Supporting Information

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

Fabien Pépineau, Sandrine Pensec, Clément Sanchez, Costantino Creton, Laurence Rozes and Laurent Bouteiller

Experimental Section

Materials
Methanol (VWR, 99%), phenyl isothiocyanate (Aldrich, 98%), and aminopropyl terminated polydimethylsiloxanes (ABCR; 0.6-0.7% amine, viscosity 100-120 cSt., ~5000 g mol\(^{-1}\) and 0.08-0.09% amine, viscosity 1800-2000 cSt., ~30000 g mol\(^{-1}\)) were used as received. 1-(2-hydroxyethyl)-2-pyrrolidone (Aldrich, 98%), chloroform (Acros, 99%), dichloromethane (Acros, 99%), dimethylsulfoxide (VWR, 99%), pentane (Acros, 99%), tetrahydrofuran (VWR, 99%), and toluene (VWR, 99%) were distilled on the proper desiccant and then stored on molecular sieves. Ti\(_{16}\)O\(_{16}\)(OEt)\(_{32}\) and \(^{17}\)O enriched Ti\(_{16}\)O\(_{16}\)(OEt)\(_{32}\) were synthesized as described elsewhere.\(^1\)

Instrumentation
\(^1\)H liquid NMR spectra were recorded in CD\(_2\)Cl\(_2\) or CDCl\(_3\) on a Bruker Avance II 300 spectrometer at 300 MHz. \(^{17}\)O liquid NMR spectra were recorded in CDCl\(_3\) on a Bruker Avance 300 spectrometer at 40.7 MHz. FTIR spectra were recorded in transmission, at room temperature on a Nicolet iS10 Thermo Scientific spectrometer. For bulk analyses, the product was pressed between two KBr disks. Analyses in solution were performed in CHCl\(_3\) using a KBr cell of 1 mm path length. SEC measurements were performed in THF at a flow rate of 1 mL/min using a Waters HPLC 515 pump, a Viscotek VE 5200 automatic injector, two columns thermostated at 40°C (PSS SDV, linear M, 8 mm x 300 mm, bead diameter: 5 \(\mu\)m, separation range: 400-10\(^3\) Da), a Viscotek 3580 differential refractive index and a Waters UV 484 detectors. Calculations were made using the Omnisec software. The calibration curve was based on polystyrene standards from Polymer Laboratories. Heats of association were measured using a MicroCal VP-ITC titration microcalorimeter. The experimental conditions have been described previously.\(^2\)

Post-functionalization of Ti\(_{16}\)O\(_{16}\)(OEt)\(_{32}\) (Ti\(_{16}\)-pyrrolidone)

In a glovebox, 1 g (0.4 mmol) of Ti\(_{16}\)O\(_{16}\)(OEt)\(_{32}\) was dissolved in 10 mL of toluene to which an excess (26 mmol, 3.36 g) of 1-(2-hydroxyethyl)-2-pyrrolidone was added. This mixture was then placed at 50 °C for 72 h after which the volatile fraction was evaporated to get a white paste. This paste was dissolved in a minimum amount of THF and the cluster was precipitated into DMSO, then again dissolved in a minimum amount of THF and finally precipitated into pentane to get 340 mg (~30 %) of a white powder.

\(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)) : see Figure S1. \(^{13}\)C NMR (75.4 MHz, CD\(_2\)Cl\(_2\)) : see Figure S2. \(^{17}\)O NMR (40.7 MHz, CDCl\(_3\)) : see Figure S3.

Thiourea terminated polydimethylsiloxane PDMS1

Under nitrogen atmosphere, 0.5 mL (4.2 mmol) of phenyl isothiocyanate were slowly dropped into a mixture of 10 g (2 mmol) of aminopropyl terminated polydimethylsiloxane
(molar mass \sim 5000 \text{ g mol}^{-1}) in 2 \text{ mL} of dichloromethane. This mixture was stirred at room temperature for 24 h, after which the solvent was evaporated. The polymer was recovered as a yellow oil after precipitation into methanol.

\textsuperscript{1}H NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \delta): 7.65 (s, 2H, Ar-NH), 7.46-7.22 (m, 10H, ArH), 6.11 (s, 2H, NH-CH\textsubscript{2}), 3.57 (dt, 4H, NH-CH\textsubscript{2}), 1.59 (m, 4H, C-CH\textsubscript{2}-C), 0.52 (m, 4H, Si-CH\textsubscript{2}), 0.08 (s, 580H, CH\textsubscript{3}), M\textsubscript{n}(RMN) = 7600 \text{ g mol}^{-1}; \textsuperscript{29}Si NMR (59.63 MHz, CDCl\textsubscript{3}, \delta): 7.25 (Si-CH\textsubscript{2}), -22.38 (O-Si-O); SEC (PS standards): M\textsubscript{n} = 12600 \text{ g mol}^{-1}, M\textsubscript{w} = 18850 \text{ g mol}^{-1}, M\textsubscript{w}/M\textsubscript{n} = 1.5; molecular weights were derived from the UV absorption signal (254 nm) due to the aromatic chain ends and calculated as previously described.\textsuperscript{3}

**Thiourea terminated polydimethylsiloxane PDMS2**

The same procedure as for PDMS1 was used with aminopropyl terminated polydimethylsiloxane of molar mass \sim 30000 \text{ g mol}^{-1}.

\textsuperscript{1}H NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \delta): 7.32 (s, 2H, Ar-NH), 7.28-7.22 (m, 10H, ArH), 6.11 (s, 2H, NH-CH\textsubscript{2}), 3.58 (dt, 4H, NH-CH\textsubscript{2}), 1.61 (m, 4H, C-CH\textsubscript{2}-C), 0.52 (m, 4H, Si-CH\textsubscript{2}), 0.08 (s, 3150H, CH\textsubscript{3}), M\textsubscript{n}(RMN) = 39000 \text{ g mol}^{-1}; \textsuperscript{29}Si NMR (59.63 MHz, CDCl\textsubscript{3}, \delta): 7.25 (Si-CH\textsubscript{2}), -22.37 (O-Si-O); SEC (PS standards): M\textsubscript{n} = 34050 \text{ g mol}^{-1}, M\textsubscript{w} = 58450 \text{ g mol}^{-1}, M\textsubscript{w}/M\textsubscript{n} = 1.7.

**Hybrid supramolecular network HSN1**

0.05 g (1.78 \times 10^{-5} \text{ mol}) of Ti\textsubscript{16}-pyrrolidone and 0.27 g (3.6 \times 10^{-5} \text{ mol}) of PDMS1 were solubilized in 0.1 mL of dichloromethane. The solvent was then gently evaporated to get a clear yellow gel.

**Hybrid supramolecular network HSN2**

0.078 g (2.78 \times 10^{-5} \text{ mol}) of Ti\textsubscript{16}-pyrrolidone and 1.94 g (5.0 \times 10^{-5} \text{ mol}) of PDMS2 were solubilized in 1 mL of dichloromethane. The solvent was then gently evaporated to get a clear yellow gel.
Figure S1. $^1$H NMR spectra of 1-(2-hydroxyethyl)-2-pyrrolidone (CD$_2$Cl$_2$, top), Ti$_{16}$-pyrrolidone (CD$_2$Cl$_2$, middle) and Ti$_{16}$ (C$_6$D$_6$, bottom).
Figure S2. $^{13}$C NMR spectra of 1-(2-hydroxyethyl)-2-pyrrolidone (C$_6$D$_6$, top), Ti$_{16}$-pyrrolidone (CD$_2$Cl$_2$, middle) and Ti$_{16}$ (C$_6$D$_6$, bottom).
Figure S3. $^{17}$O NMR spectrum of Ti$_{16}$-pyrrolidone in CDCl$_3$.

Figure S4. $^1$H NMR spectra of aminopropyl terminated PDMS (CDCl$_3$, top), and thiourea-modified PDMS1 (CD$_2$Cl$_2$, bottom).
Figure S5. $^{29}$Si NMR spectra in CDCl$_3$ of thiourea terminated PDMS1 (a) and PDMS2 (b).
The following model compounds were considered to investigate the complementarity of the pyrrolidone and thiourea moieties:

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\begin{align*}
\text{1-ethyl-2-pyrrolidone (PY)} \\
\text{1-octyl-N'-phenylthiourea (TU)}
\end{align*}
\]

\[\text{Figure S6. Isothermal Titration Calorimetry (ITC) experiment showing the heat exchange during the addition 3\textmu L aliquots of a 20mM PY solution in heptane into a 1.5mM TU solution in heptane (black curve) and the blank experiment corresponding to the dilution of the same PY solution into heptane (green curve). Heat flow versus time (a) and enthalogram obtained after integration of the heat flow curves (b).}
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The strong exothermic signal obtained during the addition of PY to TU shows that the heteroassociation (TU:PY) is stronger than the self-association (TU:TU and PY:PY). It was not possible to extract more quantitative information because of the complexity of the equilibria involved.
References

