Supporting information

Tin Sulfide and Selenide Clusters soluble in Organic Solvents with the Core Structures of Sn_4S_6 and Sn_4Se_6

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Content:

2.Supplementary of Mass Spectrometry and NMR Spectroscopy Data

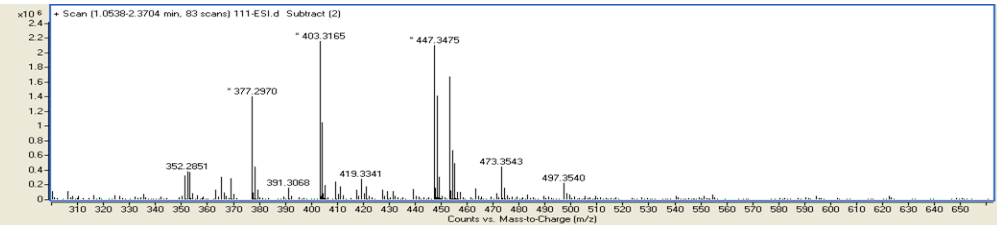


Figure S1: ESI-MS(+) mass spectrum of $LSnCl_3$ **4**

Simulations of **2** mass peaks:

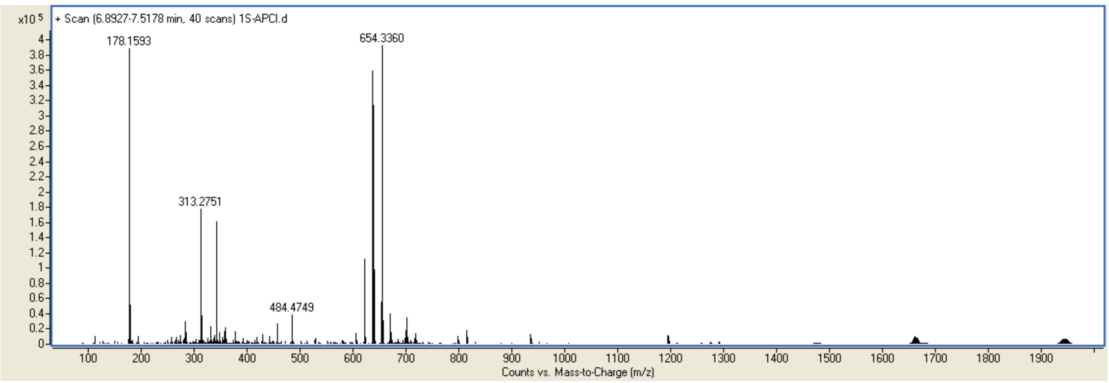
Chemical Formula: $C_{60}H_{104}N_4S_6Si_4Sn_4$

Exact Mass: 1664.18

Molecular Weight: 1661.07

m/z: 1661.18 (100.0%), 1659.18 (90.7%), 1662.18 (89.5%), 1660.18 (83.7%), 1663.18 (82.9%), 1664.18 (80.6%), 1660.17 (72.4%), 1657.18 (69.4%), 1658.17 (68.7%), 1658.18 (65.2%), 1665.18 (60.9%), 1662.17 (57.1%), 1666.18 (53.0%), 1659.17 (50.0%), 1661.17 (47.2%), 1656.17 (46.3%), 1656.18 (44.5%), 1663.17 (41.1%), 1667.18 (37.7%), 1657.17 (37.5%), 1655.18 (33.5%), 1664.17 (33.5%), 1655.17 (30.4%), 1668.18 (29.7%), 1665.17 (26.6%), 1654.18 (25.0%), 1654.17 (23.8%), 1669.18 (21.8%), 1666.17 (21.2%), 1653.18 (15.8%), 1653.17 (14.7%), 1667.17 (13.6%), 1670.18 (13.3%), 1668.17 (11.9%), 1652.18 (11.6%), 1652.17 (9.7%), 1671.18 (9.5%), 1651.18 (7.4%), 1672.18 (6.2%), 1670.17 (5.4%), 1650.18 (4.9%), 1669.17 (4.7%), 1651.17 (4.5%), 1667.19 (3.8%), 1673.18 (3.4%), 1649.18 (3.0%), 1650.17 (2.9%), 1665.19 (2.8%), 1664.19 (2.7%), 1666.19 (2.7%), 1662.19 (2.7%), 1663.19 (2.7%), 1669.19 (2.4%), 1670.19 (2.4%), 1671.17 (2.3%), 1674.18 (2.2%), 1668.19 (2.2%), 1660.19 (1.9%), 1648.18 (1.9%), 1661.19 (1.6%), 1672.19 (1.6%), 1671.19 (1.2%), 1672.17 (1.0%), 1659.19 (1.0%), 1647.18 (1.0%)

APCI-MS(+) of **2**:



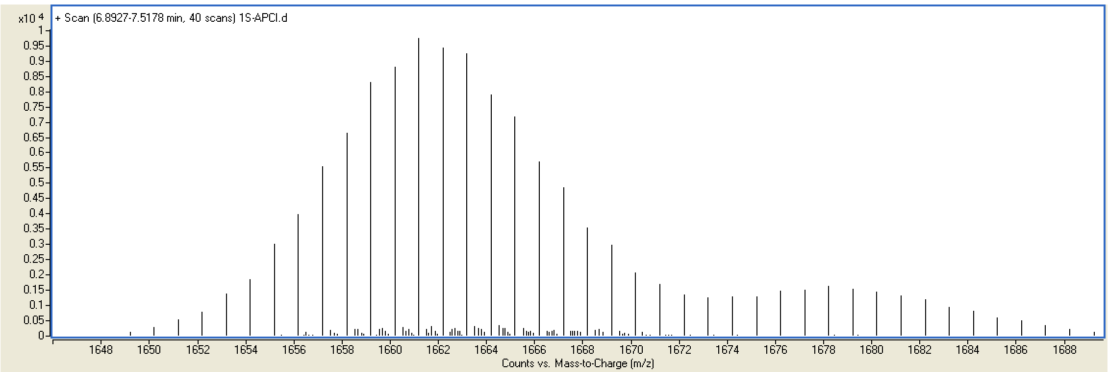


Figure S2: APCI(+) mass spectrum of **2**

Simulations of **3** mass peaks:

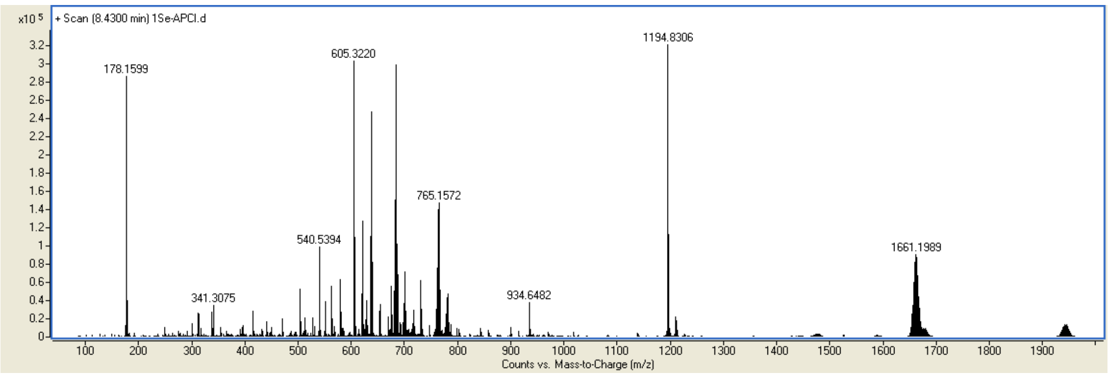
Chemical Formula: $C_{60}H_{104}N_4Se_6Si_4Sn_4$

Exact Mass: 1951.84

Molecular Weight: 1942.44

m/z: 1941.85 (100.0%), 1940.85 (99.5%), 1942.85 (99.2%), 1943.85 (95.0%), 1939.85 (93.9%), 1944.85 (90.2%), 1938.85 (88.1%), 1945.85 (81.8%), 1937.85 (77.6%), 1946.85 (74.3%), 1936.85 (68.7%), 1947.85 (63.0%), 1935.85 (57.3%), 1948.85 (54.1%), 1934.85 (47.2%), 1949.85 (44.0%), 1943.84 (43.5%), 1941.84 (40.6%), 1945.84 (39.3%), 1942.84 (37.9%), 1944.84 (37.1%), 1933.85 (36.0%), 1950.85 (35.6%), 1939.84 (31.4%), 1940.84 (31.4%), 1947.84 (30.6%), 1946.84 (29.8%), 1932.85 (27.4%), 1951.85 (26.9%), 1938.84 (22.2%), 1948.84 (21.3%), 1937.84 (21.2%), 1952.85 (20.8%), 1949.84 (20.4%), 1931.85 (19.3%), 1953.85 (15.3%), 1930.85 (13.4%), 1936.84 (12.6%), 1950.84 (12.3%), 1951.84 (12.1%), 1954.85 (10.8%), 1935.84 (10.8%), 1929.85 (8.6%), 1955.85 (7.2%), 1952.84 (5.8%), 1934.84 (5.5%), 1953.84 (5.5%), 1928.85 (5.2%), 1940.86 (5.0%), 1942.86 (4.9%), 1956.85 (4.9%), 1933.84 (4.8%), 1941.86 (4.8%), 1939.86 (4.6%), 1943.86 (4.6%), 1938.86 (4.3%), 1944.86 (4.2%), 1937.86 (3.9%), 1945.86 (3.9%), 1936.86 (3.8%), 1946.86 (3.4%), 1935.86 (3.1%), 1947.86 (3.1%), 1957.85 (3.0%), 1927.85 (2.9%), 1948.86 (2.6%), 1934.86 (2.5%), 1954.84 (2.3%), 1955.84 (2.2%), 1933.86 (2.1%), 1949.86 (2.1%), 1932.84 (1.8%), 1958.85 (1.8%), 1950.86 (1.7%), 1931.84 (1.7%), 1932.86 (1.6%), 1926.85 (1.5%), 1951.86 (1.4%), 1931.86 (1.3%), 1959.85 (1.1%), 1952.86 (1.1%)

APCI-MS(+) of **3**:



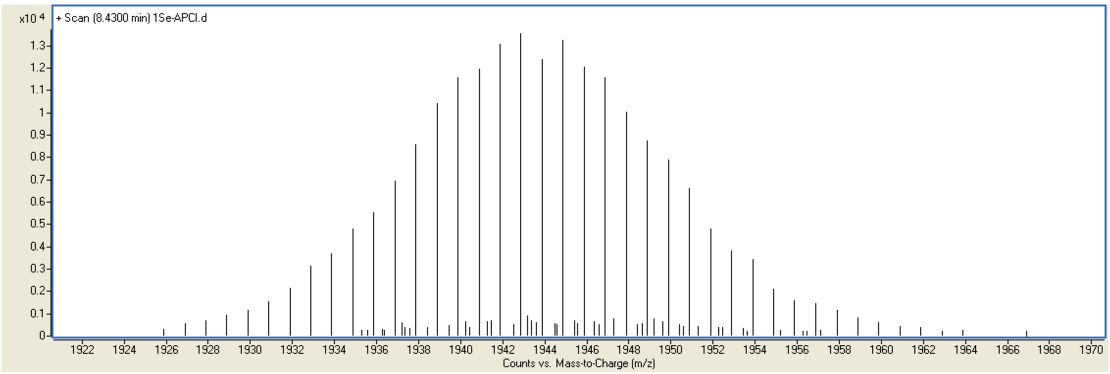


Figure S3: APCI(+) mass spectrum of **3**

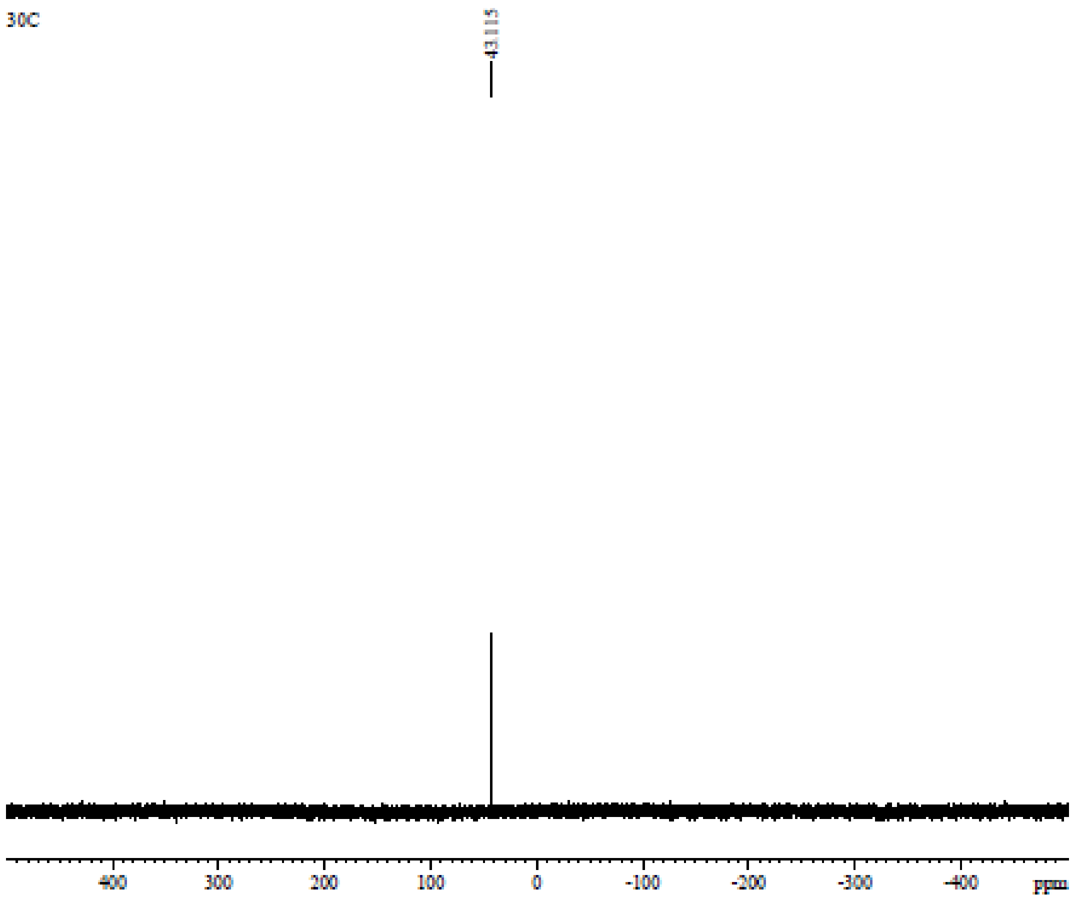
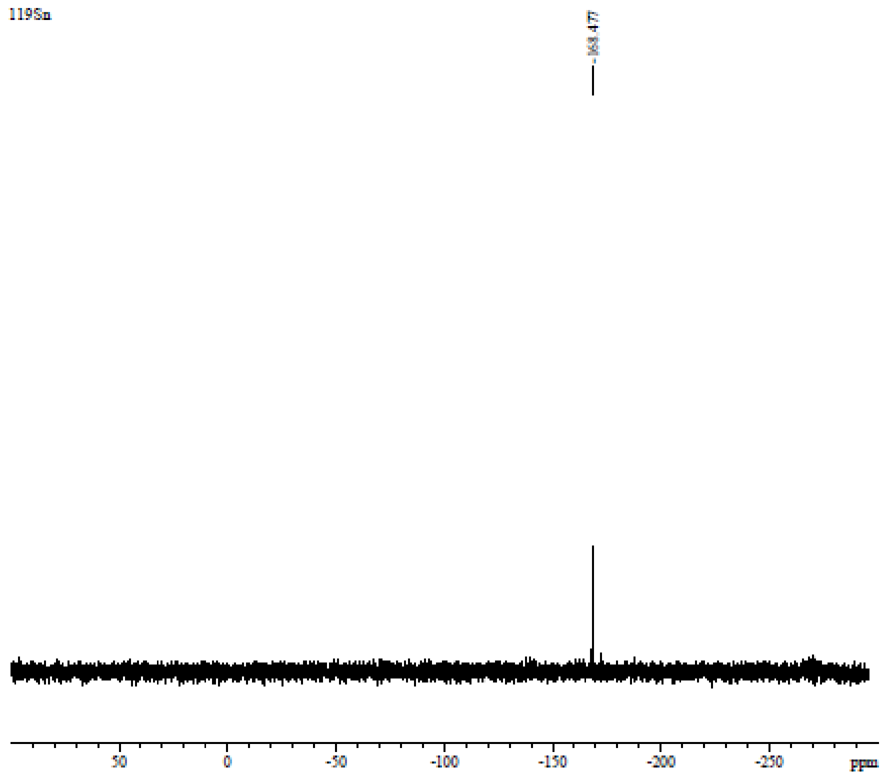


Figure S4 ^{119}Sn NMR of **2**



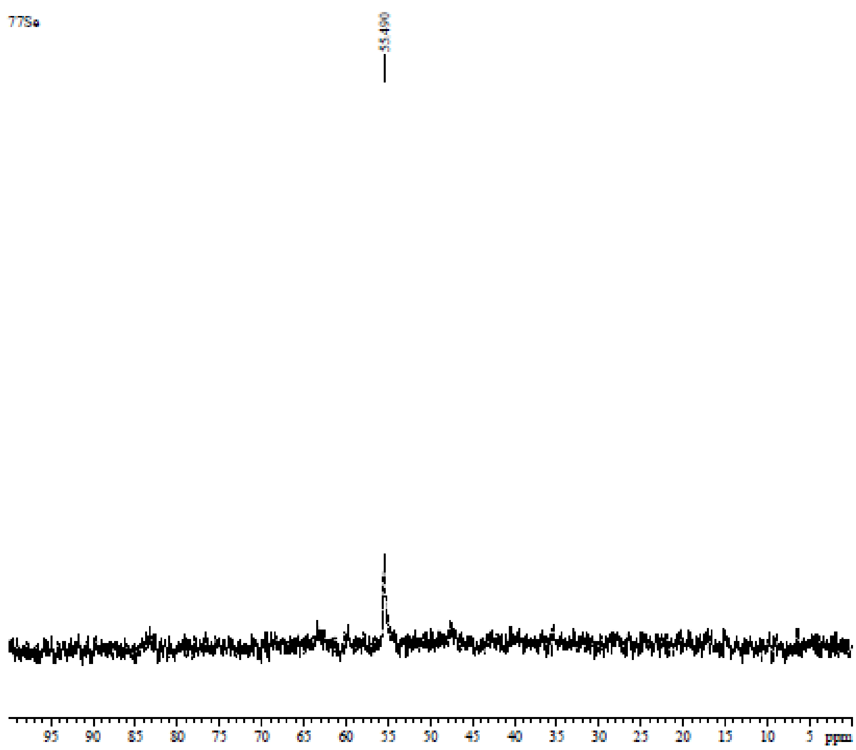
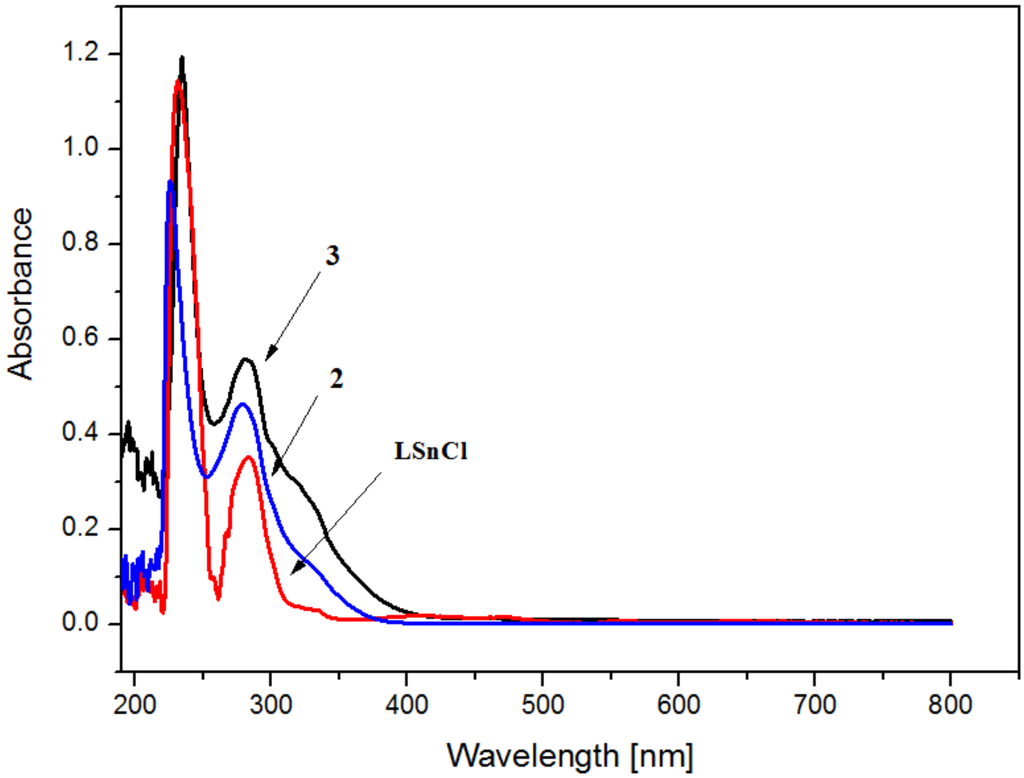


Figure S5 ^{119}Sn NMR, ^{77}Se NMR of **3**

3. Supplementary UV-Visible Absorption Spectroscopy Data

Figure S6 shows the UV-visible absorption spectra of compounds **2**, **3**, and LSnCl in THF



The spectra of **2** and **3** display two significant absorption bands, similar to the values of LSnCl recorded in THF solution. Unlike $(R^{Fc}Sn)_4Sn_6S_{10}]$ $[R^{Fc}$ = $CMe_2CH_2C(Me)$=N-N=C(Me)Fc] they are slightly red shifted.[S1] In **2** and **3** a p(S)→p(Sn) or p(Se)→p(Sn) charge transfer to the Sn-S or Sn-Se skeleton was not observed.

4. Raman data of 2 and 3

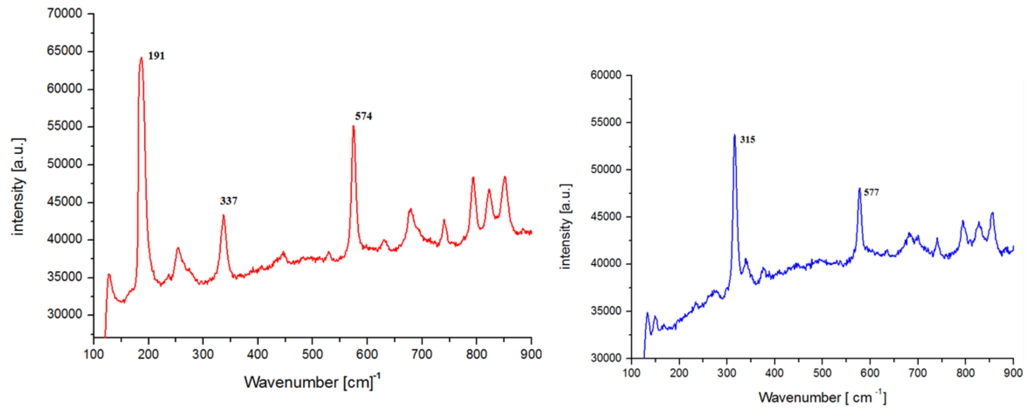
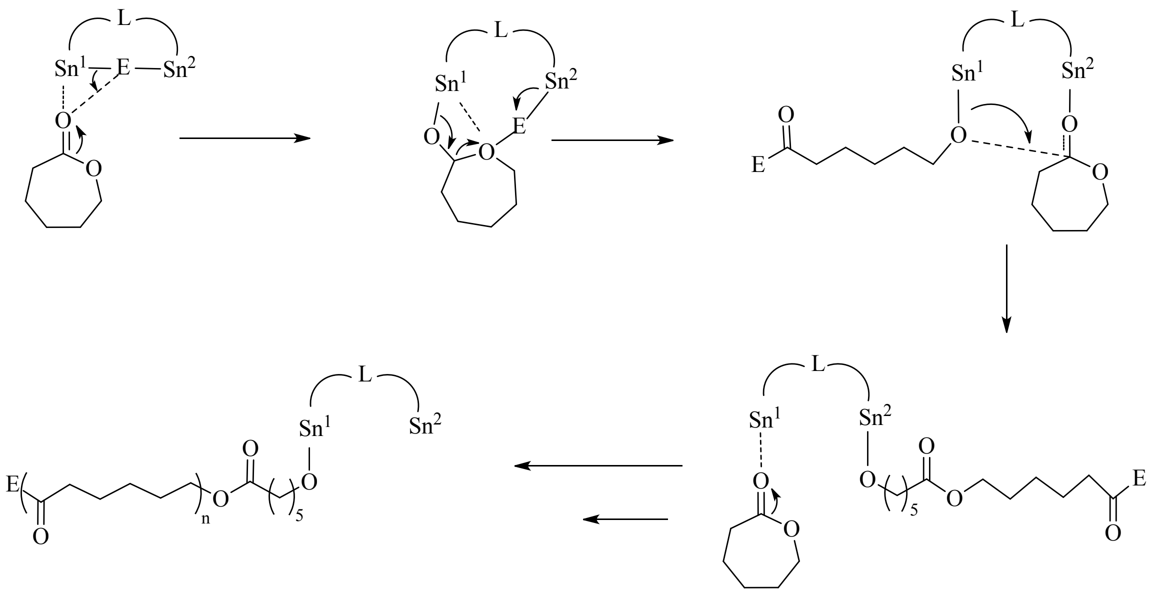


Figure S7 Resonance Raman spectra of **2** and **3** of standard samples were recorded at room temperature.

At lower wave numbers (80-900 cm^{-1}), the Raman spectra of **2** and **3** exhibit similar strong bands at 577, 574 cm^{-1}, respectively. They are the symmetric N-Sn stretching modes of the imine ligand. The Sn–S and Sn-Se stretching modes, which are IR-inactive but Raman-active, are observed at 191, 377 and 315 cm^{-1}, respectively. They are assigned to Sn–S or Sn-Se vibrations.[S2,S3]

Scheme S1. Plausible Mechanism for the Polymerization of ε-Caprolactone Initiated by **2** and **3**



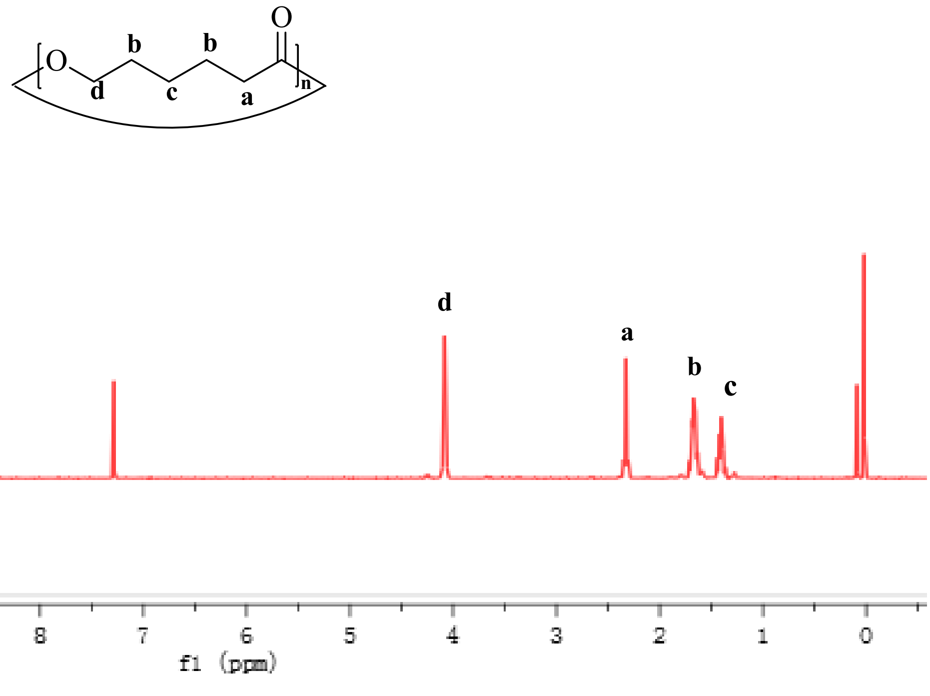


Figure S8 The ^{1}H NMR of the PCL

References

(S1) Z.You and S. Dehnen, *Inorg. Chem.*, 2013, **52**, 12332.

(S2) B. Krebs, S. Pohl and W. Schiwy, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 897.

(S3) Z. You, J. Bergunde, B. Gerke, R. Pöttegn and S. Dehnen, *Inorg. Chem.*, 2014, **53**, 12512.