Supplementary Material (ESI) for Chemical Communications

Supplementary information

Self-Assembled Titanium-Based Hybrids with Cyclopentadienyl-Titanium Network Bonding

Sana Ahmad, Bernard Jousseaume, Laurent Servant, Thierry Toupance and Cécile Zakri

Content page

Preparation of materials **1d**-**5d**

In a dry Schlenk tube under nitrogen, a mixture of water (184 µL, 10.2 mmol) and THF (5 mL) was added slowly to the stirring a solution of 4,4'-biphenylenebis(2,3,4,5-tetramethyl-cyclopentadienyl)di(trimethyltitanium) **(2b)** (1.0 g, 1.7 mmol) in THF (40 mL) via a syringe. The reaction mixture was allowed to stir for 10 min and then was left untouched to gelify. The resulting yellow gel was aged for 3 weeks. It was then washed with THF, diethyl ether and petroleum ether after centrifugation to remove the oligomers. The resulting powder was dried overnight under vacuum and the required xerogel (0.77 g, 80% yield) was obtained as a yellow powder.

The same experimental conditions were used for the preparation of other hybrids **1d**, **3d**, **4d**, **5d**.

Compound	Infrared (cm^{-1})	Raman (cm^{-1})	Assignment
$Cp^*Ti(OMe)_3$			
		405.9	Cp* ring tilt[1]
		571.8 (broad peak)	Cp* ring breath[2]
		594.9	υ(Ti-O)[3]
$PhMe_4CpTiMe_3$			
		394.9	$PhMe_4Cp$ ring tilt
		509.4	υ(Ti-Me)
		578.7	$PhMe_4Cp$ ring breath
$(PhMe_4CpTiMe_2O_{0.5})_2$			
		408.9	$PhMe_4Cp$ ring tilt
		468.4	υ(Ti-O)
		509.6	υ(Ti-Me)
		577.6 (weak)	$PhMe_4Cp$ ring breath
$(PhMe_4CpTiO_{1.5})_4$			
	305.6	312.8	$υ_s(PhMe_4Cp\text{-}Ti)$
		351.3 (weak)	$υ_{as}(PhMe_4Cp\text{-}Ti)$
	410.8	408.9	$PhMe_4Cp$ ring tilt
	444.5	468.4	υ(Ti-O)[4]
	506.2	506.7	$υ_{as}$(Ti-O)[5]
	540.9		$υ_{as}$(Ti-O)
	593.0	580.5	$PhMe_4Cp$ ring breath

Table 1: Infrared and Raman spectra of the reference compounds

1 (a) Samuel,E.; Ferner, R.; Bigorgne, M. *Inorg. Chem.* **1973**, *12*, 881 (b) Jiang, S.; Zhang, P.; Wang, Y. *Chem. Res. Chin. Univ.* **2000**, *16*, 341

2 (a) Malisch, W.; Jehle, H.; Möller, S.; Thum, G.; Reising, J.; Gbureck, A.; Nagel, V.; Fickert, C.; Kiefer, W.; Nieger, W. *Eur. J. Inorg. Chem*. **1999**, 1597 (b) Malisch, W.; Lankat, R.; Schmitzer, S.; Pikl, R.; Posset, U.; Kiefe, W. *Organometallics* **1995**, *14*, 5622 (c) Bencze, E.; Lokshin, B. V.; Mink, J.; Herrmann, W. A.; Kühn, F. E. *J. Organomet. Chem.* **2001**, *627*, 55

3 Maslowsky, E. Jr. *Vibrational Spectra of Organometallic Compounds* **1977**, Wiley-Interscience, New York

4 Bobrova, A. M.; Zhigun, I. G.; Bragina, M. I.; Fotiev, A. A. *J. Appl. Spectrosc.* **1968**, *8*, 96

5 Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Finnie, K. S.; Bartlett, J. R.; Woolfrey, J. L. *Inorg. Chem*. **1998**, *37*, 2741

Hybrid material	Infrared (cm^{-1})	Raman (cm^{-1})	Assignment
1d			
	302.8		υ_s(R_5Cp-Ti)
	410.8	409.2	R_5Cp ring tilt[1]
	464.8	473.2	υ(Ti-O)[4]
	549.6		υ_{as}(Ti-O)[5]
	608.4		R_5Cp ring breath[2]
2d			
	302.7		υ_s(R_5Cp-Ti)
	409.8	409.2	R_5Cp ring tilt
	466.7	470.3	υ(Ti-O)
	551.5		υ_{as}(Ti-O)
	594.9		R_5Cp ring breath
3d			
	302.8		υ_s(R_5Cp-Ti)
	409.8	407.6	R_5Cp ring tilt
	464.8	473.2	υ(Ti-O)
	562.2		υ_{as}(Ti-O)
	597.8		R_5Cp ring breath

Table 2: Infrared and Raman spectra of the hybrid materials

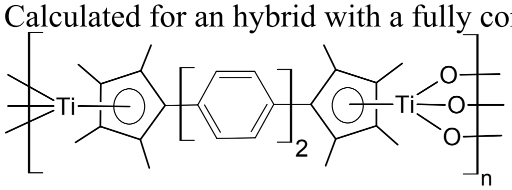
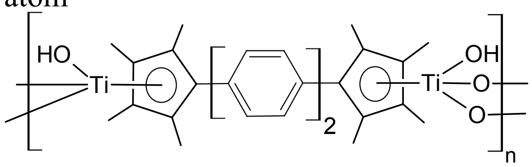
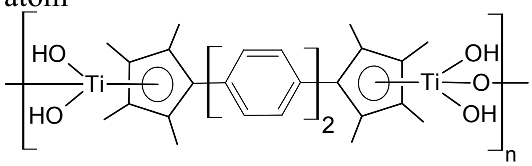
Molecular formula	Ti	C	H	O
Found	16.1	64.4	6.0	13.5
Calculated for an hybrid with a fully condensed inorganic network 	17.9	67.2	6.0	9.0
Calculated for an hybrid with one hydroxyl group on each titanium atom 	17.3	65.0	6.1	11.6
Calculated for an hybrid with two hydroxyl groups on each titanium atom 	16.8	62.2	6.3	14.0

Table 3. Microanalysis data for **2d**.

Xerogel	%C		%H		%O		%Ti	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp. *	Cal.	Exp.
1d	58.1	60.6	6.5	6.5	16.1	15.7	19.4	17.2
2d	62.9	64.4	6.3	6.0	14.0	13.5	16.8	16.1
3d	66.7	66.6	6.2	6.1	12.3	13.6	14.8	13.7
4d	53.4	53.2	5.5	5.2	13.7	-	16.4	16.2
5d	62.1	63.0	8.0	8.0	16.1	16.2	13.8	12.8

* Obtained by difference

Table 4: Elemental analyses

Hybrid		H/Ti	C/Ti	O/Ti	Spacer/Ti
1d	Theoretical	16	12	2.5	0.5
	Actual	18.0	14.1	2.7	0.56
2d	Theoretical	18.0	15.0	2.5	0.5
	Actual	17.9	16.0	2.5	0.52
3d	Theoretical	20.0	18.0	2.5	0.5
	Actual	21.6	19.5	3.0	0.54
4d	Theoretical	16	13	2.5	0.5
	Actual	15.3	13.1	-	0.51
5d	Theoretical	28	18	3.5	0.5
	Actual	30.2	19.7	3.8	0.54

Table 5: Theoretical and actual molar ratios of elements

Xerogel	Residual mass(%)	Molecular weight (g/mol)	Theoretical molecular weight (g/mol)
1d	32.2	497	496
2d	27.2	588	572
3d	24.6	650	648
4d	27.1	590	584
5d	29.8	536	488

Table 6: Residual masses after TGA of the hybrids

To discard the hypothesis that the excess of oxygen could come from a molecule of water coordinated on each titanium atom, we relied on the fact that no coordination water was reported in monocyclopentadienyltitanium oxides obtained under hydrolytic conditions,[6] and that no significant mass loss was observed by TGA before 250°C

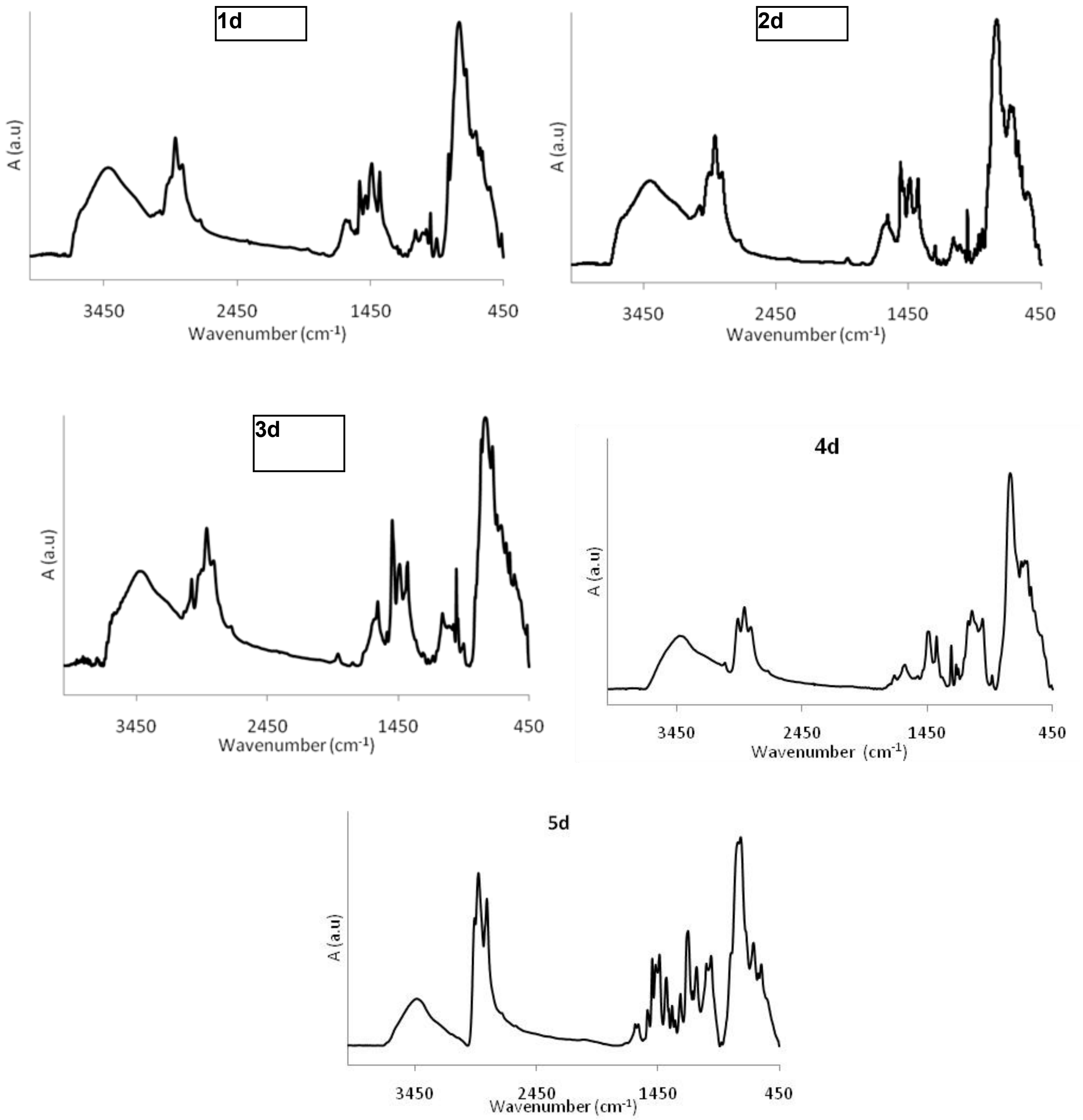


Figure 1: Infrared spectra of hybrids **1**-5**d**

6 M. Björgvinsson, S. Halldorsson, I. Arnason, J. Magull and D. Fenske, *J. Organomet. Chem.,* 1997, **544**, 207.