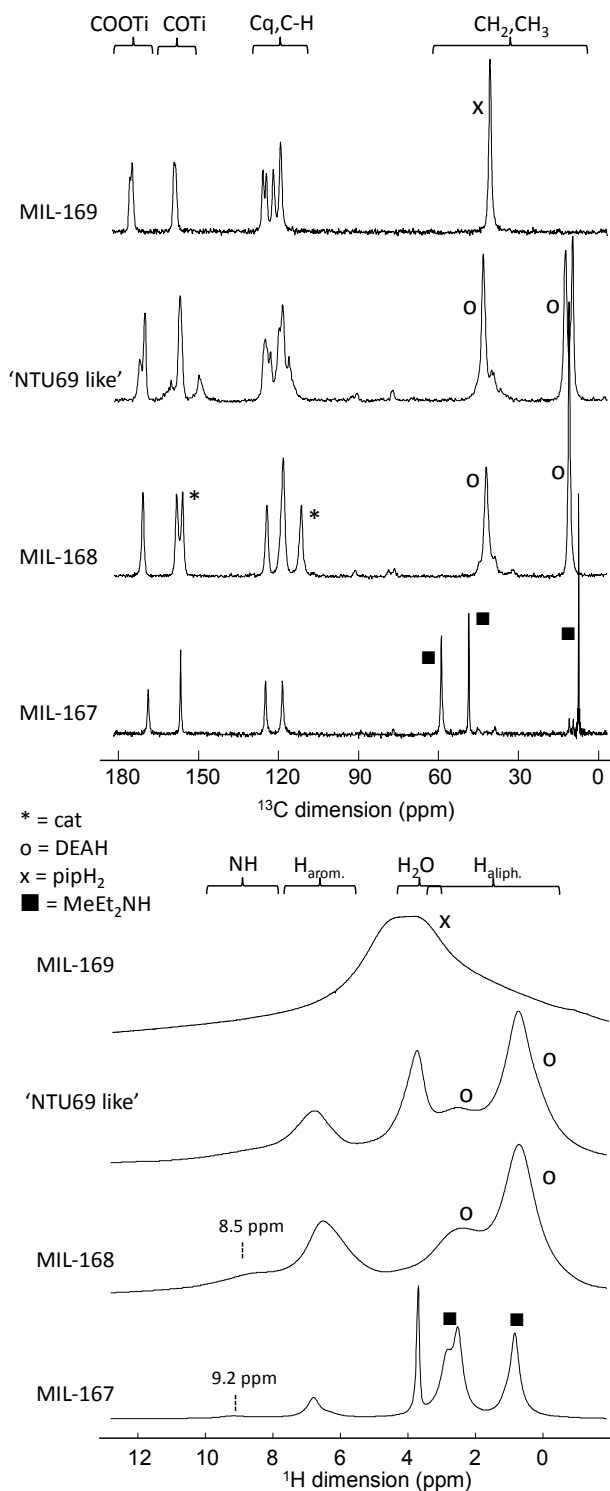


Figure 2. Crystal structures. a) Coordination sphere around the Ti(IV) ions in both NTU-9 and MIL-167; b) and c) coordination framework and the corresponding topological net for MIL-167 and NTU-9 respectively.

One (1D) and two-dimensional (2D) solid state NMR experiments were further carried out to investigate the nature of the pore content (see Figure 3 and S20). Both ^1H and ^{13}C 1D NMR spectra (Figure 3) present the signals expected for the DOBDC ligand, as well as resonances characteristics of alkyl groups. Specifically, the signals at 9, 46 and 60 ppm on the ^{13}C NMR spectrum (Figure 3, top) were attributed to diethylmethylammonium.⁴⁹ This is in agreement with

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3 the 2D ^1H - ^{13}C and ^1H - ^1H NMR correlation experiments (Figures S22 and S23), which indicate
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5 that all alkyl groups are close in space, hence likely belonging to a single molecular entity. Such
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7 tertiary ammonium could arise from reactions involving both solvents: DEF first degrades into
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9 diethylamine, which further reacts with methanol to generate diethylmethylamine.⁵⁰ An acidic
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11 proton ($\delta \sim 9.2$ ppm) as well as a signal at 3.6 ppm attributed to the ammonium and water
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13 respectively could also be identified on the ^1H NMR spectrum (Figure 3, *bottom*), finally
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15 yielding to the formula $\text{Ti}(\text{DOBDC})_{1.5}(\text{Et}_2\text{MeNH})_2 \cdot n\text{H}_2\text{O}$, in agreement with thermogravimetric
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17 and chemical analyses (see Figure S12 and Table S1).
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53 **Figure 3.** ¹H→¹³C CPMAS (10 kHz) (*top*) and ¹H MAS (30 kHz) (*bottom*) NMR spectra of
54 MIL-167, MIL-168, 'NTU-9 like' and MIL-169.
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3 In the absence of methanol in the reaction mixture, the 'NTU-9 like' solid was produced. As
4 mentioned earlier, this compound is built up from isolated TiO_6 octahedra connected through
5 three DOBDC ligands giving rise to a honeycomb 2-D layer (Figure 2).³⁹ Slight differences
6 between the calculated and experimental patterns are discernible (see Figure S2), and probably
7 arise from a variation of the interlayer content (although preferred orientation effects could not
8 be ruled out). Indeed, while Gao. *et al* formulated the NTU-9 solid as
9 $\text{Ti}(\text{HDOBDC})(\text{H}_2\text{DOBDC})_{0.5}$, signals indicating the presence of diethylammonium (DEAH)
10 were found in the ^1H and ^{13}C NMR spectra (see Figure 3 and Figure S24), suggesting a formula
11 closer to $\text{Ti}(\text{H}_x\text{DOBDC})_{1.5}(\text{DEAH})_{2-1.5x}\cdot n\text{solv}$ (solv = H_2O , DEF) for our experimental
12 conditions.
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28 Interestingly, MIL-167 and NTU-9 are built up from the same coordination motif (Figure 2a) and
29 hence, without taking into account the counter-ions, are simply polymorphs arising from a
30 different alternation of the absolute configuration Δ / Λ of the neighboring octahedral metal
31 centers. Such occurrence of polymorphic 2-D (6,3) and 3-D (10,3) networks was indeed already
32 identified by Abrahams *et al.* when using M(II) cations and 2,5-dihydroxybenzoquinone as a
33 ligand,⁴⁴ and might be associated with a templating effect of the ammonium cations.⁵¹
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35 Nevertheless, a solid similar to MIL-167 but of very poor crystallinity was obtained using a
36 mixture of acetic acid and diethylamine as a solvent (see Figure S1), indicating that the presence
37 of the diethylmethylammonium cation is not mandatory to produce the 3-D polymorph.
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49 Finally, the third compound, *i.e.* MIL-168, isolated in the presence of catechol (H_2cat),
50 crystallizes in an orthorhombic setting in the *Pbcn* space group, with an asymmetric unit
51 consisting of one Ti ion lying on a two-fold axis, half of a DOBC ligand and a catechol on a two
52 fold axis. It also contains a diethylammonium ion (DEAH) in general position, thus leading to
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3 the formula $\text{Ti}(\text{DOBDC})(\text{cat})(\text{DEAH})_2$, as confirmed by ^1H and ^{13}C NMR (Figure 3 and S24),
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5 TGA and chemical analyses (see Figure S12 and Table S1). This structure is once again built up
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7 from isolated TiO_6 octahedra, the coordinating oxygen atoms arising this time from two DOBDC
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9 ligands and one catechol moiety (Figure 4). This define 1-D zig-zag chains running parallel to
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11 each other and separated by $\text{N-H}\cdots\text{O}$ hydrogen bonded DEAH cations (see Figure S7), arising
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13 again from the degradation of DEF. The surrounding of the Ti ion presents thus strong
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15 similarities with those in MIL-167 and NTU-9, with solely one DOBDC ligand replaced by a
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17 catecholate one. Catechol was initially added to act as a modulator,^{46, 47} *i.e.* to slow down the
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19 precipitation and improve the crystallinity of the resulting solid. Here, even the use of a minor
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21 amount of catechol ($\text{cat}/\text{DOBDC} = 3/4$) leads to its insertion within the structure. This is in
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23 agreement with its stronger coordination ability compared with α -hydroxycarboxylates such as
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25 DOBDC, and indicates that it shall not be used as a modulator with such ligands.⁴⁸ Furthermore,
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27 whatever the solvothermal conditions tested, exclusively structures built up from isolated TiO_6
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29 octahedra without any inorganic ligand (oxo, hydroxo or aquo moieties) were produced. This is
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31 in sharp contrast with the case of Ti-carboxylates, in which oxo or hydroxo bridges are always
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33 found.^{9, 10, 16} Only in the case of Ti bisphosphonate systems, one could obtain such as
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35 configuration leading to pillared versions of the well-known α -TiP solid.¹³ As already
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37 exemplified in the case of Zr-based MOFs,^{48, 52} the final inorganic building unit results from the
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39 competition between both types of ligands, the organic and the inorganic ones. When switching
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41 from carboxylate^{9, 10, 16} to α -hydroxycarboxylate,³⁹ catecholate¹² or phosphonates ligands, the
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43 strength of coordination increases, hence disfavoring the presence of inorganic ligands. Similarly
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45 to the case of the Ti-phosphate chemistry under hydrothermal conditions, this effect can of
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47 course be counter-balanced through an increase of the pH favoring the inorganic condensation.¹⁵
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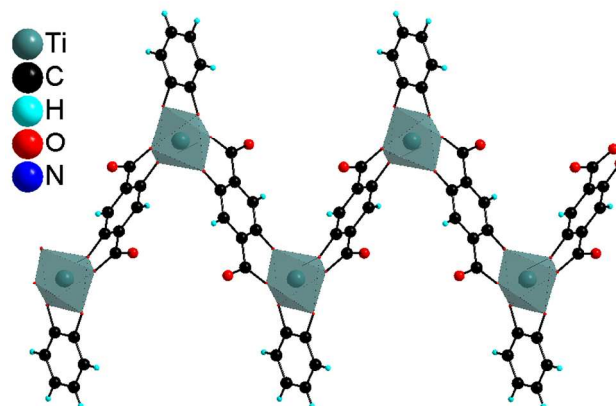
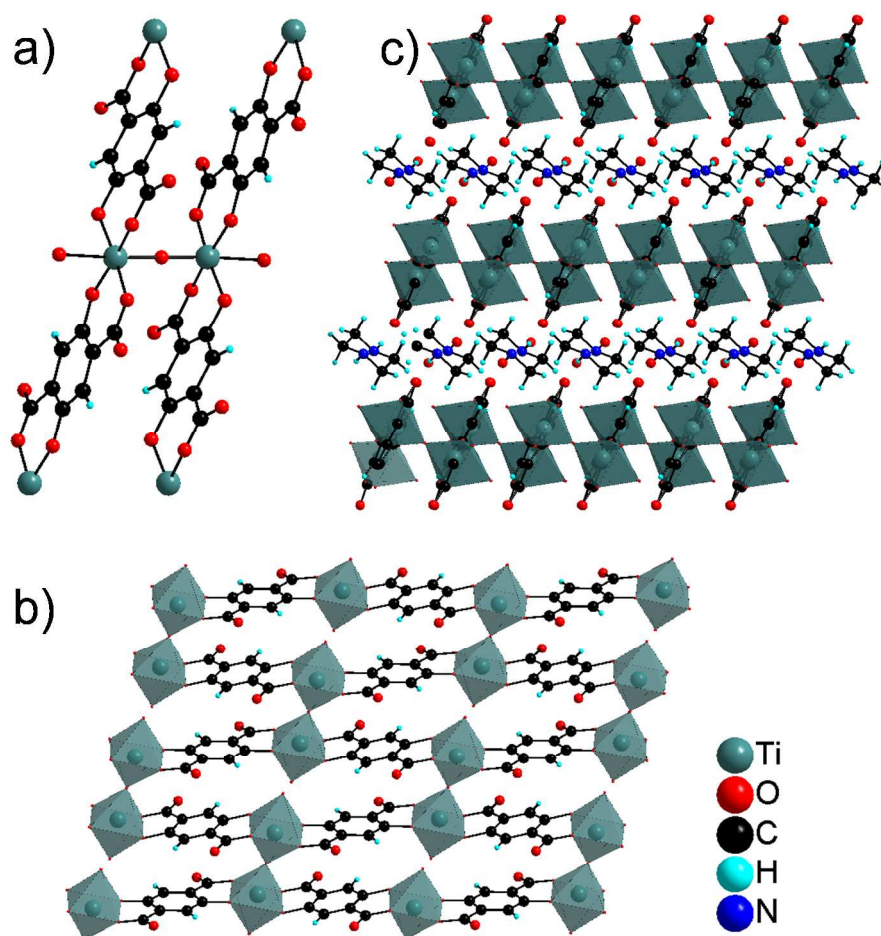


Figure 4. Crystal structure of MIL-168: 1-D coordination chain.

Thus, in order to favor the formation of more condensed inorganic units with DOBDC, drastic modifications of the synthetic conditions were applied. An increase of the pH did not lead however to any crystalline materials. Thus, we selected another possibility which consists of the use of preformed Ti oxo-clusters as a source of Ti containing oxo/hydroxo species, hoping that upon complexation with the title linkers, one might form more condensed building units. The tetrameric Ti oxalate formulated $Ti_4O_4(ox)_7(pipH_2)_3$ ($ox = oxalate$ and $pipH_2 = piperazinium$), which already contains μ_2 -oxo bridged Ti ions was thus prepared.⁵³ Upon reaction with H_2DOBDC in water (a solvent which of course favors the appearance of hydroxo or oxo ligands) a fourth microcrystalline solid, later labelled MIL-169, was isolated (see Figure 1). The structure was again solved by XRPD (see [Figure S6](#) for the final Rietveld plot), taking into account local information gained from solid state NMR. This solid crystallizes in a triclinic setting, with one oxygen atom on an inversion center, one Ti ion, two halves of a DOBDC ligand. It contains also half of a piperazinium ion and two water molecules in general position, leading to the formula $Ti_2O(DOBDC)_2(H_2O)_2(pipH_2) \cdot 2H_2O$, in agreement with 1H and ^{13}C NMR (Figure 3 and S25-27), TGA and chemical analyses (see [Figure S12](#) and Table S1). Each Ti ion is chelated by two DOBDC ligands through the 6-membered ring involving phenolate and carboxylate groups

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3 already observed in MIL-167, -168 and 'NTU-9 like'. Noteworthy, the Ti ions are associated
4 into Ti_2O_{11} dimers of octahedra bridged by a $\mu_2\text{-O}$ group and exhibit terminal water molecules
5 (Figure 5a). These dimers are then connected to each other through four DOBDC ligands to
6 afford anionic layers (Figure 5b), which are further separated by hydrogen bonded piperazinium
7 ions and free water molecules to define the whole structure (Figure 5c). Note that the dimer is
8 reminiscent of the titanyl chains of metal octahedra with alternating short (1.80 Å) and long Ti-O
9 distances (2.29 Å).
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3 **Figure 5.** Crystal structure of MIL-169. a) the $\text{Ti}_2(\text{DOBDC})_4\text{O}(\text{H}_2\text{O})_2$ dimer; b) 2-D coordination
4 network; c) stack of anionic layers separated by piperazinium ions and water molecules.
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10 11 **Thermal behavior and sorption properties**

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14 The thermal behavior of all solids was evaluated by thermogravimetric (TG) analyses and
15 temperature dependent XRPD analyses under oxygen and air, respectively. As expected, the TG
16 curves of all solids but MIL-169 present a weight loss in the low temperature regime ($50 < T <$
17 150°C) associated with the elimination of the entrapped solvent molecules (Figure S12).
18
19 Temperature dependent XRPD analysis reveals that this solvent departure is associated with
20 strong shifts in the position of the Bragg peaks in MIL-169 and ‘NTU-9 like’, while no
21 noticeable change occurs for MIL-167 (see Figures S8, S9 and S11). This is in line with the
22 structure of these solids: MIL-169 and ‘NTU-9 like’ are 2-D compounds, and thus prone to
23 shrink upon solvent departure (especially when the solvent molecules are located between the
24 layers). MIL-167, which adopts an interpenetrated 3-D structure, appears to be rather rigid
25 towards desorption.
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40 At higher temperature, all solids present a similar feature, with a combustion of the organic
41 moieties occurring around 250°C (Figure S12) and associated with the complete collapse of the
42 structures (Figures S8-S11). It is worthy to note that this temperature is significantly lower than
43 the ones observed for Ti carboxylates such as MIL-125 and MIL-125-NH₂. This is likely to arise
44 from the intrinsic reactivity of phenolate ligands with oxidants (here dioxygen), as already
45 observed with other cations.^{48, 52, 54, 55}
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55 The permanent porosity of MIL-167 was finally assessed after activation at 150°C overnight.
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57 No noticeable adsorption of N₂ at -195°C was detected. On the opposite, adsorption of CO₂ at
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near ambient conditions (15°C) leads to a type I isotherm indicative of a microporous character, with a maximal adsorption capacity around 2.1 mmol g⁻¹ at 20 bar (Figure 6). These results can be understood in light of the structure of MIL-167: although this framework is quite open, both the interpenetration and the presence of entrapped bulky diethylmethylammonium cations drastically decrease the accessible pore volume, leading finally to a modest sorption capacity.

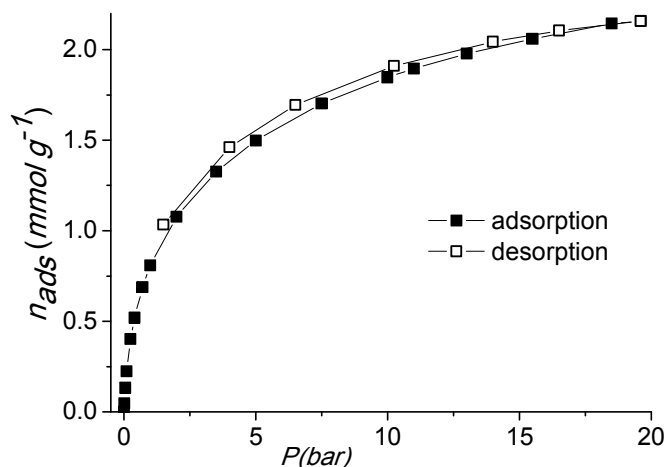
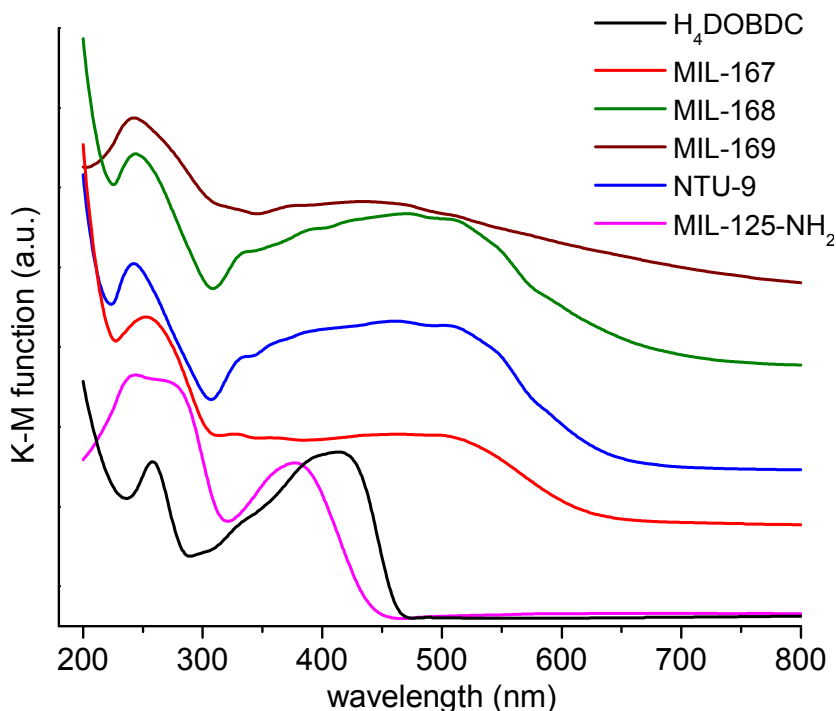


Figure 6. CO₂ sorption isotherms of MIL-167 at 15°C.

Optical properties and photocatalytic tests

The optical properties of MIL-167, MIL-168, MIL-169 and ‘NTU-9 like’ were evaluated by diffuse reflectance spectra measurements (see Supporting Information for details), the corresponding absorption spectra are shown in Figure 7, together with the ones of MIL-125-NH₂ and the H₄DOBDC ligand. The absorption spectrum of the H₄DOBDC ligand presents two main absorption bands centered about 250 and 400 nm. In sharp contrast, all coordination polymers built up from this ligand present roughly similar spectra, with a band centered at 250 nm together with a broad band covering the 300 to 600 nm window. This result was, as developed in the introduction, expected, and confirmed the occurrence of ligand to metal charge transfer typical of

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3 Ti-phenolate systems.^{39, 56} This significantly differs from Ti carboxylate compounds (see MIL-
4 125-NH₂ on Figure 7), whose absorption bands in the visible range are typically associated with
5 purely organic electronic levels.^{4, 5, 26, 27}
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35 **Figure 7.** Diffuse reflectance spectra of MIL-167, MIL-168, MIL-169 and ‘NTU-9 like’ in
36 comparison with H₄DOBDC and MIL-125-NH₂.
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41 These results prompted us to test the charge transport ability of the title solids. Time-resolved
42 microwave conductivity (TRMC) measurements^{5, 57, 58} were thus carried out on MIL-167. The
43 solid was initially grinded and drop casted on a quartz plate, and the excitation wavelength was
44 set to 500 nm, *i.e.* close to the absorption maximum. As shown in Figure S18, photoconductance
45 was found to be low ($\eta\Sigma\mu \sim 2.10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), on the whole similar to the one of MIL-125
46 derivatives,⁵ and no improvement was observed upon irradiating in the UV range (340 nm, see
47 Figure S19). This result probably arises from the fact that such structure does not offer long
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3 range pathway suitable for electronic conduction, as a possible consequence of the isolated Ti
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5 metal centers.
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8 Finally, preliminary tests were carried out to assess the photocatalytic activity of MIL-167, MIL-
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10 169 and 'NTU-9 like' for hydrogen production. The solids were suspended in a solution of water
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12 and triethylamine (acting as a proton source and a sacrificial electron donor respectively) in
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14 acetonitrile at 30-35°C, and hydrogen evolution was monitored under constant light irradiation
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16 (see Supporting Information for details). Results are shown in Figure 8, and compared with the
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18 one obtained with MIL-125-NH₂. This later was indeed already shown to act as a moderate
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20 photocatalyst in similar conditions.^{59, 60} Under UV irradiation ($\lambda = 280$ nm), a noticeable
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22 production of hydrogen was detected for MIL-167, while no activity was found for MIL-169 and
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24 'NTU-9 like' solids, suggesting that the microporosity might play a role in achieving an efficient
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26 conversion. The reaction rate was found initially 2.6 higher for MIL-167 than for MIL-125-NH₂
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28 (reaction rate = 2.9 and 7.7 $\mu\text{mol h}^{-1}$ for MIL-125-NH₂ and MIL-167, respectively), but the
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30 activity decreases with time, suggesting a deactivation of the catalyst, although XRPD analysis
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32 indicates that the structure is maintained with some splits of diffraction peaks (Figure S3), likely
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34 due to a symmetry lowering (from cubic to tetragonal, see Figure S4) associated with different
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36 pore contents. Upon switching to visible light irradiation ($\lambda = 385$ nm), a slight decrease of the
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38 hydrogen production is observed for MIL-125-NH₂ (see Figure S20), while no more hydrogen is
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40 detected for MIL-167 (data not shown). These preliminary experiments indicate that a good
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42 visible light absorption ability is not the prime criterion in determining the catalytic activity of
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44 Ti-based MOFs for hydrogen production. In the case of MIL-167, it is especially not yet fully
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46 understood why in spite of the observed LMCT no catalytic activity under visible illumination
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48 could be achieved. Deeper investigations are thus requested to shed some light on this behavior.
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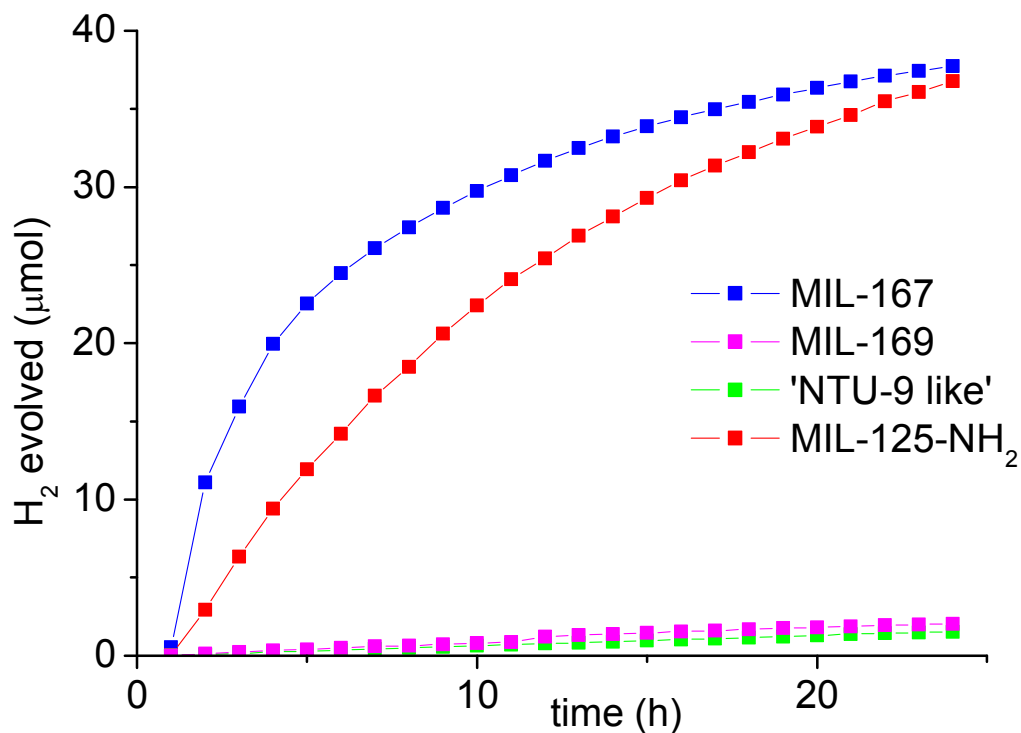


Figure 8. Photocatalytic activity of MIL-167, MIL-169, 'NTU-9 like' and MIL-125-NH₂ (30 mg) for hydrogen production: hydrogen evolution as a function of time of reaction at 40°C upon irradiation at 280 nm.

Conclusion

Upon systematically investigating under solvothermal conditions the reactivity of Ti(IV) precursors with 2,5-dihydroxyterephthalic acid (H₄DOBDC), four crystalline phases were isolated and characterized, highlighting the high degree of structural diversity of this system. Their structural analysis revealed that, in sharp contrast with the case of pure carboxylate ligands and due to the strong coordination ability of the α -hydroxycarboxylate moieties, the formation of coordination polymers built up from isolated Ti ions surrounded solely by organic ligand is favored. The appearance of more condensed motifs including inorganic oxo bridges requires specific conditions, such as the use of aqueous reaction medium and pre-condensed inorganic

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3 reactants. Thanks to ligand to metal charge transfer, all solids present a strong absorption in the
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5 visible range, much broader than the Ti carboxylate systems. Preliminary experiments reveal that
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7 such optical feature does not lead however to a direct improvement of the photocatalytic
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9 performance under visible light, and that further studies are needed to gain benefit from such
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11 characteristics.
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26 27 **Author Contributions**

28
29 The manuscript was written through contributions of all authors. All authors have given approval
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31 to the final version of the manuscript.
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35 **Supporting Information Available:** synthetic details, structure determination, solid state NMR,
36
37 TGA, IR, thermogravimetry, porosimetry, SEM imaging, catalytic tests. This material is
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39 available free of charge via the Internet at <http://pubs.acs.org>.
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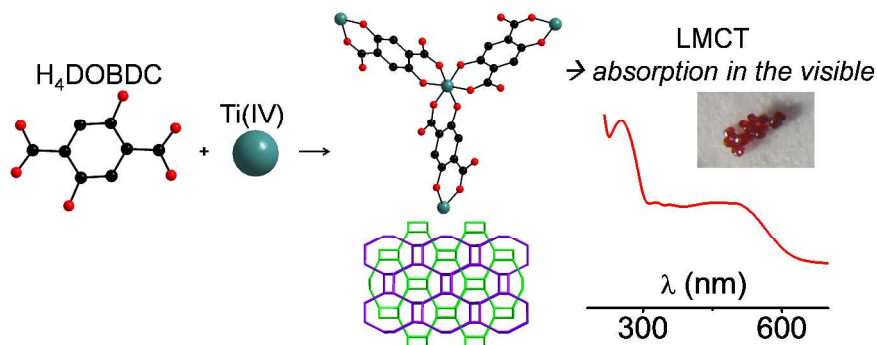
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Table of Contents Graphic



Reaction of the 2,5-dihydroxyterephthalic acid (H_4DOBDC) with $Ti(IV)$ precursors lead to the formation of four coordination polymers of various dimensionalities, all presenting a strong absorption of light in the visible range.