

Supporting Information

Self-assembly of fullerene-rich nanostructures with a stannoxane core.

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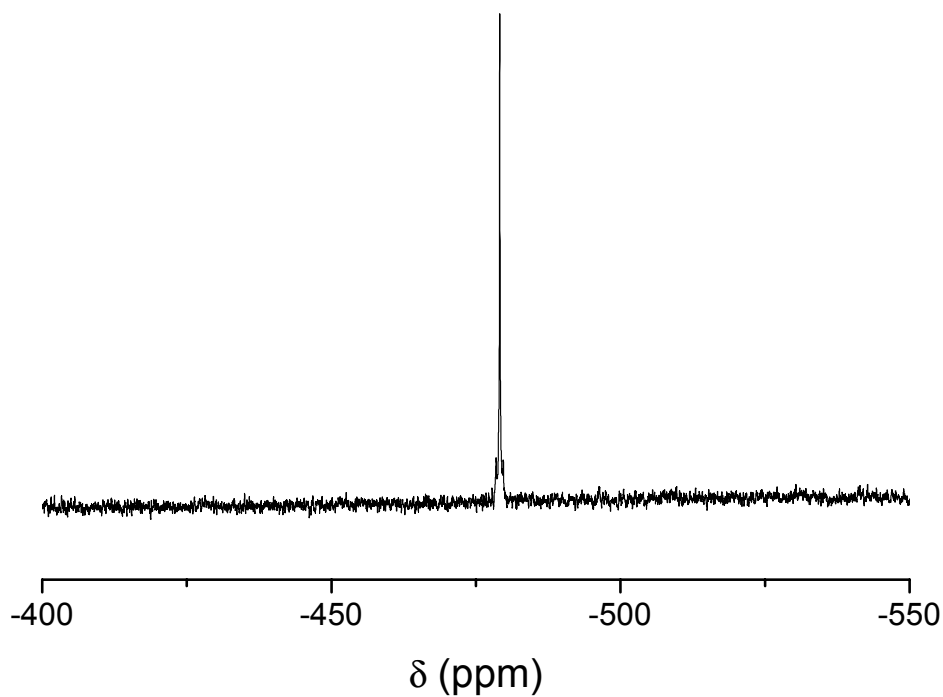


Fig. S1. ^{119}Sn NMR spectrum of **2a**.

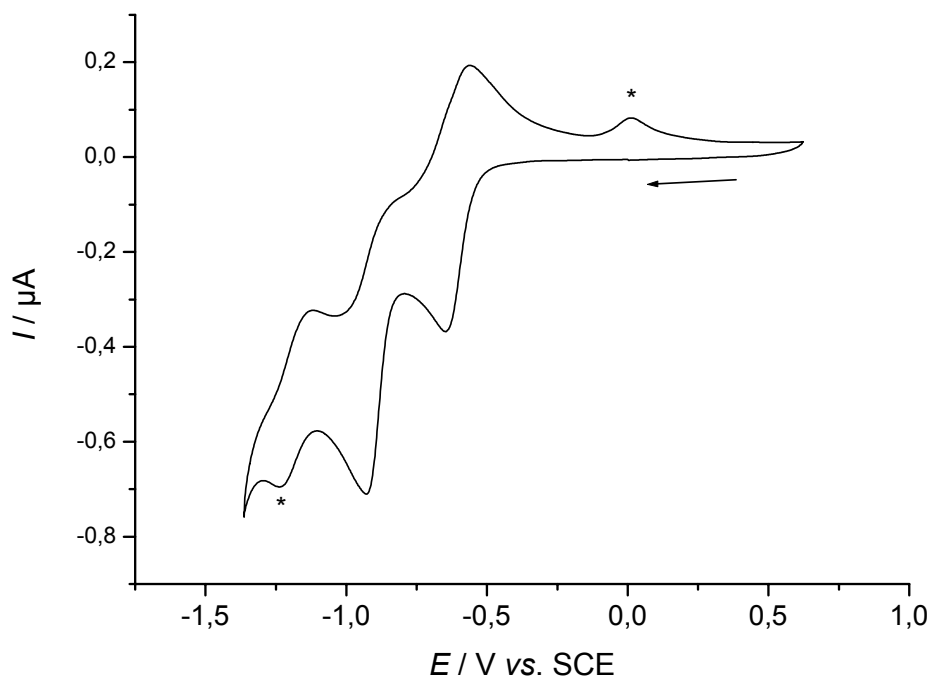


Fig. S2. Cyclic voltammogram of **2b** on a Pt electrode at $v = 0.1 \text{ Vs}^{-1}$ in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M } ^n\text{Bu}_4\text{NBF}_4$ (the second electron transfer in *cis*-2 derivatives is followed by a chemical reaction leading to an undefined electrogenerated species that gives rise to the peak indicated with a star).

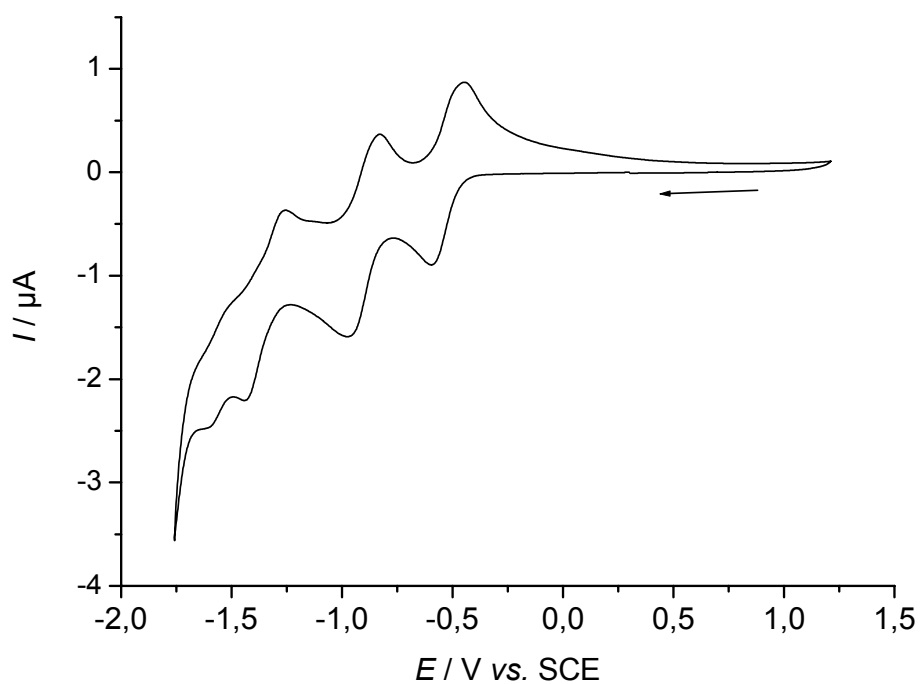
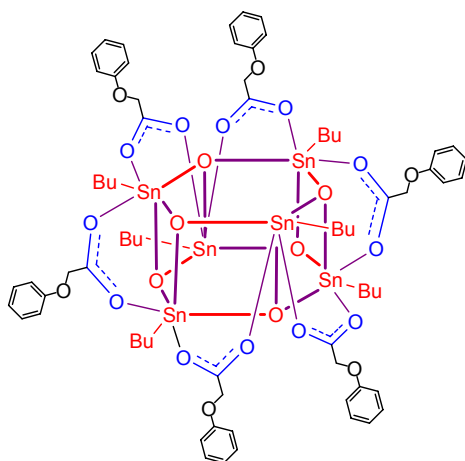


Fig. S3. Cyclic voltammogram of **2c** on a Pt electrode at $v = 0.1 \text{ Vs}^{-1}$ in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M } n\text{Bu}_4\text{NBF}_4$.

Experimental section

General. All reagents were used as purchased from commercial sources without further purification. Compounds **1b**, **1c**, and **1d** were prepared according to previously reported procedures.¹ 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 μm (230-400 mesh). TLC: Precoated glass sheets with silica gel 60 F₂₅₄ (Merck), visualization by UV light. Melting points were determined on a Electrothermal Digital Melting Point apparatus and are uncorrected. UV/Vis spectra (λ_{max} in nm (ϵ)) were measured on a Hitachi U-3000 spectrophotometer. IR spectra (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 ³¹P Channel operating at 500.33 and 186.57 MHz for ¹H and ¹¹⁹Sn, respectively. Chemical shifts are referenced to tetramethylsilane and tetramethyltin for ¹H and ¹¹⁹Sn, respectively. ¹¹⁹Sn NMR spectra were recorded with inverse gated ¹H decoupling. Elemental analysis were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France).

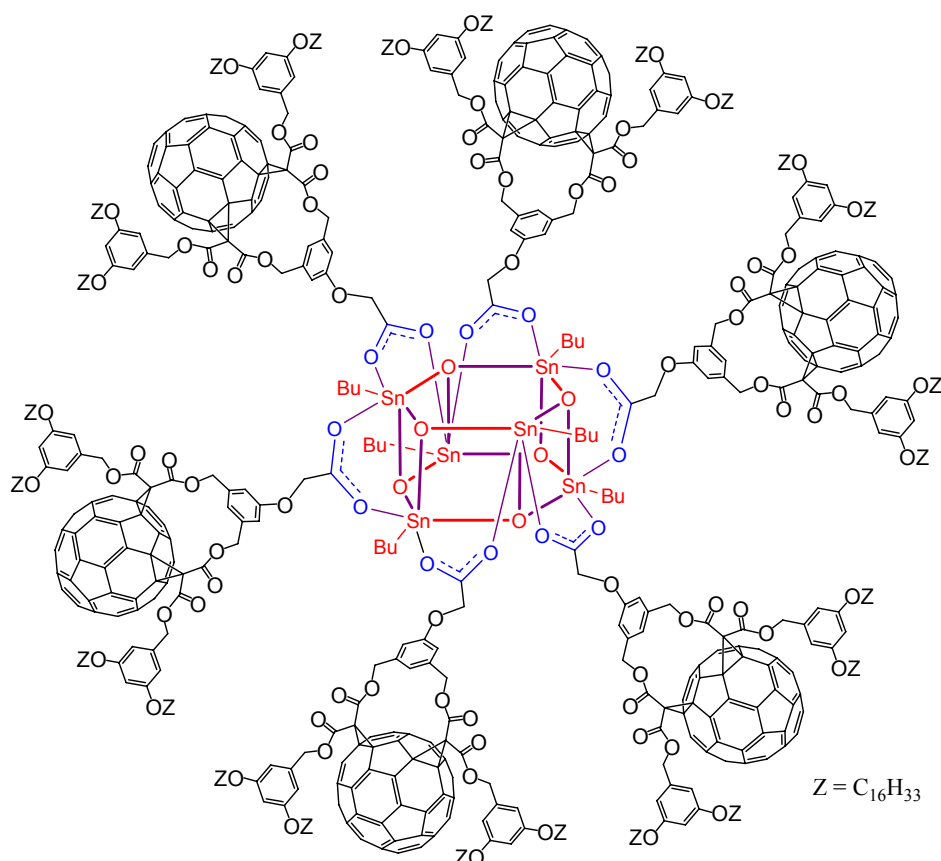
Compound 2a.



A mixture of *n*-butyl stannonic acid (686 mg, 3.29 mmol) and **1a** (500 mg, 3.29 mmol) in benzene (200 mL) was refluxed for 12h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **2a**

(1.09 g, 97 %) as a colourless solid. M.p. > 280°C; IR (KBr): $\nu = 1615, 1569$ (COO), 1221 (C-O) cm^{-1} ; ^1H NMR (500.3 MHz, CDCl_3 , 20°C): $\delta = 0.85$ (t, $J = 7$ Hz, 18 H), 1.16 (m, 12 H), 1.25 (m, 12 H), 1.48 (m, 12 H), 4.37 (d, $J = 16$ Hz, 6 H), 4.42 (d, $J = 16$ Hz, 6 H), 6.87 (m, 12 H), 6.93 (t, $J = 7$ Hz, 6 H), 7.24 (m, 12 H) ppm; ^{13}C NMR (125.8 MHz, CDCl_3 , 20°C): $\delta = 13.6, 26.2, 26.8, 27.2, 66.8, 115.0, 121.3, 129.3, 158.3, 177.1$ ppm; ^{119}Sn NMR (186.5 MHz, CDCl_3 , 20°C): $\delta = -479.1$ ppm; Anal. calcd. for $\text{C}_{72}\text{H}_{96}\text{O}_{24}\text{Sn}_6$: C 41.86, H 4.69; found: C 42.08, H 4.55.

Compound 2b.

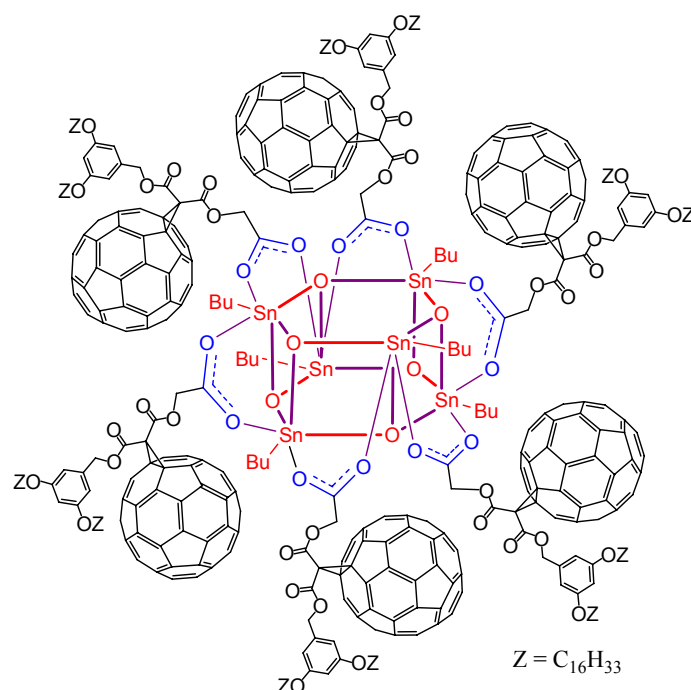


A mixture of *n*-butyl stannonic acid (20 mg, 96 μmol) and **1b** (215 mg, 96 μmol) in benzene (50 mL) was refluxed for 12h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **2b** (210 mg, 97%) as a dark orange glassy product. IR (KBr): $\nu = 1747$ (C=O) cm^{-1} ; UV/Vis [CH_2Cl_2 , nm ($\text{L mol}^{-1} \text{cm}^{-1}$)]: $\lambda_{\text{max}} = 260$ (663000), 324 (201000), 438 (23900); ^1H NMR (500.3 MHz, C_6D_6 , 20°C): $\delta = 1.00$ (m, 90 H), 1.17 (m, 24 H), 1.32-1.55 (m, 636 H), 1.75 (m, 48 H), 3.78

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(m, 48 H), 4.36 (m, 12 H), 4.96 (br m, 12 H), 5.18-5.45 (br m, 24 H), 5.76 (br m, 12 H), 6.55-6.70 (br m, 48 H), 7.31 (br s, 6 H); ^{13}C NMR (125.8 MHz, CDCl_3 , 20°C): δ 14.1, 14.3, 23.0, 26.6, 27.2, 27.6, 29.8, 30.2, 32.2, 52.1, 64.2, 66.9, 68.0, 69.3, 71.8, 71.9, 102.4, 107.8, 108.0, 108.1, 137.2, 138.2, 141.0, 142.3, 143.1, 143.9, 144.7, 145.3, 146.0, 161.0, 162.8, 163.2, 175.5 ppm; ^{119}Sn NMR (186.5 MHz, CDCl_3 , 20°C): δ = -478.8 ppm; Anal. calcd for $\text{C}_{948}\text{H}_{960}\text{O}_{96}\text{Sn}_6$: C 76.25, H 4.88; found: C 76.55, H 4.66.

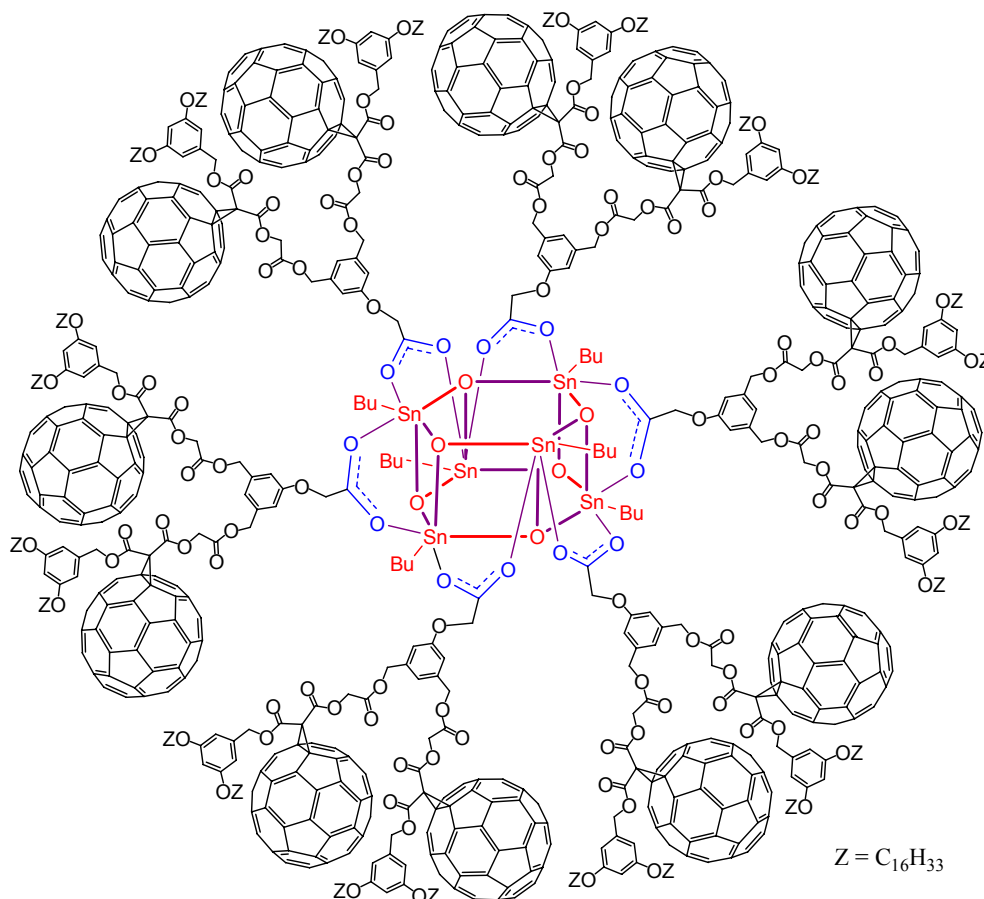
Compound 2c.



A mixture of *n*-butyl stannonic acid (29 mg, 138 μmol) and **1c** (200 mg, 138 μmol) in benzene (60 mL) was refluxed for 12h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **2c** (224 mg, 99%) as a dark red glassy product. IR (KBr): 1749 (C=O) cm^{-1} ; UV/Vis [CH_2Cl_2 , nm (L mol^{-1} cm^{-1}): λ_{max} = 258 (690000), 325 (250700), 426 (29200), 690 (1000); ^1H NMR (500.3 MHz, C_6D_6 , 20°C): δ = 1.05 (m, 54 H), 1.26-1.68 (m, 348 H), 1.85 (m, 24 H), 3.90 (m, 24 H), 5.10-5.30 (br m, 12 H), 5.62-5.78 (br m, 12 H), 6.70 (s, 6 H), 6.90 (s, 12 H); ^{13}C NMR (125.8 MHz, CDCl_3 , 20°C): δ 14.1, 14.3, 23.0, 26.6, 27.2, 27.6, 29.8, 30.1, 32.2, 52.1, 64.2,

64.4, 68.0, 69.3, 71.9, 102.4, 107.8, 137.2, 138.2, 141.0, 142.3, 143.1, 143.9, 144.7, 144.9, 145.3, 146.0, 161.0, 162.8, 163.1, 175.5 ppm; ^{119}Sn NMR (186.5 MHz, CDCl_3 , 20°C): $\delta = -476.4$ ppm; Anal. calcd for $\text{C}_{648}\text{H}_{492}\text{O}_{54}\text{Sn}_6$: C 78.98, H 5.03; found: C 78.59, H 5.05.

Compound 2d.



A mixture of *n*-butyl stannonic acid (27 mg, 130 μmol) and **1d** (400 mg, 130 μmol) in benzene (60 mL) was refluxed for 12h. The water formed in the reaction was removed by using a Dean-Stark apparatus. The solution was filtered and evaporated to dryness to yield **2d** (420 mg, 99%) as a dark red glassy product. IR (KBr): 1749 (C=O) cm^{-1} ; UV/Vis [CH_2Cl_2 , nm ($\text{L mol}^{-1} \text{cm}^{-1}$): $\lambda_{\text{max}} = 258$ (1598000), 325 (538400), 426 (55700), 690 (2450); ^1H NMR (500.3 MHz, C_6D_6 , 20°C): $\delta = 1.05$ (m, 90 H), 1.30-1.64 (m, 660 H), 1.85 (m, 48 H), 3.90 (m, 48 H), 4.45 (br s, 12 H), 4.90-5.40 (br m, 48 H), 5.65 (br s, 24 H), 6.68 (s, 12 H), 6.88 (s, 24 H), 7.00-7.22 (br m, 18 H) ppm; ^{13}C NMR (125.8 MHz, CDCl_3 , 20°C): δ 14.1, 14.3, 23.0, 26.6, 27.0, 27.5, 29.8, 30.2, 31.2, 32.2, 52.0, 62.7, 66.9, 68.1, 69.2, 69.3, 71.7, 102.3, 107.6,

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114.5, 120.7, 137.2, 138.7, 140.3, 140.9, 142.0, 142.2, 142.3, 143.1, 143.9, 144.7, 145.3, 158.6, 160.9, 163.1, 166.5, 175.5 ppm; ^{119}Sn NMR (186.5 MHz, CDCl_3 , 20°C): $\delta = -478.0$ ppm; Anal. calcd for $\text{C}_{1332}\text{H}_{984}\text{O}_{120}\text{Sn}_6$: C 80.88, H 3.57; found: C 80.69, H 3.85.

X-ray crystal structure of 2a

Crystals suitable for X-ray crystal-structure analysis were obtained by slow diffusion of Et_2O into a C_6H_6 solution of **2a**. Data were collected at 180K on a Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures were solved by direct methods using SIR92,² and refined by means of least-squares procedures on F using the programs of the PC version of CRYSTALS.³ Atomic scattering factors were taken from the International tables for X-ray Crystallography.⁴ One butyl group was disordered on two sites and refined isotropically. All other non-hydrogens atoms were anisotropically refined. Hydrogen atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. All hydrogen atoms were refined using a riding model. Drawing of molecule was performed with CAMERON⁵ with 30% probability displacement ellipsoids for non-hydrogen atoms.

References

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