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Inorganic-Cored Photoactive Assemblies: Synthesis, Structure, and Photochemical Investigations on Stannoxane-Supported Multifluorene Compounds

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Abstract: Organostannoxanes were used as inert supports for the preparation of multichromophore assemblies. The synthesis involves a single-step procedure and allows the preparation of compounds in which the number of chromophore units can be varied from one to six. Thus, the reactions of LCOOH (1-fluorenecarboxylic acid) or L′COOH (9-fluorenecarboxylic acid) with various organostannoxane precursors afforded the fluorenyl derivatives [Ph$_3$SnO$_2$CL] (**1**), [Ph$_3$SnO$_2$CL′] (**2**), [{nBu$_3$SnO$_2$CL″}$_n$] (**3**), [{nBu$_3$SnO$_2$CL′}$_n$] (**4**), [{tBu$_2$Sn(OH)O$_2$CL}$_2$] (**5**), [{tBu$_2$Sn(OH)O$_2$CL′}$_2$] (**6**), [{[nBu$_2$SnO$_2$CL]$_2$O}$_2$] (**7**) [{[nBu$_2$SnO$_2$CL′]$_2$O}$_2$] (**8**), [{nBuSn(O)O$_2$CL}$_6$] (**9**), and [{nBuSn(O)O$_2$CL′}$_6$] (**10**). Interestingly, the formation of **3** is accompanied by an unusual oxo-transfer reaction. The ligand L is oxidized at the 9-position. Compounds **1**, **3**, **5**, **7**, and **8** were characterized by X-ray crystallography. The solid-state structures of these compounds reveal rich supramolecular structures owing to multiple intermolecular interactions between the various supramolecular synthons present in these molecules. The optical behavior of **1**–**10** is primarily dictated by the fluorenyl periphery. These compounds display strong blue fluorescent emission in solution and blue-green fluorescent emission in the solid state. Fluorescence lifetimes of all of these compounds are on the nanosecond timescale, and this suggests that the emission originates from the singlet excited state to the ground state. Intermolecular interactions in the solid state lead to considerable broadening of the emission bands.

Keywords: carboxylate ligands · fluorescence · hydrogen bonds · supramolecular chemistry · tin

Introduction

There is considerable contemporary interest in the development of new organic/organometallic luminescent compounds.[1,2] This is because of the enormous potential of such materials in niche technological applications based on the possibility of using them as photo- and electroluminescent devices.[3,4] Conjugated polymers such as polyphenylenevinylene have been studied in considerable detail.[5,6] Over the past decade polyfluorenes have been actively investigated as leading electroluminescent materials.[6] This is due to their bright blue emission and high hole mobility.[7–10] Both types of polymers are tunable through chemical modifications.[11] However, in spite of their many favorable properties, one of the critical drawbacks of polymer-based materials is the lack of control over precise molecular structure. Chain-length variations, molecular weight distributions, and branching are some of the problems which arise due to the nature of the polymerization reaction. These difficulties do not pose a major problem in conventional applications of polymers.[12] However, the critical parameters for a good optoelectronic material are chemical purity and uniformity,[13] which together lead to optical purity. In comparison to polymers, small molecules with dendrimerlike structures are more amenable in terms of structural precision and easy purification.[14] Thus, the synthesis of chemically pure multichromophore

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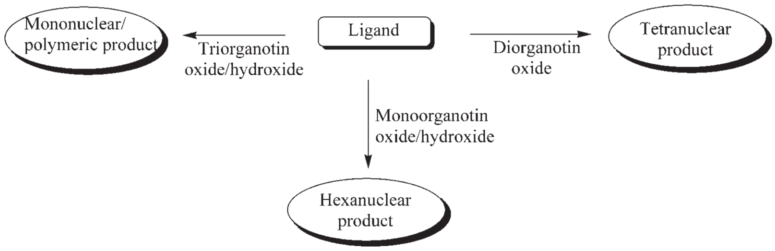
molecules becomes an important task. In this regard several synthetic methods are reported in the literature, some of which depend on supramolecular principles, and some others on more conventional synthetic principles (Figure 1).[15–18] We have been interested in organooxotin cages for some time and have recently developed new paradigms that utilize known robust synthetic methodologies to assemble a well-defined organooxotin cluster/cage with simultaneous arrangement of a functional periphery around the inorganic cluster/cage.[19] It was of interest whether such a stannoxane-based synthetic methodology can be applied to prepare multifluorene compounds. The primary emphasis of this methodology lies in its broad applicability, one-step synthetic protocol, near quantitative yield, reproducibility, and tunability in terms of the number and orientation of the photoactive groups that can be assembled around the central stannoxane core (Scheme 1). Furthermore, we expect that the stannoxane core will not interfere with the optical properties of the periphery. On the contrary, the solid-state structural arrangement of the stannoxane core would lead to intermolecular interactions involving the fluorenyl periphery. This would result in interesting solid-state optical behavior. Herein we report the synthesis and NMR spectroscopic and photochemical (solid-state and solution) characterization of compounds **1**–**10**. The crystal and molecular structures of **1**, **3**, **5**, **7**, and **8** are also reported. Interestingly, the formation of **3** is accompanied by an unusual oxo-transfer reaction.



Scheme 1. General reaction path of organotin oxide/hydroxides with carboxylic acids.

Results and Discussion

Synthesis and characterization of compounds 1–10: Organostannoxanes **1**–**10** were prepared by reaction of LCOOH (1-fluorenecarboxylic acid) and L′COOH (9-fluorenecarboxylic acid) with appropriate organotin precursors (Schemes 2–6). These were characterized by analytical and spectroscopic procedures. In the case of **1**, **3**, **5**, **7**, and **8**, X-ray crystallography was also carried out. The reactions of $(Ph_3Sn)_2O$ with LCOOH and L′COOH affords Ph_3SnO_2CL (**1**) and Ph_3SnO_2CL' (**2**) (Scheme 2). In the solid state **1** and **2** exist as discrete molecules. This was confirmed by X-ray crystal structural analysis on **1**. The solution ^{119}Sn NMR spectra of these compounds (see Experimental Section) are consistent with monomeric structures in solution.[21] Similarly the reaction of $(n\mathrm{Bu}_3\mathrm{Sn})_2\mathrm{O}$ with LCOOH and L′COOH in a 1:2 stoichiometric ratio afforded $[\{n\mathrm{Bu}_3\mathrm{SnO}_2\mathrm{CL}\}_n]$ (**3**) and $[\{n\mathrm{Bu}_3\mathrm{SnO}_2\mathrm{CL}'\}_n]$ (**4**) respectively (Scheme 3). In the solid state **3** and **4** exist as coordination polymers, as revealed by the single-crystal X-ray analysis of **3**.

However, solution ^{119}Sn NMR spectra of these compounds (see Experimental Sec-

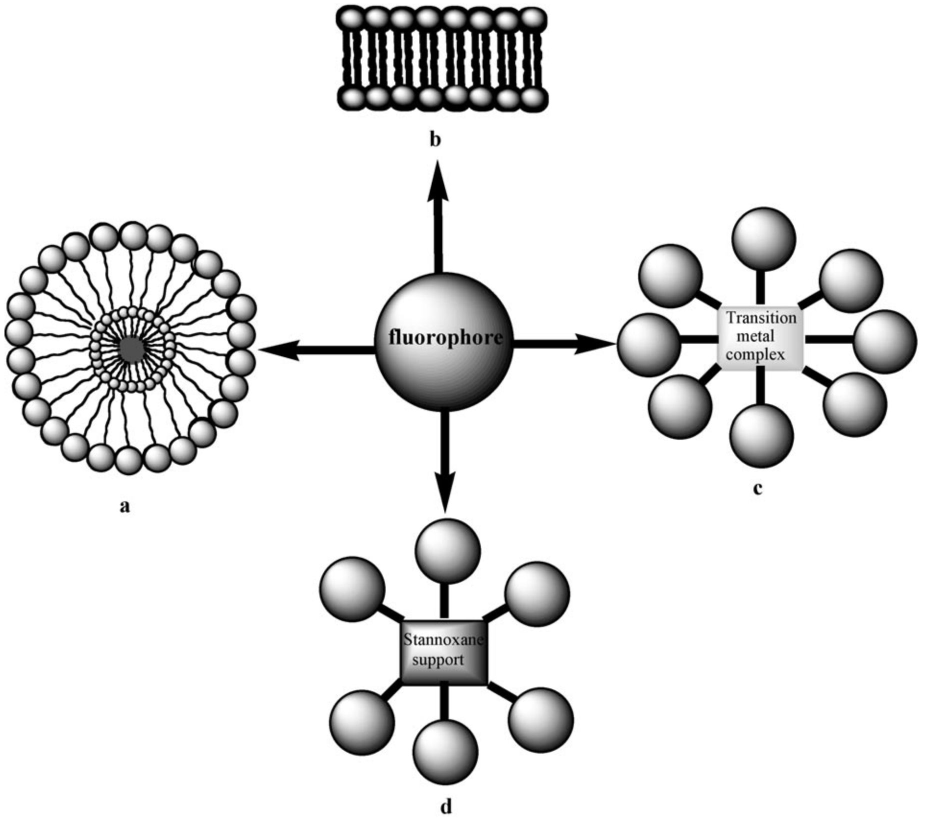
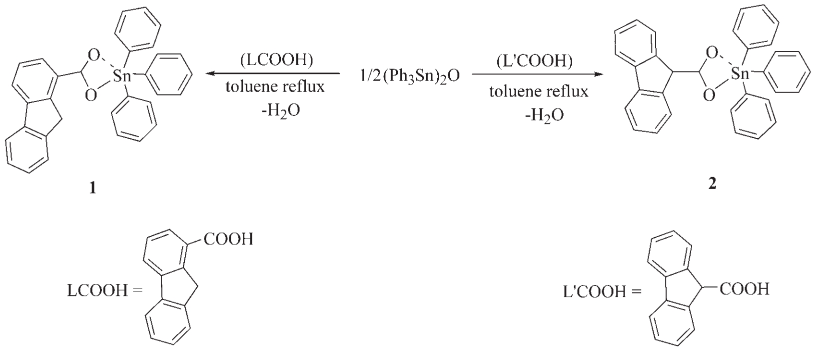
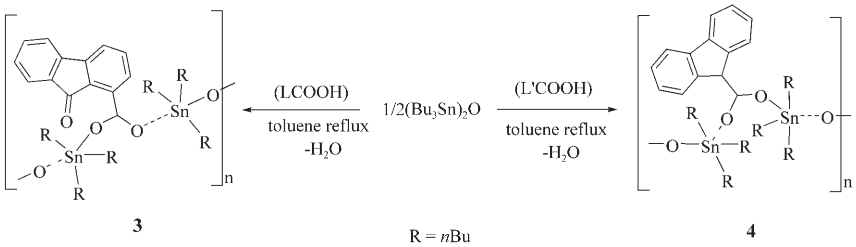


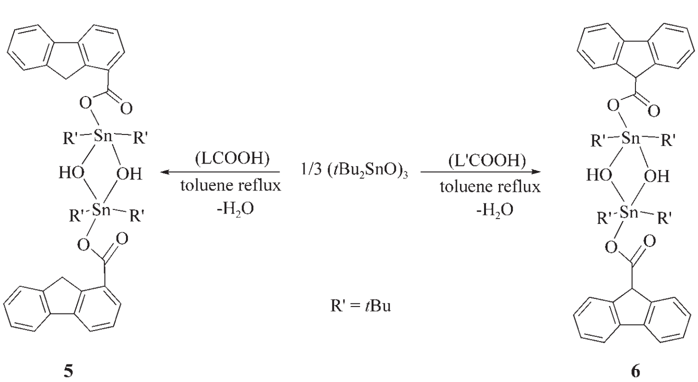
Figure 1. a) Photoactive materials assembled on a dendrimeric core.[15] b) Assembly of photoactive materials by weak interactions.[17] c) Assembly of photoactive materials on transition metal supports.[16] d) Assembly of photoactive materials on stannoxane supports.[18]



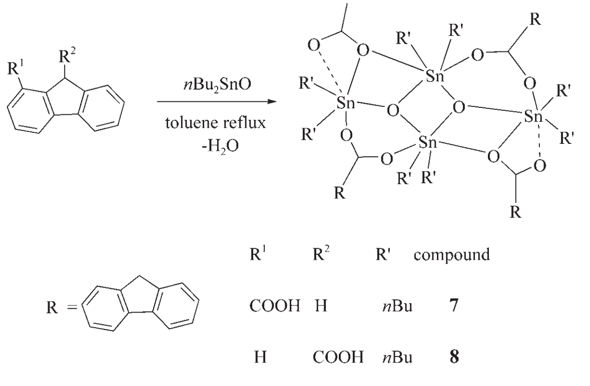
Scheme 2. Synthesis of **1** and **2**.



Scheme 3. Synthesis of **3** and **4**.

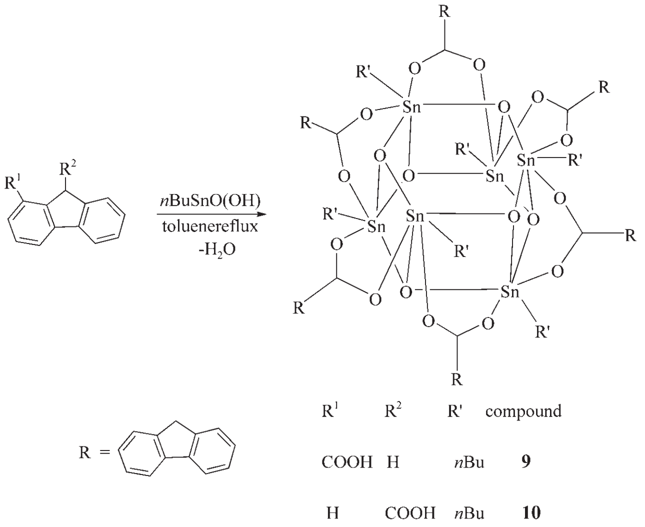


Scheme 4. Synthesis of **5** and **6**.



R^1	R^2	R'	compound
COOH	H	*n*Bu	7
H	COOH	*n*Bu	8

Scheme 5. Synthesis of **7** and **8**.



R^1	R^2	R'	compound
COOH	H	*n*Bu	9
H	COOH	*n*Bu	10

Scheme 6. Synthesis of **9** and **10**

tion) are consistent with monomeric structures in solution.[21] Interestingly, during the course of reaction the 9-position of LCOOH is oxidized with conversion of the fluorene unit to a fluorenone moiety (see Supporting Information). We were able to isolate the oxidized product only in the reaction with $(nBu_3Sn)_2O$. In contrast, the reaction of $(tBu_2SnO)_3$ with LCOOH or L′COOH (Scheme 4) afforded the hydroxyl-bridged dimers $[\{tBu_2Sn(OH)O_2CL\}_2]$ (**5**) and $[\{tBu_2Sn(OH)O_2CL'\}_2]$ (**6**). Tetranuclear compounds $[\{[nBu_2SnO_2CL]_2O\}_2]$ (**7**) and $[\{[nBu_2SnO_2CL']_2O\}_2]$ (**8**) were the only products obtained in the reaction of LCOOH or L′COOH with nBu_2SnO (Scheme 5). The solution ^{119}Sn NMR spectra of **7** and **8** reveals that the tetrameric structures found in the solid state (vide infra) are retained in solution.[21] Finally, the reaction of *n*BuSnO(OH) with LCOOH or L′COOH (Scheme 6) gave hexanuclear compounds $[\{nBuSn(O)O_2CL\}_6]$ (**9**) and $[\{nBuSn(O)O_2CL'\}_6]$ (**10**). The ^{119}Sn NMR of **9** and **10** show a single peak at $\delta =$ 484.4 and −485.0 ppm, respectively, characteristic of a prismane or drum structure in which tin is hexacoordinate (5O, 1C).[21]

X-ray crystal structures of 1, 3, 5, 7, and 8: The molecular structures of **1**, **3**, **5**, **7**, and **8** (see Figure 2) along with their bond parameters are summarized in Table 1.

Ph_3SnO_2CL (**1**) shows a discrete structure in accordance with the preference of such structures for triphenyltin arylcarboxylates.[21] The geometry around tin may be described as capped tetrahedral. Two types of tin–oxygen bond lengths are found: Sn1−O2 2.055(1) Å and Sn1−O3 2.802(2) Å. In contrast to **1**, nBu$_3$SnO$_2$CL (**3**) has a polymeric structure resulting from bridging coordination of the carboxylate ligand, which binds two neighboring tin atoms in an unsymmetrical manner: Sn4−O2 2.214(3), Sn4−O3 2.410(3) Å. The tin atom is pentacoordinate with a 3C, 2O coordination environment. The geometry around the tin atom can be described as trigonal-bipyramidal. The unit cell of **3** contains two independent coordination polymers in the asymmetric unit. The polymers have a zigzag arrangement (see Supporting Information). There is no significant interaction between the two chains in the asymmetric unit. However, an interesting aspect of this crystal structure is that the fluorenyl substituents of the two independent molecules have a mirror-image relationship with each other.

The two tin atoms of the dinuclear compound [{tBu$_2$Sn(OH)O$_2$CL}$_2$] (**5**) are bridged by two hydroxide ligands to generate a four-membered Sn_2O_2 ring. The two fluorenyl substituents are arranged almost in plane with respect to the distannoxane ring. Each tin atom is bound to one fluorene carboxylate oxygen atom (Sn1−O3, Sn2−O5). The other oxygen atom of the carboxylate group (O4 and O6) is involved in an intramolecular hydrogen bond (O1−H1···O6 1.744(3), O2−H2···O4 1.887(4) Å) with the bridging OH group. The Sn1−O4 distance is 3.490(2) Å. This is much

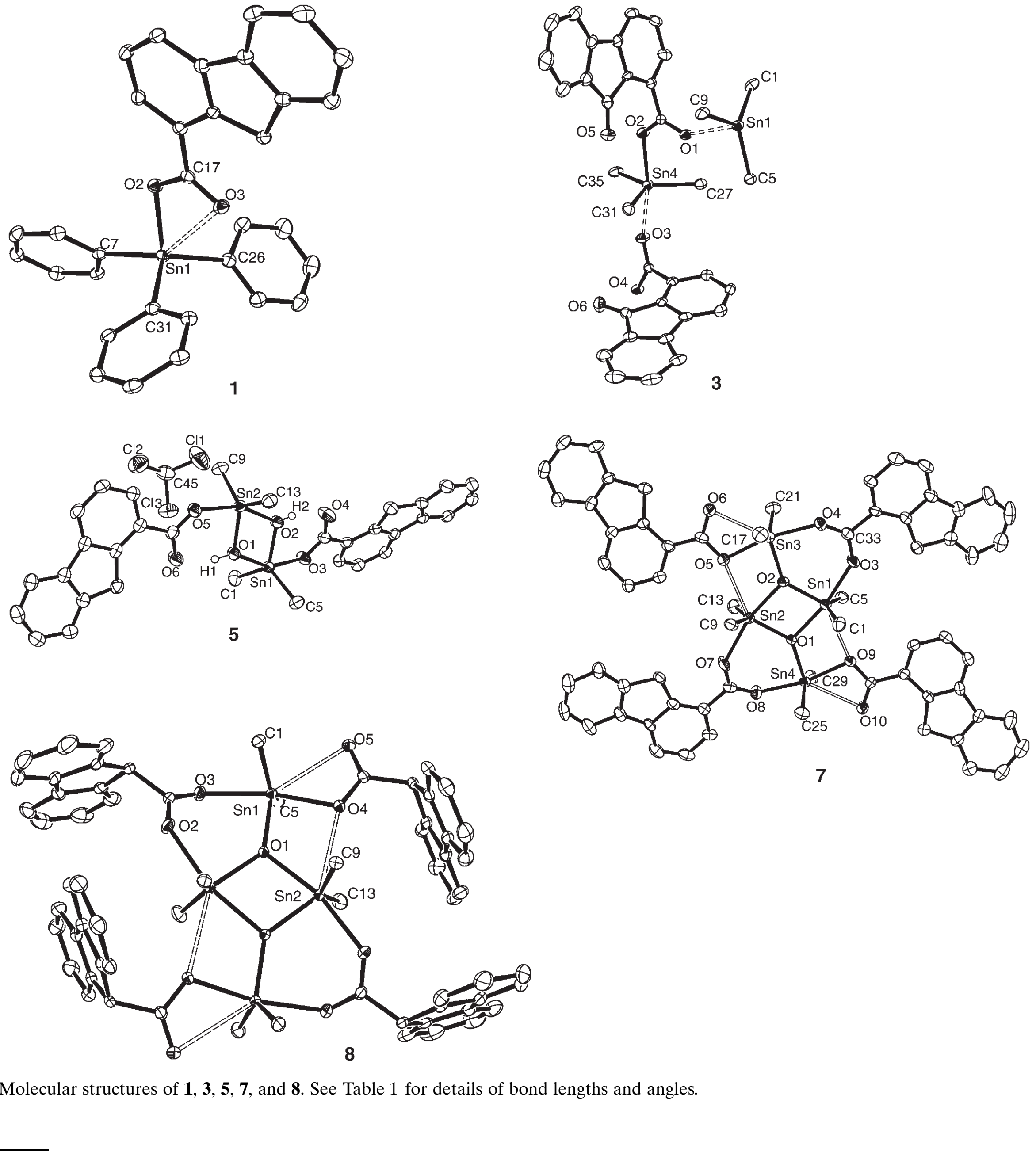


Figure 2. Molecular structures of **1**, **3**, **5**, **7**, and **8**. See Table 1 for details of bond lengths and angles.

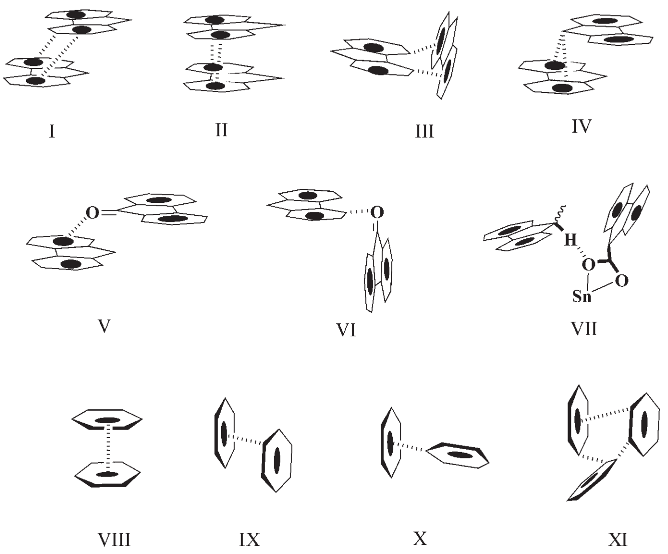
Table 1. Metric parameters for the molecular structures of **1**, **3**, **5**, **7**, and **8** (see also Figure 2).

Compd	Coordination mode of the carboxylate ligand and coordination environment around tin	Sn−O (carboxylate) bond lengths [Å]	Core Sn−O bond lengths [Å]	Bond angles [°]
1	anisobidentate chelating pentacoordinate (3C, 2O) distorted trigonal-bipyramidal	Sn1−O2 2.055(1) Sn1−O3 2.802(2)		Sn1-O2-C26 108.81(91), Sn1-O2-C7 94.55(81) Sn1-O2-C31 109.69(89), Sn1-C26-C7 118.74(92) Sn1-C26-C31 115.38(94), Sn1-C7-C31 107.56(97)
3	anisobidentate bridging pentacoordinate (3C, 2O) distorted trigonal-bipyramidal	Sn1−O1 2.427(3) Sn4−O2 2.214(3) Sn4−O3 2.410(3)		C9-Sn1-C5 120.52(16), C9-Sn1-C1 120.10(16) C9-Sn1-O4 94.02(14), C9-Sn1-O1 87.89(14) C5-Sn1-C1 118.33(16), C5-Sn1-O4 84.94(13) C5-Sn1-O1 84.97(10), C1-Sn1-O4 101.10(15) C1-Sn1-O1 86.98(15), O4-Sn1-O1 169.25(11) Sn4-C31-C27118.70(16), Sn4-C31-C35 121.30(16) Sn4-C31-O2 94.30(14), Sn4-C31-O3 87.94(14) Sn4-C27-O3 91.72(14), Sn4-O2-O3 168.71(11)
5	monodentate pentacoordinate (2C, 3O) distorted trigonal-bipyramidal	Sn1−O3 2.171(1) Sn1−O4 3.490(2) Sn2−O5 2.174(1) Sn2−O6 3.436(2)	Sn1−O1 2.186(1) Sn1−O2 2.031(1) Sn2−O1 2.041(1) Sn2−O2 2.197(1)	O1-Sn2-O5 86.31(75), O1-Sn2-C13 110.70(96) O1-Sn2-C9 121.82(95), O1-Sn2-O2 69.80(73) O5-Sn2-C13 92.09(93), O5-Sn2-C9 91.18(99) O5-Sn2-O2 155.79(73), C13-Sn2-C9 127.47(12) C13-Sn2-O2 99.83(93), C9-Sn2-O2 97.96(94)
7	isobidentate bridging and anisobidentate chelating pentacoordinate (2C, 3O) distorted trigonal-bipyramidal	Sn1−O3 2.225(5) Sn1−O9 2.735(4) Sn2−O5 2.746(4) Sn2−O7 2.277(5) Sn3−O4 2.270(5) Sn3−O5 2.190(5) Sn3−O6 2.723(4) Sn4−O8 2.258(5) Sn4−O9 2.196(5) Sn4−O10 2.738(4)	Sn1−O1 2.155(4) Sn1−O2 2.048(4) Sn2−O1 2.054(4) Sn2−O2 2.154(4) Sn3−O2 2.054(4) Sn4−O1 2.031(4)	O2-Sn1-C1 107.20(21), O2-Sn1-C5 110.43(21) O2-Sn1-O1 76.24(17), O2-Sn1−O3 92.24(21) C1-Sn1-C5 142.13(27), C1-Sn1-O1 95.52(23) C1-Sn2-C13 104.81(26), O1-Sn2-C9 111.83(20) O1-Sn2-O2 76.11(15), O1-Sn2-O7 90.03(15) C13-Sn2-C9 141.01(33), C13-Sn2-O2 103.88(27) C13-Sn3-C17 110.89(26), O2-Sn3-C21 106.27(24) O2-Sn3-O5 78.80(17)
8	isobidentate bridging and anisobidentate chelating pentacoordinate (2C, 3O) distorted trigonal bipyramidal	Sn1−O3 2.270(1) Sn1−O4 2.168(1) Sn1−O5 2.893(2) Sn2−O2 2.241(1) Sn2−O4 2.873(1)	Sn1−O1 2.009(1) Sn2−O1 2.042(1)	O1-Sn1-C5 112.61(98), O1-Sn1-C1 109.14(96) O1-Sn1-O4 81.17(74), O1-Sn1−O3 88.13(71) C5-Sn1-C1 137.05(11), C5-Sn1-O4 97.39(98) C1-Sn1-O4 98.38(96), Sn2-O1-C13 109.10(10) O1-Sn2-C9 107.52(94), O1-Sn2-O1 75.45(70) O1-Sn2-O2 89.51(78), C13-Sn2-C9 143.30(11) C13-Sn2-O1 97.38(94)

longer than that in **1**. Each tin atom in **5** is five-coordinate (2C, 3O) and has a distorted trigonal-bipyramidal geometry; two *tert*-butyl groups (C1 and C5) and one bridging hydroxy oxygen atom (O2) occupy the equatorial positions, while one carboxylate oxygen atom (O3) and the other bridging hydroxy oxygen atom (O1) are the axial ligands. The average Sn−O bond length for the nearly planar distannoxane core is 2.114(1) Å, which is comparable with literature reports (2.125 Å).[22–24]

Compounds **7** and **8** are ladder framework stannoxanes (Sn_4O_4) supported by a central Sn_2O_2 distannoxane ring.[21b–d] The fluorenyl carboxylates are involved in both anisobidentate chelating (Sn3−O5 2.190(4), Sn3−O6 2.723(4) Å) as well as isobidentate bridging coordination modes (Sn1−O3 2.225(5), Sn3−O4 2.270(4) Å). The metric parameters involved in the central Sn_2O_2 core are given in Table 1. In **8** the fluorenyl rings are involved in strong intramolecular π···π and C−H···π interactions (3.880(2) Å and 4.030(2) Å), due to which the Sn_4O_4 core is completely shielded by the four fluorenyl and eight *n*-butyl groups. Consequently, this molecule looks like a rectangular box (see Supporting Information). The ^1H NMR spectrum of **8** reveals the persistence of the intramolecular π···π interaction in solution, as indicated by the upfield shift of the affected aromatic protons of the fluorenyl substituent.

Supramolecular interactions in compounds 1, 3, 5, 7, and 8: The intermolecular solid-state interactions of photoactive molecules are of interest because these have a dramatic affect on their photophysical properties in the solid state.[25,26] Compounds **1**, **3**, **5**, **7**, and **8** provide an opportunity to understand the nature of the supramolecular interactions in organometallic-based photoactive compounds.[27,28] The interesting supramolecular structures of these compounds result from several cumulative intermolecular interactions among various supramolecular functional groups: the aromatic rings of the fluorenyl substituents, the CH_2 group of the fluorenyl ring, and the oxygen atoms of the stannoxane core. The supramolecular interactions found in compounds **1**, **3**, **5**, **7**, and **8** are summarized in Scheme 7.



Scheme 7. Fluorenyl synthons: Type I (slipped offset $\pi\cdots\pi$ stacking); Type II (face-to-face $\pi\cdots\pi$ stacking); Type III (edge-to-face $\pi\cdots\pi$ stacking); Type IV ($C{-}H\cdots\pi$ interaction). Fluorenyl and CO synthons: Type V ($C{=}O\cdots\pi$ interaction); Type VI ($C{=}O\cdots H{-}C$ interaction); Type VII ($C{=}O\cdots H{-}C$ interaction involving carboxylate O atom). Phenyl synthons: Type VIII (face-to-face $\pi\cdots\pi$ stacking); Type IX (edge-to-face $\pi\cdots\pi$ stacking); Type X (T-shaped $\pi\cdots\pi$ stacking); Type XI ($C{-}H\cdots\pi$ interaction).

The three phenyl substituents on tin in compound **1** are involved in intermolecular $\pi\cdots\pi$ interactions to generate a dimer (Figure 3a). Intermolecular $\pi\cdots\pi$ stacking between the aromatic groups of the fluorene rings of such adjacent dimers leads to a 1D chain structure, and further intermolecular $C{-}H\cdots\pi$[29–33] interaction (Types IV and XI) between neighboring chains leads to a 2D layered structure (Figure 3b). Further intermolecular $\pi\cdots\pi$ stacking[29–33] (Types I, VIII–X) and $C{-}H\cdots O{-}C$ interaction (Type VII; see Supporting Information) between such adjacent layers generates a 3D nanotubular structure (Figure 3c). The triphenyltin groups are along the walls of the tube, while the fluorene moieties bridge adjacent tubes.

Each zigzag coordination polymer chain in the crystal structure of **3** interacts with two neighboring chains on either side (Figure 4 and Supporting Information). Slipped off-set stacking (Type I) between the fluorene units of adjacent chains leads to the formation of the 2D layer structure (Figure 4a). Further, intermolecular $C{=}O\cdots\pi$[29–33] and $C{=}O\cdots H{-}C$[29–33] interactions (Types V–VII) between adjacent layers generate a 3D structure (Figure 4b). The $\pi\cdots\pi$ stacking (Types II and III) and $C{=}O\cdots\pi$ (Types V and VI) interactions appear to be the principal driving force in the solid-state luminescence properties of this compound, as evidenced by a strong red shift in the solid-state emission of this compound.

One of the two fluorene rings of **5** is involved in an intermolecular face-to-face $\pi\cdots\pi$ interaction (Type II). The second fluorene ring is involved in a $C{-}H\cdots\pi$ interaction (Type IV) with the CH_2 protons of the fluorene unit of another molecule. These interactions generate a rectangular molecular box (Figure 5). Two dimensions of the box are 15×24 Å; the box propagates into an infinite structure in the third dimension. Two *tert*-butyl groups of each distannoxane unit that makes up the rectangular box protrude into the rectangular void and render it highly hydrophobic and reduce its pore size. Because of the hydrophobicity of the void four chloroform molecules are trapped in each rectangular box (Figure 5a). The guest molecules are noninnocent and further augment the supramolecular interactions. Thus, two of the chloroform molecules are involved in $C{-}Cl\cdots\pi$[34] interaction with the fluorene moiety of distannoxane motif, while the other two chloroform molecules are involved in $Cl\cdots O{-}C$[34] interaction with the fluorene carboxylate oxygen atoms. In addition a weak $Cl\cdots Cl$ interhalogen interaction is also present. Further intermolecular $C{-}H\cdots\pi$ (Type IV) and $\pi\cdots\pi$ (Types I–III) interactions between the molecular boxes leads to their propagation into a 3D array of molecular boxes (Figure 5b and c).

A space-filling model of the crystal structure of **7** is shown in Figure 6a. Intermolecular $\pi\cdots\pi$ (Types I–III) and $C{-}H\cdots\pi$ (Type IV) interactions generate an interesting 3D structure (Supporting Information). The four fluorenyl groups of each molecule of **7** experience three different types of $\pi\cdots\pi$ interactions (Types I–III; Figure 6b). One of the edge-to-face (Type III) interactions between the fluorene rings of the adjacent molecules leads to a 2D layered structure. The adjacent layers interact with each other via one more edge-to-face (Type III) and face-to-face $\pi\cdots\pi$[29–33] (Type II) stacking leading to the formation of a 3D structure. The 3D structure contains highly hydrophobic circular voids (Figure 6a). However, the *n*-butyl substituents on the tin atoms effectively fill the void space.

In **8** the fluorenyl rings are involved in strong intramolecular $\pi\cdots\pi$ (Type III) and $C{-}H\cdots\pi$ (Type IV) interactions which generate a molecular box. Such molecular boxes extend in two dimensions by $\pi\cdots\pi$ stacking (Type III) and $C{-}H\cdots O$ interactions (Type VII) to generate a layered structure (Figure 7; Supporting Information).

Optical properties: Table 2 summarizes the absorption and photoluminescence data of compounds **1**–**10**. The absorption spectra of the organostannoxane derivatives of LCOOH and L′COOH are shown in Figures 8–10. The concentration of all the samples was kept constant at 10^{-7} M unless otherwise mentioned. Derivatives of LCOOH (**1**, **5**, **7**, and **9**) show two strong vibronically structured bands at 270 and 315 nm (Figure 8).

Compound **3** absorbs strongly at 275 nm and has a weak absorption at 320 nm and a shoulder at 400 nm (Figure 9). The shoulder appears only when the concentration of **3** exceeds 10^{-5} M. The change in absorption maxima of the compound **3** clearly indicates the presence of the 9-fluorenone moiety, as was proved by its X-ray crystal structure. Derivatives of L′COOH (**2**, **4**, **6**, **8**, and **10**) absorb strongly between 250 and 350 nm and exhibit vibronically unstructured bands (Figure 10). All the absorptions arise due to ligand-centered spin-allowed singlet $\pi\rightarrow\pi^*$ transition. Thus, the free ligands LCOOH (270, 315 nm) and L′COOH (250–

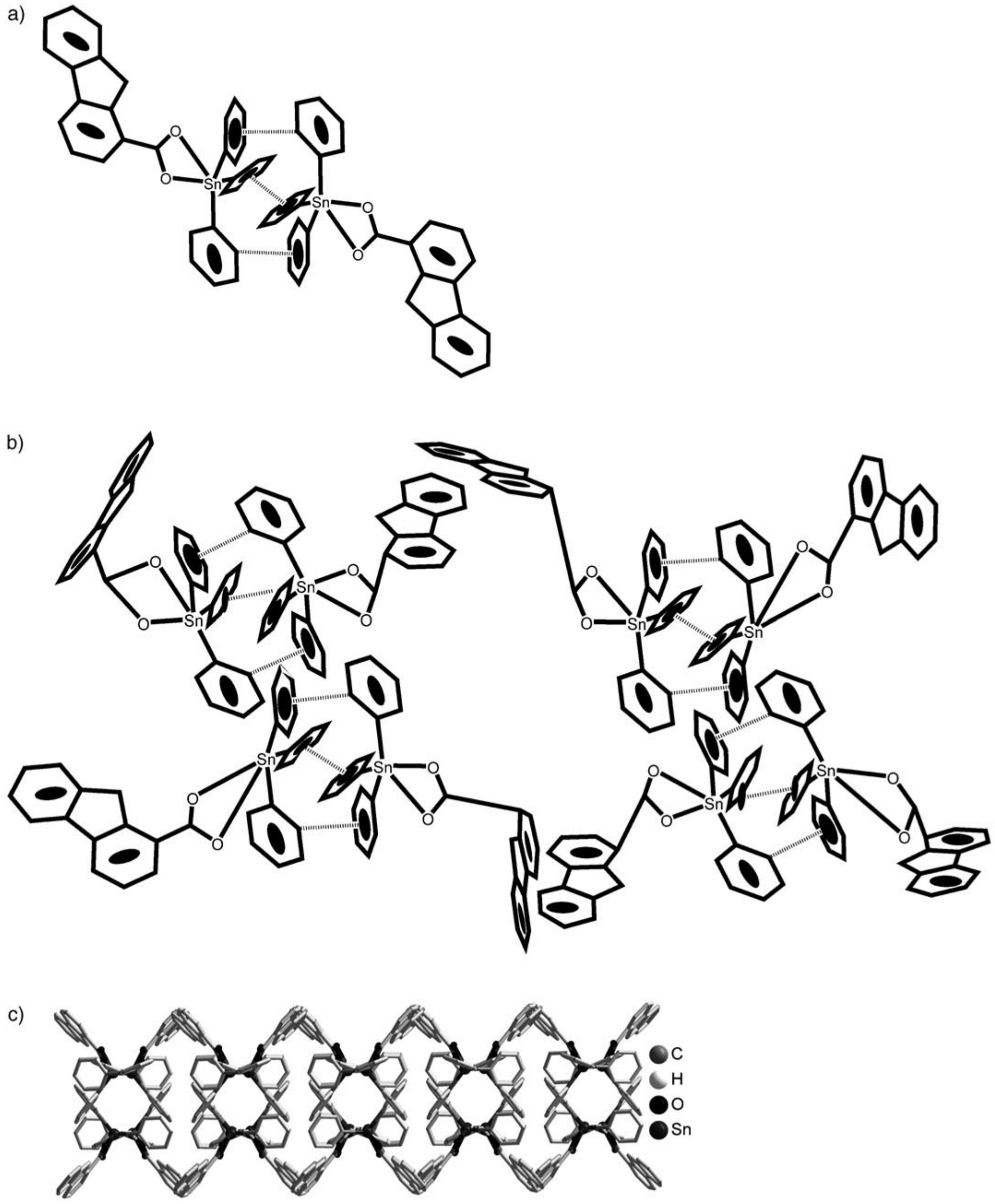


Figure 3. a) Chemdraw representation of intermolecular dimer of compound **1**. b) Chemdraw representation of 2D layered structure of compound **1**. c) Nanotubular structure of compound **1** assembled by C–H···O (2.761(6) Å), π···π (3.566(2) Å), and C–H···π (3.051(2) Å) interactions.

Table 2. Absorbance and photoluminescence data for compounds **1**–**10**.

Compd	Absorbance λ [nm] ($10^{-4}\varepsilon_{max}$)	Solution-state emission λ [nm]	Solid-state emission λ [nm]	Quantum yield	Lifetime [s]	χ^2	Crystal packing
L	265 (3.388), 313 (1.124)	355	–	0.16, 0.19	–	–	–
L′	265 (1.179), 290 (2.787)	315	–	0.13, 0.15	–	–	–
1	265 (3.225), 313 (2.153)	355	375, 450	0.15, 0.18	2.2219×10^{-9}	1.033	3D
2	280 (3.342)	365	515	0.14	$6.6549\times{}^{-10}$, 1.8821×10^{-09}	1.284	–
3	275 (2.612), 325 (1.846), 400 (1.517)	355	340, 490	0.20	7.4463×10^{-10}	0.941	3D
4	280 (3.152)	370	–	0.13	1.6919×10^{-9}	0.909	–
5	265 (5.694), 313 (2.620)	355	410	0.18, 0.21	1.0152×10^{-9}	1.199	3D
6	290 (4.284)	370	500	0.16	8.2343×10^{-10}, 2.5797×10^{-9}, 6.8652×10^{-9}	0.982	–
7	265 (6.7298), 313(2.164)	355	375, 450	0.11, 0.13	2.2199×10^{-9}	1.064	3D
8	290 (4.817)	390	505	0.25	4.9909×10^{-10} 1.1191×10^{-9}	1.100	3D
9	265 (7.016), 313 (3.123)	355	370, 454, 500	0.13, 0.25	8.2883×10^{-10} 2.2961×10^{-9}	1.255	–
10	290 (5.135)	380	495	0.23	5.2465×10^{-10} 1.6243×10^{-9}	1.246	–

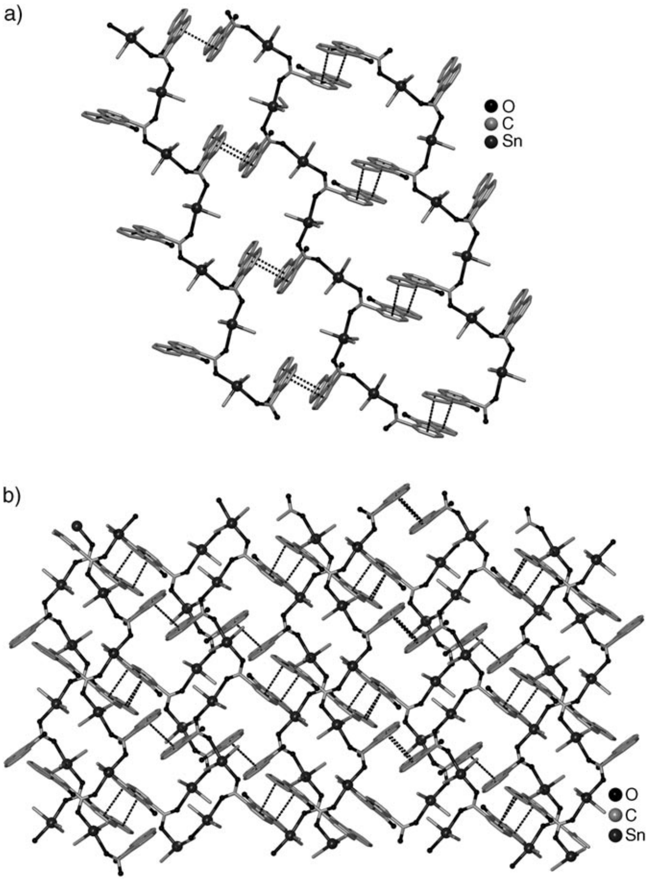


Figure 4. a) 2D layered structure of **3** arising from C–H···π (4.125(2) Å) and π···π (3.668(2) Å) intermolecular interactions. The intermolecular C=O···H–C (2.501(3) Å) and C=O···C=C (3.247(7) Å) interaction between adjacent layers lead to the 3D structure. b) Packing diagram of **3**. Only the α-C atoms of the *n*Bu groups are shown, and all the H atoms have been removed for the sake of clarity.

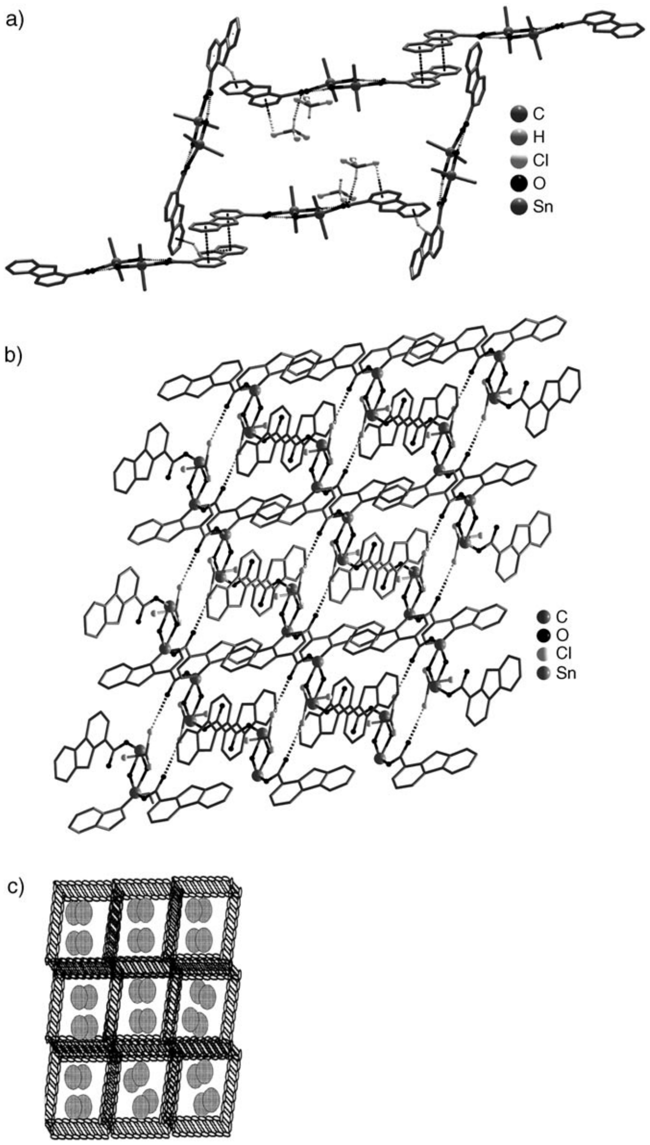


Figure 5. a) C–H···π (3.581(5) Å) and π···π (3.803(7) Å) interactions in the supramolecular rectangular box of **5**. Chloroform molecules are trapped inside the rectangular box and are involved in C–H···O (2.506(2) Å), C–Cl···π (3.703(1) Å), C–Cl···O (3.040(3) Å), and C–Cl···Cl-C (3.787(2) Å) interactions. b) Packing diagram of **5**. Only the α-C atoms of the *t*Bu groups are shown, and all the hydrogen atoms have been removed for the sake of clarity. c) Schematic representation of the arrangement of molecular rectangular boxes. Note the guest chloroform molecules in the voids of molecular boxes.

345 nm) (Supporting Information) also display absorption bands similar to those of the organostannoxane compounds derived therefrom. The absorption maxima in **1**, **5**, **7**, and **9** are invariant and do not depend on the number of fluorenyl units in the compounds; however, compounds **8** and **10** show slight bathochromic shifts versus the free ligands (Figure 10; Supporting Information). In contrast the molar extinction coefficients of all the organostannoxanes are related to the number of fluorenyl units; an increase in the number of fluorenyl units leads to an increase in the molar extinction coefficient.

When excited at their respective maximum absorption wavelengths, the organostannoxane-supported multifluorene compounds emit strongly. The fluorescence spectra of these compounds do not show any vibronically structured bands. Similar to the absorption spectra, the fluorescence spectra are not red-shifted with increasing number of fluorenyl groups (Figures 11–14). Instead, fluorescence intensity increases. Except for compound **3**, other compounds derived from LCOOH (**1**, **5**, **7**, and **9**) emit strongly at 355 nm (Figure 11) and the emission peaks are independent of excitation wavelength (excitation at 275 or 315 nm gives the same emission maxima). In the case of **3** excitation at 275 or 320 nm (Figure 12) results in emission at 350 nm, while excitation at 400 nm results in an emission band at 450 nm (Figure 12). Compounds **2**, **4**, **6**, **8**, and **10** emit strongly between 365 and 395 nm (Figure 13). Compound **10** shows a slightly red-shifted emission in comparison with other compounds (Figure 13). The fluorescence quantum yields of the compounds (determined relative to that of quinine sulfate; Table 2) are in the range of 11–20 %, and the fluorescence lifetimes of all of these compounds are on the nanosecond timescale, and this suggests that the emission originates

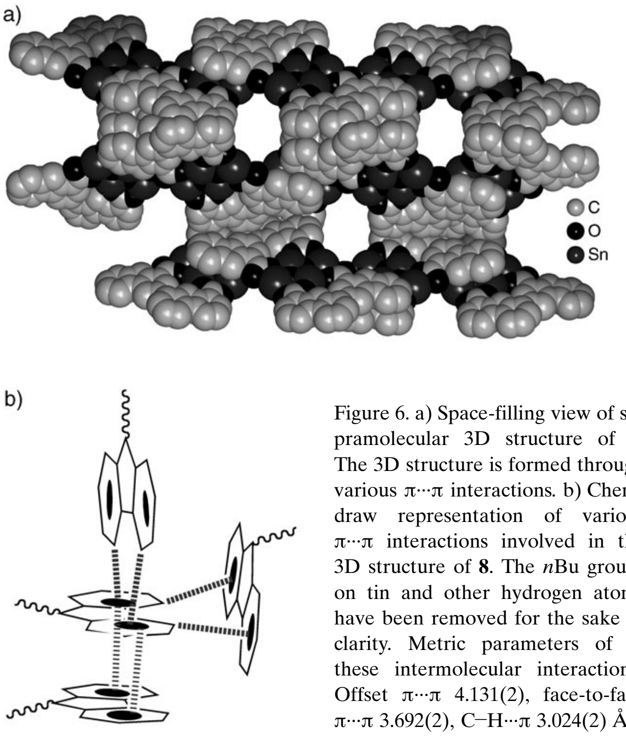


Figure 6. a) Space-filling view of supramolecular 3D structure of **8**. The 3D structure is formed through various π···π interactions. b) Chemdraw representation of various π···π interactions involved in the 3D structure of **8**. The *n*Bu groups on tin and other hydrogen atoms have been removed for the sake of clarity. Metric parameters of in these intermolecular interactions: Offset π···π 4.131(2), face-to-face π···π 3.692(2), C–H···π 3.024(2) Å.

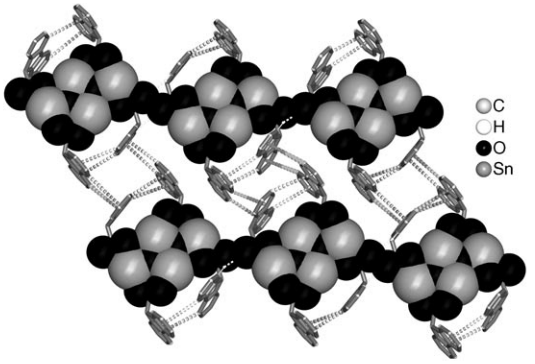


Figure 7. The 2D sheetlike structure of **8** formed via intermolecular C–H···π, π···π, and C–H···O interactions. Metric parameters of these intermolecular interactions: C–H···O–C 2.563(2), C···π 3.703(2), C–H···π 2.863(4) and 4.444(1), C–H···C=C 2.782(1) Å.

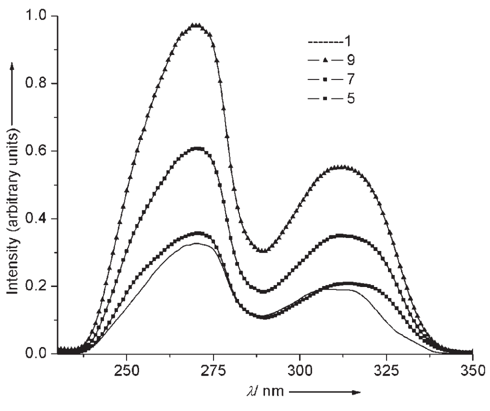


Figure 8. Absorption spectra of **1**, **5**, **7**, and **9** in chloroform.

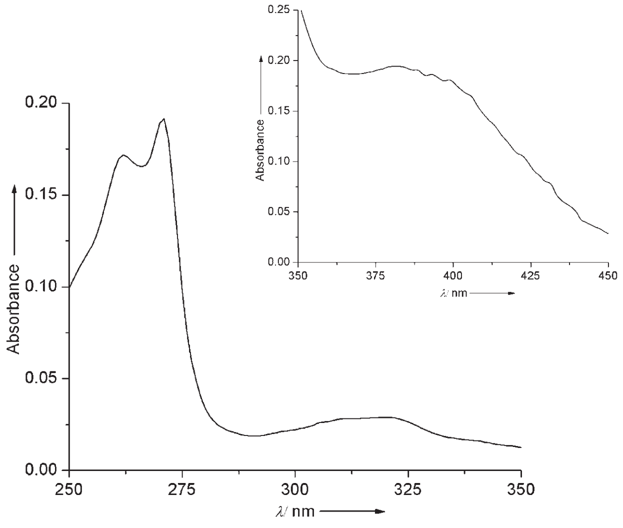


Figure 9. Absorption spectrum of **3** in chloroform. Inset shows the shoulder at 400 nm.

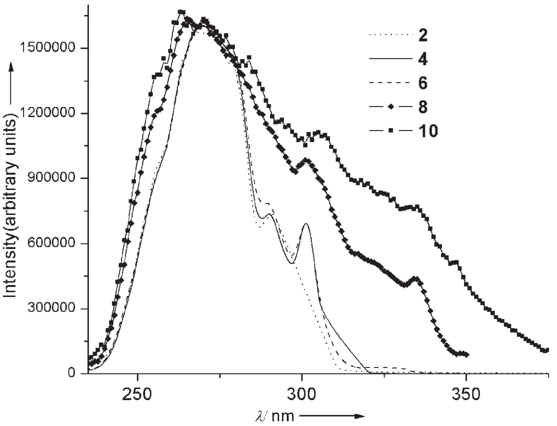


Figure 10. Normalized excitation spectra of **2**, **4**, **6**, **8**, and **10** in chloroform.

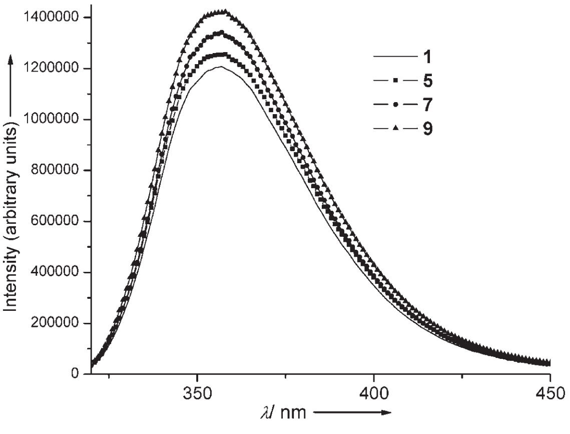


Figure 11. Normalized emission spectra of **1**, **5**, **7**, and **9** in chloroform.

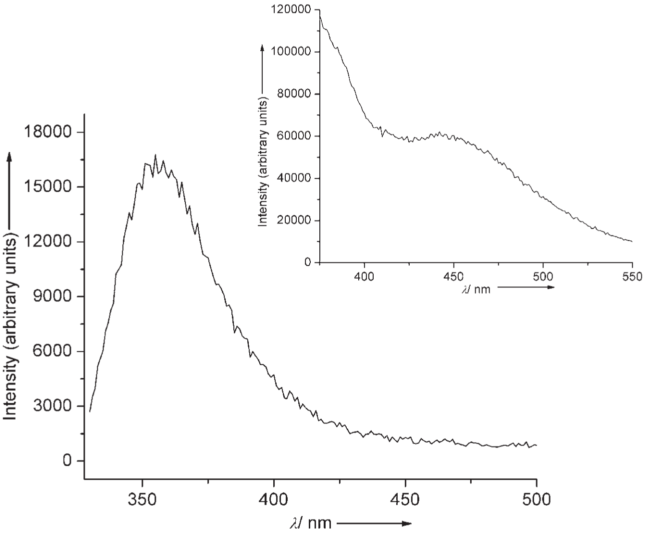


Figure 12. Emission spectra of **3** in chloroform. The inset shows the emission peak at 450 nm (excitation at 400 nm).

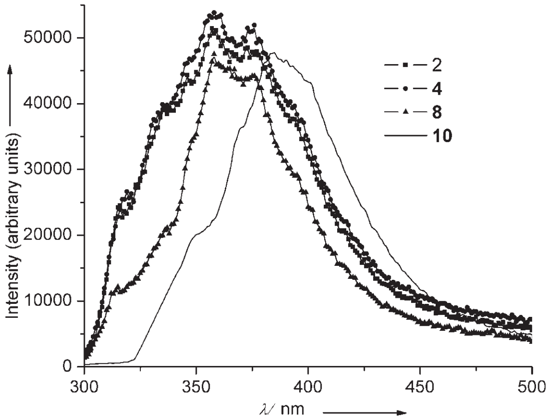


Figure 13. Normalized emission spectra of **2**, **4**, **8**, and **10**.

from the singlet excited state to the ground state. (Figure 14; Supporting Information).

Thin-film photoluminescence: Thin films of all the compounds were prepared by spin coating on quartz substrates from their chloroform solutions. The thin-film photoluminescence (PL) spectra of compounds **1**–**10** retain most of the spectral features of the solution state. However, slight to moderate red shifts are observed in the emission maxima in the solid state in comparison to the solution state (Figures 15–17). The largest red shifts occur for **9** and **10**, which bear six fluorenyl units. In solution compounds **1**–**10** are good blue emitters (emission maxima between 330 and 410 nm), but in the solid state these compounds, with the exception of **3**, exhibit a greenish blue band with an emission maximum at 490 nm in addition to the blue bands at 355–390 nm observed in solution. The striking red shift of about 100 nm in the solid state is presumably due to the various intermolecular interactions observed for these compounds.[7,25]

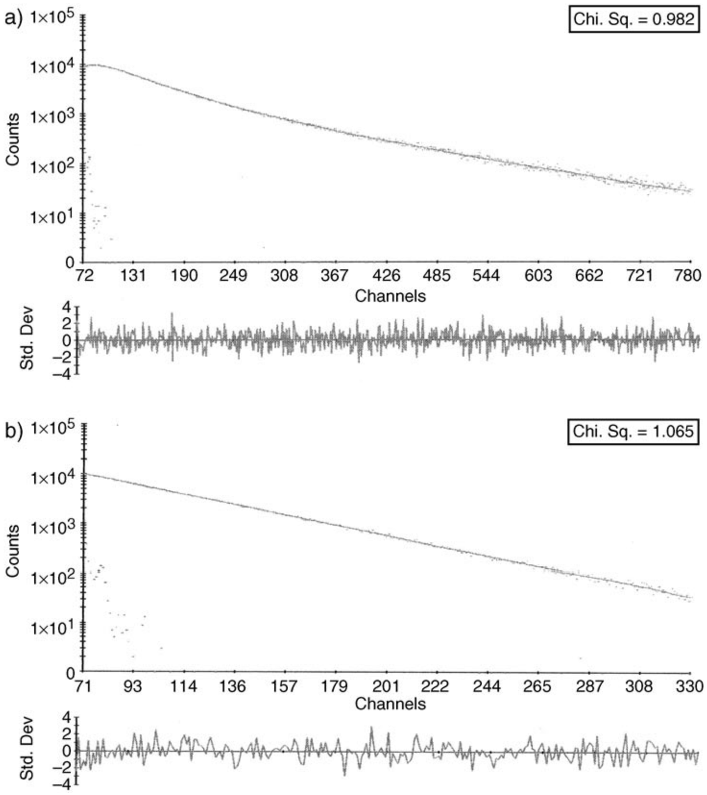


Figure 14. Photoluminescence time decay spectra of compound **6** (a) and **7** (b).

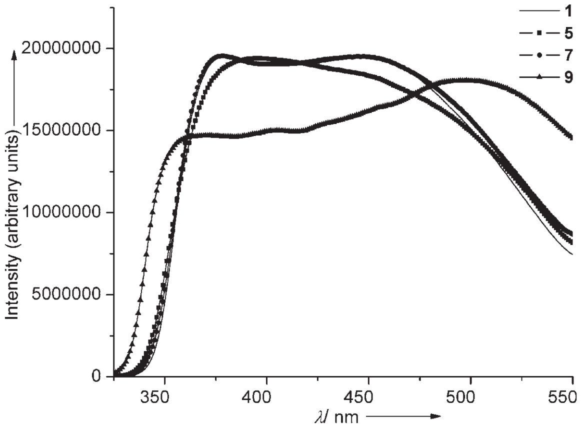


Figure 15. Solid-state luminescence spectra of **1**, **3**, **5**, **7**, and **9**.

The behavior of compound **3** is slightly different from the rest of the family. In the solid state its emission is red shifted by about 50 nm versus solution.

Whereas in solution excitation at 275 and 315 nm leads to one emission band at 350 nm, in the solid state two emission bands at 350 and 490 nm are observed. Excitation at 400 nm gives a single emission band at 490 nm. The intensity of the latter is much higher in comparison to the emission bands generated in the former excitation.

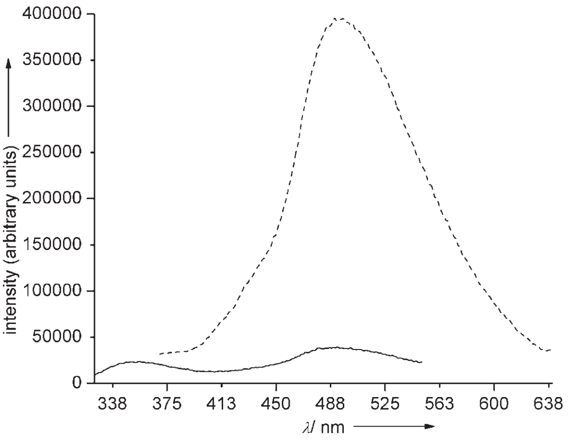


Figure 16. Solid-state luminescence spectra of **3**. Solid line: Spectrum obtained by excitation at 275 nm. Broken line: Spectrum obtained by excitation at 400 nm.

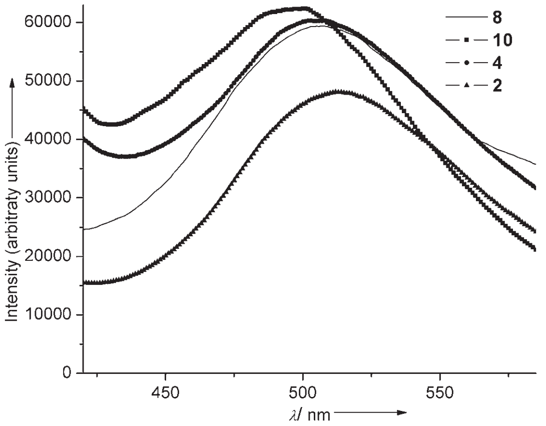


Figure 17. Solid-state luminescence spectra of **2**, **4**, **6**, **8**, and **10**.

Conclusion

We have shown that organostannoxane cores effectively support a multichromophore periphery. The stannoxane-based synthetic strategy provides a reliable and robust procedure for modulating the number and orientation of chromophores in a given molecule, and accordingly we were able to synthesize compounds **1**–**10** in which the number of fluorenyl units could be varied from one to six. The solid-state structures of **1**, **3**, **5**, **7**, and **8** reveal rich supramolecular structures owing to multiple intermolecular interactions between the various supramolecular synthons present in these molecules. The optical behavior of **1**–**10** is primarily dictated by the fluorenyl periphery, and the stannoxane units serve their role very well. The fluorescence bands of L and L′ are well resolved and highly intense in **1**–**10**, which display strong blue fluorescence emission in solution and blue-green fluorescence emission in solid state that involve ligand-centered $\pi\rightarrow\pi^*$ transitions. Various intermolecular interactions in the solid state lead to broad emission bands. Such features are of interest in lighting applications. We are also evaluating the performance of these new organostannoxane-supported multichromophore assemblies in organic light-emitting diode (OLED) devices.

Experimental Section

General: Solvents were freshly distilled over suitable drying agents. $(Ph_3Sn)_2O$, $(n\mathrm{Bu}_3Sn)_2O$, $n\mathrm{Bu}_2SnO$, nBuSnO(OH), 1-fluorenecarboxylic acid, and 9-fluorenecarboxylic acid (Aldrich) were purchased and used as such without further purification. $(t\mathrm{Bu}_2SnO)_3$ was prepared according to a literature procedure.[19] Thin films for solid-state luminescence were made by spin coating ($c=12\,\mathrm{mg\,mL^{-1}}$ for all compounds, except for **9** and **10** ($c=10\,\mathrm{mg\,mL^{-1}}$)). Spin coating was carried out for 60 s at 2500 rpm, and the coating dried under high vacuum for 2 h.

Instrumentation: Melting points were measured on a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out by using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. ^{1}H and ^{119}Sn NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer from $CDCl_3$ solutions (unless otherwise specified) with shifts referenced to tetramethylsilane and tetramethyltin for ^{1}H and ^{119}Sn, respectively. ^{119}Sn NMR spectra were recorded under broadband-decoupled conditions. UV/Vis spectra were recorded on a Perkin Elmer UV/Vis Spectrometer Lamda 20. Excitation and emission spectra were obtained with Fluorolog Spectro Fluorymeter. Thin-film photoluminescence spectra were obtained with a Kimmon (IK5352 R-D) IK Series He–Cd laser. Emission lifetimes were measured by an IBH 5000U (Source: UV LED (Nano LED-03); Detector: TBX-04 picosecond single-photon detection module. Spectral response: 185–650 nm; timing jitter: 200 ps or better (<180 ps typical).

General synthetic procedure for 1–10: A stoichiometric mixture of the organotin precursor and ligand in toluene (80 mL) was heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean–Stark apparatus. The reaction mixture was filtered and evaporated to afford the corresponding products, which were purified by recrystallization.

[Ph_3SnO_2CL] (1): $(Ph_3Sn)_2O$ (0.20 g, 28 mmol), 1-fluorenecarboxylic acid (0.12 g, 0.56 mmol). Yield: 0.26 g (81 %). M.p. 180 °C; elemental analysis (%) calcd for $C_{32}H_{24}O_2Sn$: C 68.73, H 4.33; found: C 68.20, H 4.10; ^{1}H NMR (400 MHz): $\delta=8.04$ (d, $J=7.56$ Hz, 1H, fluorenyl), 7.83–7.87 (m, 5H phenyl), 7.71 (d, $J=7.56$ Hz, 1H, fluorenyl), 7.51 (d, $J=7.32$ Hz, 1H, fluorenyl), 7.23–7.31 (m, 3H, fluorenyl), 7.4–7.43 (m) and 7.76–7.78 (m) (15H, phenyl), 4.24 ppm (s, 2H, CH_2COO); ^{119}Sn NMR (150 MHz): $\delta=-112.5$ ppm (s). Light yellow, prismlike crystals suitable for single-crystal X-ray diffraction was obtained by slow diffusion of n-hexane into a solution of **1** in chloroform at room temperature.

[Ph_3SnO_2CL'] (2): $(Ph_3Sn)_2O$ (0.20 g, 28 mmol), 9-fluorenecarboxylic acid (0.12 g, 0.56 mmol). Yield: 0.30 g (93 %). M.p. 170 °C; elemental analysis (%) calcd for $C_{32}H_{24}O_2Sn$: C 68.73, H 4.33; found: C 68.30, H 4.20; ^{1}H NMR (400 MHz): $\delta=7.59$- 7.67 (m), 7.50–7.55 (m) and 7.26–7.33 (m), 7.18–7.22 (m) (23H, fluorenyl and phenyl), 4.88 ppm (s, 1H, CHCOO); ^{119}Sn NMR (150 MHz): $\delta=-102.5$ ppm (s).

[{$n\mathrm{Bu}_3SnO_2CL''$}$_n$] (L″ = 9-fluorenone) (3): $(n\mathrm{Bu}_3SnO)_2$ (0.20 g, 0.34 mmol), 1-fluorenecarboxylic acid (0.14 g, 0.67 mmol). Yield: 0.27 g (79 %). M.p. 130 °C (decomp); elemental analysis (%) calcd for $C_{26}H_{34}O_3Sn$: C 60.84, H 6.67; found: C 60.25, H 6.15; ^{1}H NMR (400 MHz): $\delta=8.28$ (d, $J=7.8$ Hz, 1H, fluorenyl), 7.89 (d, $J=7.8$ Hz, 1H, fluorenyl), 7.70 (d, $J=7.32$ Hz, 1H, fluorenyl), 7.62 (d, $J=7.32$ Hz, 1H, fluorenyl), 7.40 (t, $J=7.38$ Hz, 1H, fluorenyl), 7.24 (t, $J=7.32$ Hz, 2H, fluorenyl), 1.55 (m, 6H, $\mathit{CH_2}CH_2CH_2CH_3$), 1.29 (m; 12H, $CH_2\mathit{CH_2}\mathit{CH_2}CH_3$), 0.85 ppm (t; $J=7.32$ Hz, 9H, $CH_2CH_2CH_2\mathit{CH_3}$); ^{119}Sn NMR (150 MHz): $\delta=-130.1$ ppm. Light yellow, prismlike crystals of **3** suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in toluene/dichloromethane (1/1).

[{$n\mathrm{Bu}_3SnO_2CL'$}$_n$] (4): $(n\mathrm{Bu}_3Sn)_2O$ (0.20 g, 0.34 mmol), 9-fluorenecarboxylic acid (0.14 g, 0.67 mmol). Yield: 0.29 g (85 %). M.p. 150 °C; elemental analysis (%) calcd for $C_{26}H_{35}O_2Sn$: C 62.67, H 7.08; found: C 62.32, H

6.95; ^{1}H NMR (400 MHz): $\delta=7.68$ (d, $J=7.56$ Hz, 2H, fluorenyl), 7.61 (d, $J=7.56$ Hz, 2H, fluorenyl), 7.34 (t, $J=7.56$ Hz, 2H, fluorenyl) 7.27 (t, $J=7.56$ Hz, 2H, fluorenyl), 4.88 (s, 1H, -C*H*−COO), 1.59–1.45 (m, 12H, C*H*$_2$C*H*$_2$CH$_2$CH$_3$), 1.33–1.22 (m, 6H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.70 ppm (t, $J=7.32$ Hz, 9H, CH$_2$CH$_2$CH$_2$C*H*$_3$); ^{119}Sn NMR (150 MHz): $\delta=-139.1$ ppm.

[{*t*Bu$_2$Sn(OH)O$_2$CL}$_2$] (5): (*t*Bu$_2$SnO)$_3$ (0.20 g, 0.27 mmol), 1-fluorenecarboxylic acid (0.17 g, 0.81 mmol). Yield: 0.28 g (76 %). M.p. 176 °C; elemental analysis (%) calcd for $C_{44}H_{56}O_6Sn_2$: C 57.55, H 6.15; found: C 57.23, H 6.00; ^{1}H NMR (400 MHz): $\delta=8.07$ (d, $J=7.8$ Hz, 2H, fluorenyl), 7.92 (d, $J=7.56$ Hz, 2H, fluorenyl), 7.74 (d, $J=7.56$ Hz, 2H, fluorenyl), 7.54 (d, $J=7.08$ Hz, 2H, fluorenyl), 7.43 (t, $J=7.56$ Hz, 2H, fluorenyl), 7.25–7.34 (m, 4H, fluorenyl), 4.28 (s, 4H, CH$_2$COO), 1.44 ppm (s, 36H, *t*Bu); ^{119}Sn NMR (150 MHz): $\delta=-212.6$ ppm (s). Light yellow crystals suitable for single-crystal X-ray diffraction were obtained by slow diffusion of methanol into a solution of **5** in chloroform at room temperature.

[{*t*Bu$_2$Sn(OH)O$_2$CL′}$_2$] (6): (*t*Bu$_2$SnO)$_3$ (0.20 g, 0.27 mmol), 9-fluorenecarboxylic acid (0.17 g, 0.81 mmol). Yield: 0.31 g (85 %). M.p. 158 °C (decomp); elemental analysis (%) calcd for $C_{44}H_{56}O_6Sn_2$: C 57.55, H 6.15; found: C 57.50, H 5.98; ^{1}H NMR (400 MHz): $\delta=7.62$ (d, $J=7.32$ Hz, 4H, fluorenyl), 7.53 (d, $J=7.56$ Hz, 4H, fluorenyl), 7.28 (t, $J=7.56$ Hz, 4H, fluorenyl), 7.20 (t, $J=7.32$ Hz, 4H, fluorenyl), 4.85 (s, 2H, CHCOO), 1.13 ppm (s, 18H, *t*Bu); ^{119}Sn NMR (150 MHz): $\delta=-213.2$ ppm (s).

[{[*n*Bu$_2$SnO$_2$CL]$_2$O}$_2$] (7): *n*Bu$_2$SnO (0.12 g, 0.48 mmol), 1-fluorenecarboxylic acid (0.10 g, 0.48 mmol). Yield: 0.18 g (82 %). M.p. 290–293 °C (d); elemental analysis (%) calcd for $C_{88}H_{108}O_{10}Sn_4$: C 58.70, H 6.05; found: C 58.23, H 5.79; ^{1}H NMR (400 MHz): $\delta=7.90$–7.92 (m, 8H, fluorenyl), 7.76 (d, $J=7.04$ Hz, 4H, fluorenyl), 7.54 (d, $J=7.08$ Hz, 4H, fluorenyl), 7.44 (m, 4H, fluorenyl), 7.27–7.35 (m, 8H, fluorenyl), 4.26 (s, 8H, CH$_2$COO), 1.51–1.72 (m, 32H, C*H*$_2$C*H*$_2$CH$_2$CH$_3$), 1.22–1.35 (m, 16H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.69–0.82 ppm (m, 24H, CH$_2$CH$_2$CH$_2$C*H*$_3$); ^{119}Sn NMR (150 MHz): $\delta=-216.6$ (s), −221.2 ppm (s). Light yellow, prismlike crystals suitable for single-crystal X-ray diffraction were obtained by slow diffusion of methanol in to a solution of **7** in chloroform at room temperature.

[{[*n*Bu$_2$SnO$_2$CL′]$_2$O}$_2$] (8): *n*Bu$_2$SnO (0.12 g, 0.5 mmol), 9-fluorenecarboxylic acid (0.10 g, 0.5 mmol). Yield: 0.19 g (86 %). M.p. 257 °C (decomp); elemental analysis (%) calcd for $C_{88}H_{108}O_{10}Sn_4$: C 58.70, H 6.05; found: C 58.10, H 5.60; ^{1}H NMR (400 MHz): $\delta=7.41$–7.42 (m, 8H fluorenyl), 7.36–7.38 (m, 8H fluorenyl), 7.15–7.24 (m, 16H, fluorenyl), 4.57 (s, 4H, CHCOO), 0.65–0.67 (m), 0.78–0.85 (m), 1.05–1.21 (m) and 1.39–1.51 ppm (m) (72H, C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$); ^{119}Sn NMR (150 MHz): $\delta=-198.1$ (s), −220.5 ppm (s). Dull yellow, prismlike crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in toluene/dichloromethane (50/50).

[{*n*BuSn(O)O$_2$CL}$_6$] (9): *n*BuSnO(OH) (0.15 g, 0.72 mmol), 1-fluorenecarboxylic acid (0.15 g, 0.72 mmol). Yield: 0.23 g (75.0 %). M.p. 290 °C (decomp); elemental analysis (%) calcd for $C_{108}H_{108}O_{18}Sn_6$: C 53.91, H

Table 3. Crystal data collection and refinement parameters for **1**, **3**, **5**, **7**, and **8**.

	1	**3**	**5**	**7**	**8**
formula	$C_{62}H_{48}O_4Sn_2$	$C_{24}H_{28}N_4O_4Sn$	$C_{45}H_{57}Cl_3O_6$ Sn_2	$C_{88}H_{108}O_{10}Sn_4$	$C_{88}H_{108}O_{10}Sn_4$
M	1094.38	555.19	1037.64	1800.50	1800.50
T [K]	293(2)	100(2)	213(2)	213(2)	100(2)
λ [Å]	0.71069	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$C12/c1$	$P\bar{1}$	$P2(1)/c$	$Pna2(1)$	$C2/c$
a [Å]	30.81(5)	10.8481(7)	9.235(2)	17.1840(3)	14.4517(8)
b [Å]	9.17(5)	21.2515(13)	24.074(5)	21.2470(4)	22.8025(13)
c [Å]	19.81(5)	21.7740(13)	22.016(3)	22.7070(5)	25.1497(15)
α [°]	90.00(5)	101.2840(10)	90	90	90
β [°]	118.75(5)	90.7340(10)	109.61(3)	90	103.685(10)
γ [°]	90.00(5)	91.5070(10)	90	90	90
V [Å^3]	4909(3)	4920.2(5)	4610.8(15)	8291(3)	8052.4(8)
Z	4	8	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.481	1.499	1.495	1.442	1.485
μ [mm^{-1}]	1.067	1.075	1.301	1.247	1.284
$F(000)$	2208	2256	2104	3664	3664
crystal size [mm]	0.1 × 0.2 × 0.1	0.2 × 0.3 × 0.1	0.4 × 0.4 × 0.3	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
θ [°]	2.34 to 28.29	2.00 to 28.31	1.96 to 24.20	1.77 to 24.27	1.67 to 28.30
index ranges	$-40 \leq h \leq 40$ $-12 \leq k \leq 10$ $-14 \leq l \leq 26$	$-14 \leq h \leq 14$ $-28 \leq k \leq 23$ $-24 \leq l \leq 29$	$-10 \leq h \leq 10$ $-27 \leq k \leq 27$ $-23 \leq l \leq 24$	$-18 \leq h \leq 19$ $-24 \leq k \leq 24$ $-25 \leq l \leq 25$	$-18 \leq h \leq 19$ $-30 \leq k \leq 21$, $-30 \leq l \leq 32$
reflections collected	16045	33084	29210	51264	25093
independent reflections	6058 [R(int) = 0.0280]	23450 [R(int) = 0.0348]	7147 [R(int) = 0.0407]	13061 [R(int) = 0.0644]	9362 [R(int) = 0.0268]
completeness to theta	99.2 %	95.7 %	96.4 %	98.1 %	93.6 %
absorption correction	SADABS	SADABS	not applied	semiempirical	semiempirical
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	6058/0/316	23450/0/1081	7147/0/526	13061/329/917	9362/0/463
GOF on F^2	1.053	1.008	1.043	0.884	1.058
final R indices [$I > 2\sigma(I)$]					
$R1$	0.0348	0.0592	0.0248	0.0354	0.0319
$wR2$	0.0896	0.1224	0.0632	0.0600	0.0790
R indices (all data)					
$R1$	0.0399	0.0851	0.0296	0.0582	0.0412,
$wR2$	0.0927	0.1336	0.0651	0.0636	0.0830
largest difference peak/hole [e Å^{-3}]	1.114/−0.678	1.864/−1.429	0.391/−0.502	1.322/−0.572	1.692/−0.995

4.52; found: C 53.23, H 4.20; ^{1}H NMR (400 MHz): $\delta = 7.88–7.90$ (m, 12H, fluorenyl), 7.72–7.75 (m, 6H, fluorenyl), 7.50–7.52 (m, 6H, fluorenyl), 7.42 (m, 6H, fluorenyl), 7.25–7.33 (m; 12H fluorenyl), 4.25 (s; 12H; CH_2COO), 1.50–1.70 (m), 1.20–1.33 (m) and 0.67–0.80 ppm (m), (54H; $CH_2CH_2CH_2CH_3$); ^{119}Sn NMR (150 MHz) $\delta = -484.4$ ppm.

[{*n*BuSn(O)O$_2$CL'}$_6$] (10): *n*BuSnO(OH) (0.15 g, 0.72 mmol), 9-fluorenecarboxylic acid (0.15 g, 0.72 mmol). Yield: 0.20 g (65.0 %). M.p. 278 °C (decomp); elemental analysis (%) calcd for $C_{108}H_{108}O_{18}Sn_6$: C 53.91, H 4.52; found: C 53.25, H 4.05; ^{1}H NMR (400 MHz): $\delta = 7.58–7.67$ (m), 7.43–7.45 (m), 7.22–7.27 (m), 7.16–7.18 (m), 7.10–7.12 (m), and 7.01–7.05 (m), (48H, fluorenyl), 4.62 (s, 6H, CHCOO), 1.42–1.47 (m, 12H, $CH_2CH_2CH_2CH_3$) and 1.17–1.04 (m, 24H, $CH_2CH_2CH_2CH_3$), 0.76 ppm (m, 18H, $CH_2CH_2CH_2CH_3$); ^{119}Sn NMR (150 MHz) $\delta = -485.0$ ppm (s).

X-ray crystallography: Crystal data for **1** and **3** were collected on a Bruker Smart diffractometer, while those of **5**, **7**, and **8** were collected on Bruker AXS Smart Apex diffractometer (Table 3). All structures were solved by direct methods using SHELXS-97[20] and refined by full-matrix least-squares techniques on F^2 using SHELXL-97.[20] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC-604710 (**1**), CCDC-604711 (**3**), CCDC-604712 (**5**), CCDC-604713 (**7**), and CCDC-604714 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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