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# Supramolecular design for polymer/titanium oxo-cluster hybrids: An open door to new organic-inorganic dynamers

Fabien Périneau,<sup>a,b</sup> Sandrine Pensac,<sup>a</sup> Clément Sanchez,<sup>b</sup> Costantino Creton,<sup>c</sup> Laurence Rozes<sup>b</sup> and Laurent Bouteiller<sup>\*a</sup>

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Hybrid materials from organic polymers and inorganic solids often possess enhanced properties compared to their isolated constituents, if intimate mixing is achieved. We report a new approach combining inorganic nanobuilding blocks and  
10 supramolecular interactions, exemplified by a titanium oxo cluster bearing four hydrogen bond acceptors and a telechelic PDMS with two hydrogen bond donors. With these simple components, we demonstrate that well chosen supramolecular interactions can be used to obtain new hybrid dynamers  
15 having the intrinsic properties of the inorganic component (such as photochromism) and improved mechanical properties, due to the supramolecular cross-linking of the polymer chains.

Hybrid materials combining organic polymers and inorganic  
20 solids are remarkably versatile systems, which often display enhanced properties compared to their isolated components.<sup>1</sup> In order to further improve their properties, the key is to control their nanostructure. Therefore, a nanobuilding block (NBB) methodology was recently developed to reach such  
25 nanostructured hybrids.<sup>2</sup> This approach consists in functionalizing molecularly defined inorganic clusters with organic moieties able to initiate a polymerization, to copolymerize with an organic monomer, or to be grafted on a  
30 polymer matrix may limit phase separation and afford materials with a homogeneous distribution at the 10-nanometer scale.

In order to push the NBB concept further and to introduce some flexibility in the design, we propose to investigate the  
35 feasibility of a supramolecular approach. Indeed, supramolecular chemistry has been successfully used in polymer science,<sup>3</sup> where the reversibility brought by weak (but controlled) interactions can improve processing, can yield self-healing materials,<sup>4</sup> and can afford pathways to  
40 thermodynamically stable materials. Moreover, the potential of coupling inorganic components by well defined supramolecular synthons has been well demonstrated in the case of metallic nanoparticles,<sup>5</sup> and polyoxometallates.<sup>6</sup> Of course, supramolecular chemistry has also been widely used  
45 to enhance interactions between the components of organic polymers/inorganic hybrid materials.<sup>7</sup> However, these studies were restricted to relatively coarse inorganic components or to unspecific supramolecular interactions. Our aim is therefore to investigate the potential of functionalizing well-defined  
50 inorganic clusters with highly specific supramolecular synthons in order to form new polymer/inorganic NBB hybrid materials: hybrid dynamers.

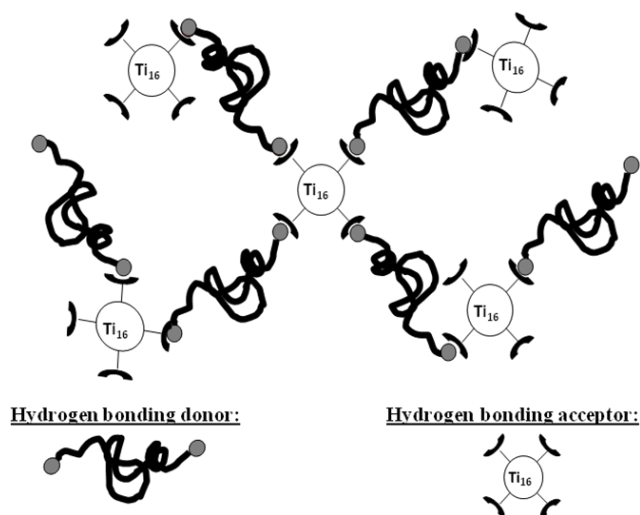
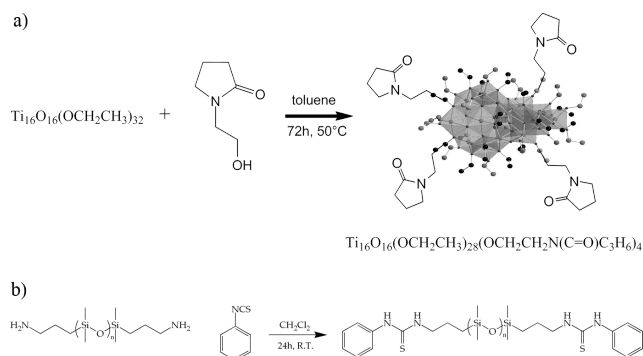


Fig. 1 Schematic representation of the hybrid supramolecular network composed of titanium oxo-clusters and PDMS.  
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The design of our hybrid supramolecular network is schematized in Fig. 1. It consists in the association of two complementary elementary units via hydrogen bonding. In order to avoid phase separation, each unit must be capable of  
60 hetero-association with its counterpart while preventing any homo-association. We chose the following system: a structurally well-defined titanium oxo-cluster NBB bearing hydrogen bond acceptors and a telechelic polydimethylsiloxane with hydrogen bond donor chain ends.  
65 The functional titanium oxo-cluster was synthesized from the known  $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$  (labelled “ $\text{Ti}_{16}$ ”). The structure of  $\text{Ti}_{16}$  oxo-cluster is based on an inorganic oxo core composed of 16  $\text{TiO}_6$  octahedra surrounded by 32 ethoxy ligands. Half of these ligands bridge two titanium atoms while the other 16 ligands,  
70 the terminal ligands, are linked to only one titanium atom. These terminal ethoxy groups can be selectively exchanged by transalcoholysis or transesterification reactions in organic solvents.<sup>8</sup> The post-modification of  $\text{Ti}_{16}$  leads to functional NBBs which can be further employed in the build up of  
75 hybrid materials.<sup>9</sup> In our case, the terminal ethoxy groups of  $\text{Ti}_{16}$  were partially exchanged by 1-(2-hydroxyethyl)-2-pyrrolidone in toluene at 50°C for 72h (see Fig. 2a).  $^1\text{H}$  NMR analyses show that 4 of the 32 ethoxy groups of the  $\text{Ti}_{16}$  were exchanged by pyrrolidone ligands (Fig. S1).<sup>10</sup> Additionally,  
80  $^{17}\text{O}$  NMR analyses were performed to assess the integrity of the oxo core of  $\text{Ti}_{16}$ -pyrrolidone. Here, the  $\text{Ti}_{16}$  precursor was prepared from conventional  $\text{Ti}(\text{OR})_4$  alkoxide and  $^{17}\text{O}$  enriched water. Consequently, the organic ligands keep their low natural abundance and the NMR spectrum only displays

resonances relative to the  $^{17}\text{O}$  of the oxometallic core. The resonances observed on the spectrum (Fig. S3) can be attributed as follows:  $\mu_2\text{-O}$  (753 ppm),  $\mu_3\text{-O}$  (567 ppm, 564 ppm, 562 ppm, 558 ppm) and  $\mu_4\text{-O}$  (385 ppm) and prove that the core of the cluster is not affected by the exchange of the peripheral ligands.

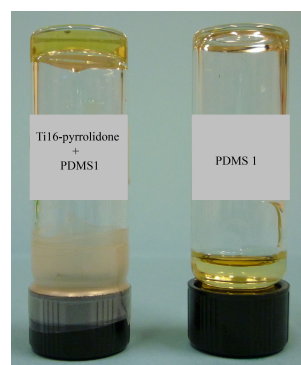


**Fig. 2** Synthesis of  $\text{Ti}_{16}$ -pyrrolidone (a) and thiourea terminated PDMS (PDMS1 and PDMS2) (b).

The carbonyl functions of the pyrrolidone ligands are simple, yet efficient hydrogen bond acceptors. The complementary unit to be placed on the polymer therefore needs to bear a strong hydrogen bond donor. This group must fulfill two other requirements: (i) it should not be able to exchange with the cluster ligands; and (ii) it should be a weak hydrogen bond acceptor, to avoid competing with the desired hetero-association. The thiourea synthon was chosen because it is known to be a strong hydrogen bond donor together with a weak hydrogen bond acceptor (Fig. S6).<sup>11</sup> Two samples of thiourea terminated polydimethylsiloxanes were prepared from telechelic aminopropyl terminated polydimethylsiloxanes of different molar masses by reaction with phenyl isothiocyanate (Fig. 2b).  $^1\text{H}$  NMR analyses confirms the modification of the aminopropyl terminated PDMS as proved by the presence at 7.65 ppm and at 6.11 ppm of singlets corresponding to the N-H protons (Fig. S4). This is correlated with the disappearance at 1 ppm of the  $\text{NH}_2$  protons (Fig. S4). The molar mass of the polymers was determined by  $^1\text{H}$  NMR and SEC to be about 8000 g/mol and 35000 g/mol for PDMS1 and PDMS2, respectively.  $^{29}\text{Si}$  NMR showed evidence of only two kinds of silicon atoms in the PDMS, that is, terminal silicon atoms and silicon atoms from the backbone of the macromolecular chain (Fig. S5).

The hybrid supramolecular network was prepared by mixing equimolar amounts of  $\text{Ti}_{16}$ -pyrrolidone and the thiourea-modified PDMS1 in  $\text{CH}_2\text{Cl}_2$ . Upon evaporation of the solvent, the pale yellow liquid became a transparent gel as shown in Fig. 3. This qualitative observation reveals two important features. First, the dispersion of the cluster in the polymer matrix is homogeneous, as proved by the following blank experiment: mixing in the same conditions the non-functional cluster  $\text{Ti}_{16}$  and a non-functional PDMS (trimethyl-terminated) yields a precipitate.<sup>12</sup> Second, the gelation of the sample is characteristic of multi-topic interactions between the constituents.<sup>13</sup> The gel formation probably results from the

association, via hydrogen bonding, of the N-H groups of the PDMS with the  $\text{C}=\text{O}$  groups of the cluster, eventually leading to a three dimensional hybrid network. Indeed, hydrogen bonding is demonstrated by FTIR analysis in the region of the N-H functions of thiourea groups, as shown in Fig. 4. The spectrum of thiourea terminated PDMS1 in  $\text{CHCl}_3$  shows two bands located at 3410 and 3393  $\text{cm}^{-1}$ , which can be attributed to free N-H groups adjacent to the aliphatic and aromatic groups, respectively.<sup>14</sup> The absence of a band at 3200-3300  $\text{cm}^{-1}$  confirms the lack of hydrogen bond in dilute solution. However, in bulk, the spectrum of the same polymer shows an additional large band at 3250  $\text{cm}^{-1}$ , which corresponds to hydrogen bonded N-H groups (with the thiocarbonyl and/or the oxygen atoms of the siloxane chains as acceptors). The bulk spectrum of the hybrid supramolecular network HSN1 also shows a strong band at 3300  $\text{cm}^{-1}$ . Moreover, the disappearance of the band at 3400  $\text{cm}^{-1}$  proves that hydrogen bonding is enhanced when  $\text{Ti}_{16}$ -pyrrolidone is introduced in the polymer. Therefore,  $\text{Ti}_{16}$ -pyrrolidone is equipped with stronger hydrogen bond acceptors than the polymer.

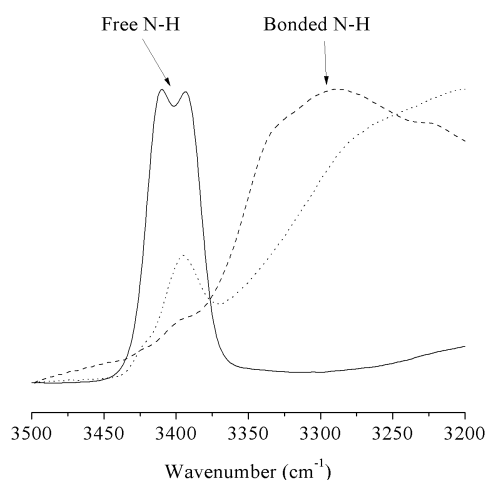


**Fig. 3** Qualitative comparison between the hybrid supramolecular network HSN1 (left) and the thiourea-modified PDMS1 (right).

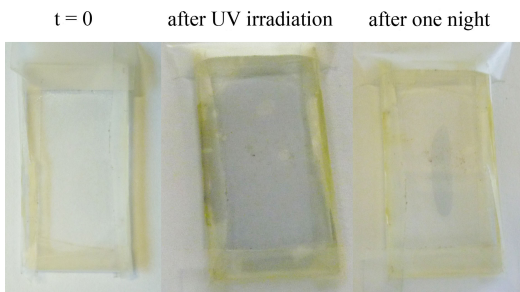
Similarly, adding equimolar amounts of  $\text{Ti}_{16}$ -pyrrolidone to the thiourea-modified PDMS2 increased significantly the viscosity of the material. The fact that a very viscous oil is obtained with the higher molar mass polymer (HSN2), whereas a gel is obtained for HSN1 is probably due to the lower concentration of hydrogen bonding groups in HSN2, and possibly to a larger proportion of supramolecular macrocycles.

Therefore, introducing hydrogen bonding groups on both cluster and polymer matrix seems to be a reliable way to homogeneously disperse the cluster into the polymer matrix and therefore impart the material with the intrinsic properties of the cluster. For example, titanium oxo-based hybrids are known to present a photochromic behavior when exposed to UV light.<sup>15</sup> Indeed, a stable darkening of samples has been assigned to an efficient trapping of photo-excited electrons as small polarons ( $\text{Ti}^{3+}$ ) due to sample irradiation by UV photons and the concomitant rapid scavenging of the photo-excited holes by the organic domains. Thus, a hybrid supramolecular network HSN1 sample was placed between two quartz plates and exposed to UV light. It went from pale yellow to grey-blue in a few minutes, and after irradiation, the color faded in the presence of air in a few hours (Fig. 5). This experiment

could be repeated several times, showing the reversibility of the photochromic phenomenon.



**Fig. 4** FTIR spectra showing N-H absorption bands of thiourea-modified PDMS1 in  $\text{CHCl}_3$  (straight line) or in bulk (dotted line), and hybrid supramolecular network HSN1 in bulk (dashed line).



**Fig. 5** Photochromic behaviour of the hybrid supramolecular network HSN1. Left: initial sample; middle: sample right after UV irradiation; right: sample one night after UV irradiation.

We have reported the synthesis of a titanium oxo cluster bearing four hydrogen bond acceptor groups and telechelic polydimethylsiloxanes with two hydrogen bond donors. With these particularly simple components, we demonstrate that well chosen supramolecular interactions can be used to obtain homogeneous hybrid materials having the intrinsic properties of the inorganic component (such as photochromism) and improved mechanical properties, due to the supramolecular cross-linking of the polymer chains. The ability of the NBBs to be post-modified and functionalized in a controlled manner allows the easy tuning of the reversible crosslinking density and leads to hybrid dynamers with tunable mechanical properties and specific properties inherent to the nature of the metallic oxo-core.

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## Notes and references

<sup>a</sup> UPMC Univ Paris 06, UMR 7610, Chimie des Polymères, F-75005 Paris, France; CNRS, UMR 7610, Chimie des Polymères, F-75005 Paris, France. E-mail: laurent.bouteiller@upmc.fr

- <sup>b</sup> UPMC Univ Paris 06, UMR 7574, Chimie de la Matière Condensée de Paris, F-75005, Paris, France; CNRS, UMR 7574, Collège de France, Chimie de la Matière Condensée de Paris, F-75005, Paris, France
- <sup>c</sup> Physico-chimie des Polymères et des Milieux Dispersés, UMR 7615, UPMC-CNRS-ESPCI, 10 rue Vauquelin 75231 Paris cedex 05, France
- † Electronic Supplementary Information (ESI) available: Experimental section and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{29}\text{Si}$  NMR spectra. See DOI: 10.1039/b000000x/
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