Supplementary Material (ESI) for Chemical Communications

Supporting Information

A Doubly Folded Spacer in a Self-Assembled Hybrid Material

Hicham Elhamzaoui,' Bernard Jousseaume, Thierry Toupance, Cécile Zakri, Monique Biesemans, Rudolph Willem and Hassan Allouchi,*

Laboratoire de Chimie Organique et Organométallique, UMR 5802, Université Bordeaux 1, 351 cours de la Libération, 33405 Talence, France, Centre de Recherche Paul Pascal,UPR 8641, avenue A. Schweitzer, 33600 Pessac, France High Resolution NMR Centre (HNMR), Department of Polymer Science and Structural Chemistry, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050 Brussels (Belgium) and Laboratoire de Chimie Physique PIMIR, EA 2098, Faculté de Pharmacie, 31 Avenue Monge, 37200 Tours, France

Experimental

1: tin tetrachloride (0.9 ml, 7.65 mmol) was added to a solution of 4,4'-bis(5-(tricychlohexylstannyl)pentyloxymethyl)biphenyl (3 g, 2.82 mmol) in dry toluene (100 ml) under a nitrogen atmosphere in a Schlenk tube. After stirring for 72h at room temperature, the liquid phase was removed and white precipitated obtained was taken up in dry acetonitrile. The solution was extracted with pentane (5x50ml) and evaporated. The obtained solid was dissolved in dry THF (100 ml). The solution was subsequently evaporated to give pure **1.** Crystals suitable for X-ray analysis were grown from a toluene solution.

Yield: 2.09 g, 96%; m.p. 159°C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ = 1.76 (m, 4H), 2.19 (m, 4H, $^{1}J_{Sn-H}$ = 314 Hz), 2.58 (m, 4H, $^{2}J_{Sn-H}$ = 92 Hz), 3.78 (t, 4H) 4.78 (s, 4H), 7.44 (d, 4H), 7.63 (d, 4H); ^{13}C NMR (62.9 MHz, $C_2D_2Cl_4$): 24.7 ($^{2}J_{Sn-C}$ = 75 Hz), 29.9 ($^{3}J_{Sn-C}$ = 34 Hz), 38.9 ($^{1}J_{Sn-C}$ = 801 Hz), 72, 72.6, 127.1, 128.7, 134.7, 140.3; ^{119}Sn NMR (74.6 MHz, $C_2D_2Cl_4$, 25°C): –142.2; ^{117}Sn CPMAS NMR (89.13 MHz): δ = -163; elemental analysis calc (%) for $C_{22}H_{28}Cl_6O_2Sn_2$: C 34.12, H 3.64, Cl 27.46, O 4.13, Sn 30.65; found: C 33.72, H 3.63, Cl 27.14, O 4.57, Sn 30.97.

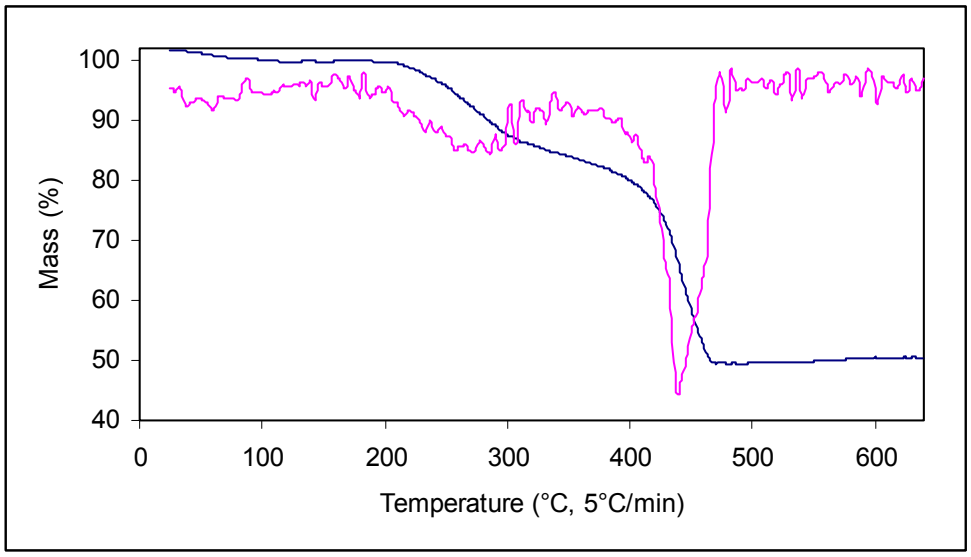
2: a 2.5M solution of BuLi (8 ml, 20 mmol) was added to a solution of propyne (5ml, 87.5 mmol) in dry toluene (50 ml) in a 500-ml 3-necked flask under nitrogen at – 78°C. After stirring for 15 min, a solution of **1** (2 g, 2.58 mmol) in 200 ml of dry toluene was added at -78°C. After stirring for 15 h at room temperature, the suspension was filtered over dry $MgSO_4$, the solvent was evaporated under vacuum to give **2** as an oil.

Yield: 1.29 g, 63%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, 4H, $^{2}J_{Sn-H}$ = 77 Hz), 1.76 (m, 8H), 1.90 (s, 18H, $^{4}J_{Sn-H}$ = 15 Hz), 3.53 (m, 4H) 4.54 (s, 4H), 7.41 (d, 4H), 7.57 (d, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): 5.3 ($^{3}J_{Sn-C}$ = 15 Hz), 14.9 ($^{1}J_{Sn-C}$ = 635 Hz), 22.4 ($^{3}J_{Sn-C}$ = 29 Hz), 33.0 ($^{2}J_{Sn-H}$ = 87 Hz), 69.7, 72.6, 76.8($^{1}J_{Sn-C}$ = 806 Hz), 107.8 ($^{2}J_{Sn-C}$ = 168 Hz), 127.1, 128.2, 137.8, 140.3; ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 25°C): δ = –252.1; elemental analysis calc (%) for $C_{40}H_{46}O_2Sn_2$: C 60.34, H 5.82, O 4.02, Sn 29.81; found: C 60.14, H 6.01, O 4.30, Sn 28.76.

3: a solution of HCl and water (0.137 ml of 1 N HCl in 1.35 ml H_2O, 76.4 mmol) in THF (3.39 g) was added to a solution of **2** (0.76 g, 1 mmol) in dry THF (6 g) in a Schlenk tube under nitrogen. The mixture gelified after 6 days at room temperature and was aged for 28 days. The solid was then filtered, washed with THF (3x50 ml) and dried under vacuum at 120°C for 3 h.

Yield: 0.40 g, 65%; elemental analysis calc (%) for $C_{22}H_{28}O_5Sn_2$: C 43.33, H 4.63, O 13.12, Sn 38.92; found: C 44.31, H 4.95, O 13.51, Sn 37.22.

Thermogravimetric analysis of 3



The mass of residual SnO_2 at 640°C corresponds to a molecular mass of 608 to be compared to a theoretical mass of 609.85 ($C_{22}H_{28}O_5Sn_2$) for **6.**

Solid state CPMAS spectrum of 1 (blue line: spectrum; red line simulated spectrum)**.**