

**Supporting Information**

**Modular construction and hierarchical gelation of organooxotin  
nanoclusters derived from simple building blocks**

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## Synthesis of compounds 1-5b

A mixture of the appropriate carboxylic acid (**1-5a**, 1 equiv.) and *n*BuSn(O)OH (1 equiv.) in benzene was refluxed for 12 h using a Dean-Stark trap. After cooling, the solution was filtered and evaporated to dryness to afford the corresponding hexameric organostannoxane derivatives (**1-5b**) in almost quantitative yields. The drum-like structure of these compounds made up of a prismatic Sn<sub>6</sub>O<sub>6</sub> core was confirmed by their <sup>119</sup>Sn NMR spectrum recorded in C<sub>6</sub>D<sub>6</sub> which shows a single resonance at *ca.* -480-484 ppm (typical examples are depicted in Fig. S1). This chemical shift is characteristic of a drum-shaped structure with six equivalent Sn atoms coordinated by 5 oxygens and one carbon.<sup>1</sup>

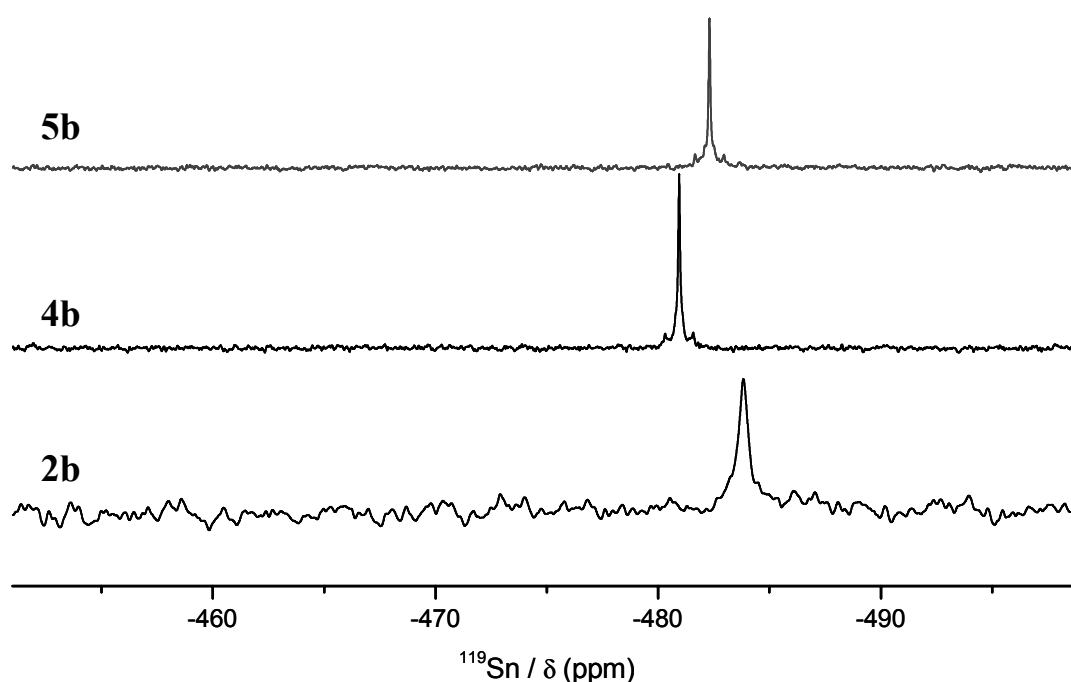


Fig. S1. <sup>119</sup>Sn NMR spectra (C<sub>6</sub>D<sub>6</sub>) of **2b**, **4b** and **5b**.

## Experimental section

**General.** All reagents were used as purchased from commercial sources without further purification. Compounds **1a** and **1b** were prepared according to previously reported procedures.<sup>2</sup> All reactions were performed in standard glassware. Evaporation was done

using water aspirator and drying *in vacuo* at  $10^{-2}$  Torr. Column chromatography: Merck silica gel 60, 40-63  $\mu\text{m}$  (230-400 mesh). TLC: Precoated glass sheets with silica gel 60 F<sub>254</sub> (Merck), visualization by UV light. Melting points were determined on a Electrothermal Digital Melting Point apparatus and are uncorrected. UV/Vis spectra ( $\lambda_{\text{max}}$  in nm ( $\epsilon$ )) were measured on a Hitachi U-3000 spectrophotometer. IR spectra ( $\text{cm}^{-1}$ ) were determined on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AV 500 spectrometer equipped with a 5 mm triple resonance inverse probe with dedicated  $^{31}\text{P}$  Channel operating at 500.33 and 186.57 MHz for  $^1\text{H}$  and  $^{119}\text{Sn}$ , respectively. Chemical shifts are referenced to tetramethylsilane and tetramethyltin for  $^1\text{H}$  and  $^{119}\text{Sn}$ , respectively.  $^{119}\text{Sn}$  NMR spectra were recorded with inverse gated  $^1\text{H}$  decoupling. Elemental analyses were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France).

### Compound 1b

A mixture of *n*-butyl stannonic acid (620 mg, 2.96 mmol) and **1a** (2.00 g, 2.96 mmol) in benzene (200 mL) was refluxed for 12 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **1b** (2.56 g, 99 %) as a colourless glassy product.<sup>3</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta$  = 0.95 (t,  $J$  = 7 Hz, 18 H), 1.11 (m, 54 H), 1.48 (m, 360 H), 1.74 (m, 12 H), 2.01 (m, 12 H), 3.47 (t,  $J$  = 7 Hz, 12 H), 3.79 (m, 24 H), 4.35 (m, 12 H), 7.87 (s, 12 H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta$  = 15.0, 15.1, 23.7, 23.8, 23.9, 30.4, 30.45, 30.7, 30.8, 30.85, 30.9, 30.95, 31.1, 31.2, 31.3, 31.35, 31.4, 31.45, 31.6, 32.9, 33.1, 31.15, 63.3, 69.6, 74.1, 109.9, 127.7, 145.4, 154.3, 169.8 ppm; Anal. calcd. for  $\text{C}_{282}\text{H}_{516}\text{O}_{36}\text{Sn}_6$ : C 65.93, H 10.01; found: C 64.89, H 9.97.

### Compound 2b

A mixture of *n*-butyl stannonic acid (300 mg, 1.44 mmol) and **2a** (1.09 g, 1.44 mmol) in benzene (200 mL) was refluxed for 12 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **2b** (1.28 g, 99%) as a colourless glassy product.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta$  = 0.96 (m, 54 H), 1.08 (t,  $J$  = 7 Hz, 18 H), 1.39 (m, 360 H), 1.63 (m, 36 H), 1.76 (m, 36 H), 1.89 (m, 12 H), 2.03 (m, 12 H), 2.33 (m, 12 H), 3.95 (m, 24 H), 4.18 (m, 12 H), 7.72 (s, 12 H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta$  = 14.0, 14.1, 22.8, 22.8, 22.9, 26.4, 26.4, 26.6, 27.7, 28.2, 29.4, 29.5, 29.6, 29.65, 29.7, 29.75, 29.8, 29.85, 29.9, 30.3, 30.7, 32.0, 32.0, 32.1, 32.2, 68.5,

68.9, 70.8, 73.1, 109.2, 127.9, 143.1, 152.9, 173.6 ppm;  $^{119}\text{Sn}$  NMR (186.5 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta = 483.8$  ppm; Anal. calcd. for  $\text{C}_{318}\text{H}_{588}\text{O}_{36}\text{Sn}_6$ : C 67.01, H 10.40; found: C 66.66, H 10.13.

### Compound 3b

A mixture of *n*-butyl stannonic acid (344 mg, 1.65 mmol) and **3a** (300 mg, 1.65 mmol) in benzene (100 mL) was refluxed for 12 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **3b** (614 mg, 99%) as a colourless glassy product.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta = 0.95$  (t,  $^3J = 7$  Hz, 18H), 1.61 (m, 12H), 1.92 (m, 12H), 2.20 (m, 12H), 3.37 (s, 36H), 6.59 (t,  $^4J = 2$  Hz, 6H), 7.64 (d,  $^4J = 2$  Hz, 12H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta = 14.7, 27.4, 28.6, 28.8, 55.5, 106.3, 108.9, 136.7, 161.7, 174.4$  ppm;  $^{119}\text{Sn}$  (186.5 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta = -482.3$  ppm; Anal. calcd. for  $\text{C}_{78}\text{H}_{108}\text{O}_{30}\text{Sn}_6$ : C 41.86, H 4.86; found: C 41.86, H 4.76.

### Compound 4b

A mixture of *n*-butyl stannonic acid (695 mg, 3.33 mmol) and **4a** (300 mg, 3.33 mmol) in benzene (100 mL) was refluxed for 12 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **4b** (872 mg, 99%) as a colourless glassy product.  $^1\text{H}$  NMR (500.3 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta = 0.93$  (t,  $J = 7$  Hz, 18 H), 1.46 (m, 12 H), 1.78 (m, 12 H), 2.06 (m, 12 H), 3.14 (s, 18 H), 3.76 (d,  $J = 17$  Hz, 6 H), 3.86 (d,  $J = 16$  Hz, 6 H) ppm;  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta = 14.4, 27.5, 28.3, 28.6, 59.3, 71.8, 180.2$  ppm;  $^{119}\text{Sn}$  NMR (186.5 MHz,  $\text{C}_6\text{D}_6$ , 293 K):  $\delta = 480.9$  ppm; Anal. calcd. for  $\text{C}_{42}\text{H}_{84}\text{O}_{24}\text{Sn}_6$ : C 29.93, H 5.02; found: C 29.84, H 4.83.

### Compound 5b

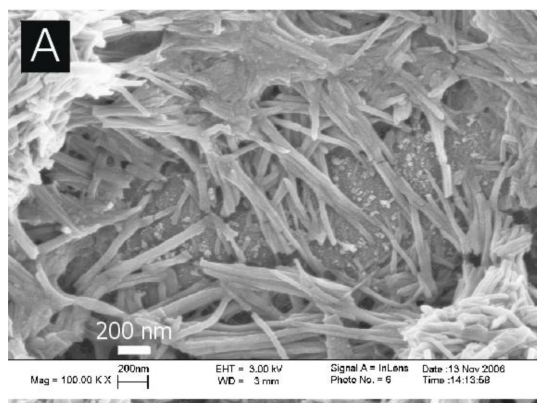
A mixture of *n*-butyl stannonic acid (1.71 g, 8.19 mmol) and **5a** (1.00 g, 8.19 mmol) in benzene (200 mL) was refluxed for 12 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **5b** (2.35 g, 84 %) as a colourless solid (m.p.  $> 280^\circ\text{C}$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 293 K):  $\delta = 0.95$  (t,  $J = 7$  Hz, 18 H), 1.50 (m, 24 H), 1.91 (m, 12 H), 7.42 (t,  $J = 7$  Hz, 12 H), 7.52 (t,  $J = 7$  Hz, 6 H), 8.11 (d,  $J = 7$  Hz, 12 H) ppm;  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{CD}_2\text{Cl}_2$ , 293 K):  $\delta = 13.4, 26.3, 27.1, 27.5, 128.0, 130.0, 132.5, 133.2, 172.8$  ppm;  $^{119}\text{Sn}$  NMR (186.5 MHz,  $\text{CD}_2\text{Cl}_2$ ,

293 K):  $\delta = 482.3$  ppm; Anal. calcd. for  $C_{66}H_{84}O_{18}Sn_{6.1}/2C_6H_6$ : C 43.24, H 4.58 ; found: C 43.16, H 4.29.

### General Comments

It is worth noting that the  $^{119}\text{Sn}$  NMR spectra of the starting stannonic acid and of partially reacted compounds, including dimeric intermediates, are significantly different from the one observed for the final compounds.<sup>1</sup> All of our reactions were monitored by  $^{119}\text{Sn}$  NMR spectroscopy and several signals were observed as long as the self-assembly process was not finished. Chandrasekhar and co-workers have reported several X-ray crystal structures of hexameric organostannoxane derivatives obtained from substituted benzoic acids.<sup>4</sup> The  $^{119}\text{Sn}$  NMR spectra of all these derivatives show a single peak around  $-480$  ppm.

### SEM Image of Gelator **5b**



FEGSEM image of gelator **5b** as xerogel from bromonaphthalene.

### References

1. V. Chandrasekhar, C. G. Schmid, S. D. Burton, J. M. Holmes, R. O. Day and R. R. Holmes, *Inorg. Chem.* 1987, **26**, 1050.
2. J.-F. Nierengarten, J.-F. Eckert, Y. Rio, M. P. Carreon, J.-L. Gallani and D. Guillon, *J. Am. Chem. Soc.* 2001, **123**, 9743.
3. Characterization of compound **1b** by  $^{119}\text{Sn}$  NMR was attempted. However due to gelation during the experiment, the spectrum was always broad and poorly resolved.

4. V. Chandrasekhar, K. Gopal, S. Nagendran, A. Steiner, S. Zacchini, *Cryst. Growth Des.* **2006**, *6*, 267.