From a bulk solid to thin films of a hybrid material derived from the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ oxo-cluster and poly(4-vinylpyridine)

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From a bulk solid to thin films of a hybrid material derived from the $[Ti_{10}O_{12}(cat)_8(py)_8]$ oxo-cluster and poly(4-vinylpyridine)

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Abstract:

In this work, we report the formation of a coloured inorganic-organic hybrid material generated from the $[Ti_{10}O_{12}(cat)_8(py)_8]$ oxo-cluster and poly(4-vinylpyridine). In this material, the linkage between the titanium oxo-cluster and the organic polymer implies Ti-N coordination bonds. Vibrational spectroscopies (FT-IR and Raman scattering) and thermo gravimetric analysis prove the quantitative incorporation of the cluster in the polymeric matrix with no degradation of the inorganic core of the starting complex and highlight the good homogeneity of the resulting materials. The solid-state NMR measurements (^{13}C CP-MAS) also reveal that the hybrid material results only from the substitution of the labile pyridine ligands within $[Ti_{10}O_{12}(cat)_8(py)_8]$ by the pyridines of the P4VP polymer. Next, the functionalization of SiO_2 surfaces with monolayer or multilayer films composed of alternate layers of the oxo-cluster and of the polymer is detailed. The thickness of these films, as evaluated by ellipsometry, ranges from a few nanometers to tens of nanometers for the monolayer films and the multilayer films respectively.

Inorganic-organic hybrids¹ are fascinating materials owing to the synergetic influence of the organic and inorganic constituents on the overall properties of these materials. Hybrid materials have found applications in various fields such as photo-catalysis,² biology and medicine,³ functional coatings,⁴ micro-optics and micro-electronics.⁵ Titanium oxo-clusters are particularly attractive nano-building blocks (NBBs) for the generation of hybrid materials, as their highly diverse structures⁶ are usually perfectly established, as the degree of condensation O/Ti is controlled and as, in some cases, their integrity is preserved during the assembly with the organic counter-part. Sanchez *et al* have reviewed the different bottom-up strategies permitting to synthesize inorganic-organic hybrid materials based on titanium oxo-cluster.⁷ A first strategy involves the NBBs in the presence of templating agents such as surfactants, amphiphilic or double hydrophilic block copolymers leading to the formation of mesostructured hybrid arrangements.⁸ A second strategy implies a copolymerization between an organic monomer and polymerizable groups decorating the inorganic core of the oxo-cluster.⁹ In this case, these oxo-clusters are generally synthesized through a post-functionalization step. Therefore, strong covalent bonds are created in such hybrid materials between the oxo-clusters and the organic polymer matrix.

Figure 1: Molecular structure of (a) [Ti₁₀O₁₂(cat)₈(py)₈] and (b) P4VP polymer. The sketch of the complex evidences the S_4 -symmetry. The two inequivalent catecholato ligands are differently coloured (in orange and blue). The pyridine ligands are coloured in green. The titanium atoms and the oxygen atoms are in blue and red respectively. The hydrogens are omitted for clarity.

In that context, we have reported a robust S_4 -symmetry titanium-based architecture bearing catecholato (cat) and pyridine (py) ligands.¹⁰ This neutral complex formulated as [Ti₁₀O₁₂(cat)₈(py)₈] displays a tetrahedral inorganic core decorated by catecholato ligands (the

molecular crystal structure of the complex is shown in Figure 1a). In solution, the pyridine ligands are labile and can be exchanged by substituted pyridine ligands.¹¹ Furthermore, this complex shows the distinguishing feature of absorbing visible light owing to charge transfer between the lone pair of oxygen atoms and the empty 3d orbitals of the Ti(IV) ions.¹²

Colour is indeed a major property to be considered when titanium(IV)-based hybrid materials have to be designed. This requirement arises from the possibility to generate photo-active hybrids acting in the visible domain, in opposition to TiO₂ that is mostly a UV-active material. Thus, great efforts are actually devoted to generate coloured titanium(IV) hybrids or coloured titanium oxo-cluster NBBs as hybrid precursors.¹³

Therefore, [Ti₁₀O₁₂(cat)₈(py)₈] could be viewed as a promising nano-object precursor to access unprecedented hybrids by exploiting the labile behaviour of the nitrogen monodentate ligands.

In this work, we report an unique way to form inorganic-organic hybrid coloured materials and thin films based on the [Ti₁₀O₁₂(cat)₈(py)₈] architecture. In these systems, the linkage of the titanium oxo-cluster and the organic polymer implies Ti-N coordination bonds. The preparation and the full characterization of the bulk hybrid material and the related thin films derived from the [Ti₁₀O₁₂(cat)₈(py)₈] oxo-cluster and poly(4-vinylpyridine) (P4VP) are described hereafter.

Synthesis and thermal characterization

The incorporation of metallic complexes within a polymeric matrix is known to modify the initial properties of the polymer as the viscosity or the glass transition. Complexation of P4VP with transition metal complexes such as copper,¹⁴ nickel,¹⁵ cadmium¹⁶ or ruthenium¹⁷ complexes has already been reported. Thus, we take advantage of the labile behaviour of the pyridine ligands in [Ti₁₀O₁₂(cat)₈(py)₈] to coordinate the P4VP polymer to this oxo-cluster. A chloroform solution of [Ti₁₀O₁₂(cat)₈(py)₈] is added dropwise to a chloroform solution of P4VP (average MW ~60,000 g.mol⁻¹) to generate hybrids named as P4VPTiXX% (where XX % represents the mass percentage calculated as the mass of [Ti₁₀O₁₂(cat)₈(py)₈] divided by the total mass of the solid mixture (P4VP and [Ti₁₀O₁₂(cat)₈(py)₈]). Importantly, we distinguish the name of the initial complex ([Ti₁₀O₁₂(cat)₈(py)₈]) with the oxo-cluster incorporated in the polymeric matrix labelled as Ti10. Only for hybrids where XX % are superior or equal to 10%, we notice the formation of an orange precipitate, which is isolated and dried under vacuum. For hybrids with lower mass percentage, the resulting solutions are concentrated

under vacuum to afford the desired hybrids. Following this procedure, P4VPTiXX% where XX = 1, 2, 3, 4, 5, 10, 13, 15, 17, 20, 33 and 50 are obtained. The isolated solids are analysed by thermogravimetric analysis (TGA) and the thermograms obtained for [Ti₁₀O₁₂(cat)₈(py)₈], P4VP, P4VPTi20%, P4VPTi33% and P4VPTi50% are shown in Figure 2a. These analyses are performed under air to determine the percentage of residual TiO₂ obtained at high temperature.

Figure 2: a) Thermograms obtained under air at 10°C.min⁻¹ for the analysis of P4VP, P4VPTi20%, P4VPTi33% and P4VPTi50%. b) Mass percentage of residual TiO₂ at 700°C (calculated and experimental).

Two weight losses are observed for the P4VP analysis. The first one ($\approx 6\%$) is attributed to the dehydration of the polymer at around 150°C whereas the most important loss (94%) at 420°C is linked to the degradation of the polymer. The thermograms of the three analysed hybrids, that are dissimilar to those of P4VP and [Ti₁₀O₁₂(cat)₈(py)₈] (see supporting information), show very close similarity. Interestingly, a pronounced weight loss assigned to the total or partial degradation of the P4VP backbone within the hybrids is observed at 340°C. The decrease of the thermal stability ($\Delta T \approx 80^\circ\text{C}$) of the organic polymeric chain within the hybrid material in comparison with the P4VP is proposed to arise from the coordination of the oxo-cluster to the P4VP pyridine rings. The Lewis acid character of titanium (IV) coordinated by the pyridines explains this decrease of thermal stability. Next, a second pronounced weight loss occurs originating from the degradation of the rest of the organic matter within these hybrids. An excellent match is found between calculated percentages of residual TiO₂ and those determined experimentally at 700°C for all the analysed hybrids (see the table in Fig. 2b). Overall, this thermal analysis proves that the synthetic procedure applied to generate

the hybrid materials is quantitative since all the titanium within the oxo-cluster is efficiently incorporated in polymeric matrix. In order to gain deeper information about the interaction existing between the oxo-cluster and the P4VP component, these hybrids are then studied by vibrational spectroscopy.

Infrared and Raman spectroscopy

The most relevant region to analyse by infrared spectroscopy (FT-IR) for these materials is between 1570 and 1675 cm^{-1} that is assigned to the stretching of the pyridine C-N bonds (Figure 3a). As it was already observed for the coordination of transition metals to pyridine rings,¹⁸ upon coordination to the cluster the C-N stretch band of P4VP is shifted towards higher energies ($\Delta\nu \approx 20 \text{ cm}^{-1}$). Clearly, for P4VPTi50% the C-N stretch band assigned to the coordinated pyridine C-N bonds is more intense in comparison with the one recorded for P4VPTi20%. Owing to its complexity, it is impossible to assign the Ti-N and Ti-O stretches in the region between 900 cm^{-1} and 400 cm^{-1} (see Figure 3b). However, a band at $\nu = 475 \text{ cm}^{-1}$ clearly increases when the amount of the oxo-cluster incorporated in the polymer increases. This band may be assigned to the Ti-N stretches according previous studies.¹⁹ Also, the infrared spectrum of P4VPTi20% is subtracted to the spectrum of P4VP to verify if the structural integrity of the oxo-cluster within the hybrid is identical to $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$. This subtracted spectrum resembles strongly to the infrared signature of $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$, however it appears also some differences in particular in the region around 1600 cm^{-1} (Figure 3b). This indicates that the main core of the oxo-cluster within the material remains identical as $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$, but also that chemical interactions occur between the polymer matrix and the cluster.

Figure 3: a) Infrared spectra of P4VP, P4VPTi20%, P4VPTi33% and P4VPTi50% (region between 1570 and 1675 cm⁻¹). The bands marked with the blue spot are attributed to the C-N stretch of the free pyridine rings, while those marked with the red spot are attributed to the C-N stretch of the coordinated pyridine rings. b) Infrared spectra of P4VP, P4VPTi20%, P4VPTi33% and P4VPTi50% (region between 900 and 400 cm⁻¹). c) Subtracted spectrum P4VPTi20% minus P4VP and superimposition with the infrared spectrum of [Ti₁₀O₁₂(cat)₈(py)₈].

In addition to the infra-red analysis, the Raman spectra are recorded for [Ti₁₀O₁₂(cat)₈(py)₈] and for the hybrid materials P4VPTiXX% (XX = 1, 3, 5, 10, 15, 20). The assignments of several vibrational bands of the [Ti₁₀O₁₂(cat)₈(py)₈] spectra were carried out (the spectrum is shown in the Supporting Information).

Figure 4: a) Superimposition of the P4VPTiXX% (XX = 1, 3, 5, 10, 15, 20) Raman spectra. b) Plot of the intensity of the band situated at 1490 cm^{-1} as a function of XX in P4VPTiXX% (XX = 1, 3, 5, 10, 15, 20). The baseline of all the spectra are corrected and brought to the same intensities by using the peak situated at 993 cm^{-1} which corresponds to the ν_8 vibration mode of P4VP.²⁰

According to the literature, the band at 1295 cm^{-1} corresponds to the C-O elongation while the elongations of the C-C bonds are centred between 1495 cm^{-1} and 1580 cm^{-1} .²¹ Importantly, the elongation of the Ti-O bonds is found at 633 cm^{-1} . This wavenumber is fully consistent with the Raman shift obtained for the Ti-O bonds in a related complex.²² The normalized Raman spectra extracted from the analysis of the hybrid materials are displayed in Figure 4a. Furthermore, the spectra display vibration bands found either in the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ spectra or P4VP spectra and new bands (see Supporting information). A linear increase of several bands correlated to the amount of titanium incorporated within the analysed material is observed. The plot of the relative intensity of the most intense band at 1490 cm^{-1} versus P4VPTiXX% (XX = 1, 3, 5, 10, 15, 20) (Figure 4b) proves their linear relationship. This confirms the conclusions settled by the TGA studies, which indicate that the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ cluster is quantitatively incorporated in the organic P4VP matrix in course of the synthesis of the hybrid material.

Importantly, for all the hybrid materials tested, when the Raman measurement is performed at various points of a given sample, very similar spectra in terms of energy and intensity are recorded. This reflects the good homogeneity of these solids.

¹³C CP-MAS Analysis

These solids were also studied through solid-state ¹³C CP-MAS NMR. The spectra of P4VP, [Ti₁₀O₁₂(cat)₈(py)₈] and P4VPTi20% are recorded and discussed in relation to the solid-state ¹³C NMR signature of a powder mixture composed of [Ti₁₀O₁₂(cat)₈(py)₈] and P4VP (20% w/w) (see Figure 5). The ¹³C CP-MAS NMR spectrum of [Ti₁₀O₁₂(cat)₈(py)₈] (Figure 5d) shows only signals in the aromatic region with three large regions and for the most deshielded carbons four sharp signals at $\delta = 159.07$ ppm, 156.30 ppm, 155.74 ppm, 153.26 ppm. These signals are undoubtedly attributed to the C-O resonances within this S₄-symmetry complex. An identical observation for the complex in solution had been made.¹⁰ Concerning the ¹³C CP-MAS NMR signature of P4VP (Figure 5c), in addition to the two very large signals in the aromatic region attributed to the resonance of the pyridine carbons, a large signal around 40 ppm is observed belonging to the alkyl carbons of the polymer. Very similar spectra to the one obtained for P4VP (Figure 5c) are recorded for the hybrid material P4VPTi20% (Figure 5b), and for the powder mixture composed of [Ti₁₀O₁₂(cat)₈(py)₈] and P4VP (20 % w/w) (Figure 5a).²³

Figure 5: ^{13}C CP-MAS NMR spectrum of a) a powder mixture composed of $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ and P4VP (20 % w/w); b) P4VPTi20%; c) P4VP and d) $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$.

Next, the P4VPTi20% spectrum is subtracted from the spectrum of P4VP (figure 6a) and the powder mixture spectrum is subtracted from the spectrum of P4VP (Figure 6b). Clearly, there is no relationship between these two calculated spectra. The trace displayed in Figure 6b appears almost identical to the spectrum of $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ (Figure 6c), indicating that the spectrum of the mixture (Figure 5a) solely results from the superimposition of the spectra of its two constituents, *i.e.* those of $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ and P4VP. Furthermore, it shows that the mixing of the two powders does not affect the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ molecular structure. In contrast the second trace exhibits no similarity with the Ti10 spectrum (Figure 6a). This approach proves that P4VPTi20% results from the assembly of the P4VP polymer with the cluster. Additionally, according to infrared analysis, there is no doubt that the $\text{Ti}_{10}\text{O}_{12}(\text{cat})_8$ core with the hybrid material remains the same as the one established by X-ray analysis for $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$. Consequently, this indirectly proves again that the formation of the hybrid material results only from the substitution of the labile pyridine ligands within $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ by the pyridine rings of the P4VP polymer.

Figure 6: Subtracted ^{13}C CP-MAS NMR spectra: a) P4VP minus P4VPTi20%, b) the P4VP minus the powder mixture of $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ and P4VP (20 % w/w). For comparison purposes, the NMR spectrum of $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ is shown in c).

Light absorption properties

Titanium(IV)-based hybrid materials absorbing light in the visible domain is a really active domain driven by potential unprecedented photoredox properties of these materials.¹³ As $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ is highly absorbing in the visible domain ($\lambda_{\text{max}} = 411 \text{ nm}$, $\varepsilon = 10800 \text{ L.mol}^{-1}.\text{cm}^{-1}$),¹⁰ we investigate the solid-state UV-Visible optical properties of P4VPTi20%, P4VPTi33% and P4VPTi50%. Figure 7 displays the Kubelka-Munk function²⁴ extracted from diffuse reflectance spectra recorded for these materials as well as for P4VP and $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ alone. The hybrid materials absorb light in the visible domain below 650 nm whereas P4VP only absorbs in the UV domain. The spectra of the hybrid materials closely resemble to the one recorded for $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$. The absorption edges are found to be 2.05 eV, 2.0 eV and 1.95 eV for P4VPTi20%, P4VPTi33% and P4VPTi50% respectively. Concerning solid-state emission properties, P4VP is a good light emitter (425 nm) upon excitation at 330 nm. For the hybrids polymers even for very low Ti loading *i.e.* P4VPTi1%, several excitation wavelengths are tested but no emission could be detected. Obviously, the

oxo-cluster acts as a fluorescence quencher. This result linked to the emission properties of the hybrid is unsurprising since the same observation was made for monomeric titanium-based complexes.²⁵

Figure 7: $F(R)$ recorded for P4VPTi20%, P4VPTi33%, P4VPTi50%, P4VP and $[Ti_{10}O_{12}(cat)_8(py)_8]$. $F(R)$ is the Kubelka-Munk function.²⁴

Surfaces functionalized by hybrid thin films

The conception of functional “smart” surfaces is a constant demand in modern material science. Also, it is well known that P4VP forms films on glass or quartz surfaces through hydrogen bonds, allowing the grafting on this surface of metal complexes or nanoparticles.²⁶ Therefore, we have examined the formation of hybrid films incorporating the cluster *via* the functionalization of a surface by the P4VP. The schematic principle of the functionalization of a surface is shown in Figure 8.

Figure 8: A schematic representation of the procedure for the two steps functionalization of a surface by a hybrid thin film based on the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ cluster. A first step concerns the formation of a P4VP thin film interacting with the surface through hydrogen bonds. In the next step, the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ complex is coordinated to the P4VP anchored onto the surface. It should be mentioned that the precise number of P4VP pyridines linked to the cluster could not be determined. Multilayers are generated starting from the surface functionalized with the hybrid film after multiple treatments with the P4VP solution followed by the cluster solution.

In a first attempt, a quartz surface (microscope slide) beforehand treated by a piranha solution is dipped into an ethanol P4VP solution (1% w/w). The UV-visible transmission spectrum of the functionalized quartz slides displays a band centred at $\lambda = 260$ nm attributed to the $\pi \rightarrow \pi^*$ transitions of the P4VP pyridines. The resulting quartz surface is then treated with a second solution containing the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ complex. Although no clear modification of the surface appearance is noticed to the naked eye, a large continuous weak band in the visible region below $\lambda = 550$ nm is detected by UV-visible spectroscopy (see Supporting Information). It is noteworthy that the same result is obtained when the cleaned glass surface is directly immersed in the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ solution without a pretreatment with P4VP.

Next, the thickness of these films is evaluated by ellipsometry. As this technique requires reflective surfaces, the films were prepared on silicon wafers with a native SiO_2 layer which were cleaned with a Piranha solution. The surface chemistry of the substrate is thus similar for silicon wafers as for quartz or glass slides, and one can assume that the thin film structure and thickness is identical on those substrates. As the complex refractive index of the hybrid material is not known, we impose a constant refractive index in the fitting procedure of the ellipsometry data, which leads to thickness values that are slightly different from the real ones, but which are close enough to monitor with a good precision the growth of the thin films on the substrate.²⁷ The measured values are compiled in table 1. The values given are an average of the thickness measured on >10 points on the surface, and the standard deviation (which is much higher than the instrumental standard deviation) thus represents the homogeneity of the thin film.

The wafer is first immersed in a P4VP ethanol solution with concentration of 0.01 % w/w, 0.1 % w/w or 1% w/w. The homogeneity of the films is correlated to the P4VP solution concentration. For the two higher concentrations *i.e.* 0.1 % w/w and 1% w/w, the thickness of the films are respectively found to be 0.8 ± 0.2 nm and 0.9 ± 0.2 nm (see Table 1). The measurements performed at different spots on the wafers show no significant variation of the film thickness, therefore we conclude that the thin films cover homogeneously the silicon wafer surfaces. At the 0.01 % w/w concentration, the results are not reproducible and important thickness differences are determined by varying the spots of measurement on the wafer. These wafers homogeneously covered by the P4VP polymer are next dipped in a CH_2Cl_2 solution of $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ ($c = 5.10^{-4}$ mol.L⁻¹). The thickness of the hybrid films are only few nanometers. As mentioned just before, we highlighted that $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ could be directly grafted on a glass surface without the presence of the P4VP film. However, the ellipsometry study clearly indicates an inhomogeneous deposition of the cluster with thickness ranging from 25.3 to 81.6 nm. This indicates undoubtedly the presence of aggregates rather than a homogeneous sediment at the surface. Also, this proves the indispensable beforehand functionalization of SiO_2 surfaces by P4VP to generate homogeneous films incorporating the cluster.

Film	Thickness (nm)
P4VP-1%	0.9 ± 0.2
P4VP-0.1%	0.8 ± 0.2
P4VP-1% - Ti_{10}	3.2 ± 0.3
P4VP-0.1% - Ti_{10}	4.0 ± 1
LbLx2	9.2 ± 1.0
LbLx3	16.1 ± 1.9

Table 1: Thickness of the hybrid films evaluated by ellipsometry.

Furthermore, the process can be repeated several times in order to build alternated layers of polymer and cluster on the surface by using a layer-by-layer approach.²⁸ Clearly, we observe that the thickness of the film increase with the number of layers adsorbed.

Overall, our approach allows to generate LbL hybrid films and to control the amount of oxo-cluster deposited on the surface. Also, the thickness of the films could be tuned by varying the number of layers.

Conclusion

We have reported an oxo-cluster-based hybrid material absorbing light in the visible domain. The straightforward synthesis permitting to access to this material requires only very accessible starting materials as $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8(\text{py})_8]$ and poly(4-vinylpyridine) and does not require particular care. The strategy allowing the formation of the hybrid material is unique for titanium oxo-cluster-based hybrid material, as it takes advantage of the labile behaviour of the pyridine ligands decorating the inorganic core of the complex. Importantly, the incorporation of the oxo-cluster in the organic polymeric matrix is quantitative and does not lead to any degradation or modification of the $[\text{Ti}_{10}\text{O}_{12}(\text{cat})_8]$ backbone. Furthermore, the resulting solid is homogenous as proven by Raman spectroscopy and ^{13}C CP MAS NMR investigations.

Finally, we have shown that SiO_2 surfaces can be functionalized following a Layer-by-Layer approach by alternate depositions of P4VP and of the titanium oxo-cluster. The thickness of the thin film can thus be finely tuned by varying the number of deposition steps, down to 4 nm for a monolayer. Current investigations are devoted to characterize the physical properties of these films and hybrid materials. In particular, efforts are actually focused on the study of the interactions of these materials with light.

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We warmly thank Dr. J. Raya for solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra measurement.

Experimental part

All reagents and products were purchased from Sigma Aldrich, Alfa Aesar or TCI and used as received. Solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer at ambient temperature with a magic angle spinning rate of 12.0 kHz. Elemental analysis was performed at the Service Commun d'Analyses, University of Strasbourg (France). The elemental analyses were performed on a Flash 2000 instrument (Thermo Fisher Scientific) for C, H and N elements. All Raman spectra were recorded with an InVia Renishaw spectrum equipped with a CCD (charge coupled device) as a detector. All experiments were carried at a resolution of 1 cm^{-1} with an exposure time of 10 s and an excitation wavelength of 514 nm provided by an Argon STELLAR laser. Infrared (IR) spectra were recorded with a Perkin-Elmer FT-IR

spectrometer. Solid-state measurements were performed on a Perkin-Elmer LS 55 spectrometer. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Pyris 6 TGA analyzer.

For the thickness measurements a spectroscopic ellipsometer was used (SE800, SENTECH). The film was modeled as a single layer with a constant complex refractive index $n = n_0 + i n_1$, with $n_0=1.465$ and $n_1=36$. The thickness of the cleaned SiO₂ substrate was fixed at 2.4 nm.

Synthesis of P4VPTiXX% hybrid material

To a stirred solution of P4VP (60 mg) in CHCl₃ (5 mL) was added dropwise under agitation the appropriate amount of [Ti₁₀O₁₂(cat)₈(py)₈] dissolved in CHCl₃ (3 mL). The precipitate was filtered, washed several times with CHCl₃ and then dried under vacuum during one night before analysis. When no precipitate was formed, the solvent was removed by evaporation under vacuum and the residue was dried before analysis.

Functionalization and grafting of the [Ti₁₀O₁₂(cat)₈(py)₈] complex on a silicon wafer

The functionalization of the different substrates was performed by dip-coating. Prior to functionalization, the substrate was cleaned with a Piranha solution for 15 min, rinsed with distilled water and dried under argon.

Poly(4-vinylpyridine) deposition: the clean substrate was immersed in a solution of P4VP (0.01%, 0.1% or 1%) in ethanol. After 2 h, the substrate was washed several times with ethanol and dried under argon.

[Ti₁₀O₁₂(cat)₈(py)₈] grafting: the titanium complex was grafted on the previously functionalized P4VP surfaces by placing the substrate in a 5.10⁻⁴ M solution of [Ti₁₀O₁₂(cat)₈(py)₈] in chloroform. After 2 hours, the surface was rinsed several times with chloroform and dried under argon.

Multilayers were generated from a silicon wafer firstly dipped in a P4VP solution in ethanol (1 %) and next immersed in a 5.10⁻⁴ M solution of [Ti₁₀O₁₂(cat)₈(py)₈] in dichloromethane. After 2 hours, the surface was rinsed with ethanol and dried under argon. Next, this functionalized wafer is immersed in a P4VP solution in dichloromethane (1 %) followed by a treatment with the [Ti₁₀O₁₂(cat)₈(py)₈] solution.

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