Articles

α,ω-Bis(trialkynyltin) Compounds with a Linear or Cross-Shaped Spacer

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The preparation of arylene-, alkylene-, or dimethylenediphenyl-bridged bis(trichlorotin) compounds with two or three phenyl rings from the reaction of the corresponding hexacyclohexyl derivatives with tin tetrachloride is described. Hexachlorides with mixed aryl−alkyl bridges were prepared in the same way. When arylene-bridged ditins were substituted on aryl rings with alkoxy groups, it was necessary to use hexamethyl derivatives instead of the cyclohexyl compounds to obtain the corresponding hexachlorides. In these compounds, weak inter- and/or intramolecular interactions were detected by X-ray analysis. The ditin hexachlorides were transformed into the corresponding hexaalkynyl derivatives, precursors for hybrid materials.

For the past few years, research on hybrid materials constitutes a growing field in which organometallic chemistry has an important place. In class 2 hybrid materials,[1] the organic and the inorganic components are linked through covalent bonds, which requires the design and development of appropriate synthetic schemes necessary for the preparation of suitable precursors for these materials. Main approches to hybrid materials are based on silicon derivatives since silicon−carbon bonds of various types usually are stable toward sol−gel conditions, in which acidic, basic, or fluoride-catalyzed hydrolyses are used. Some functional groups can even be incorporated into the organic part of the hybrid materials and remain unchanged in the hybrid material after the whole preparative process, hydrolysis, aging, and drying. [1] It was reported recently that the disilylated compounds proved to be excellent precursors for various types of microporous or mesoporous silicas.[2] In that case, with aliphatic spacers, the duration of the gelification process is a function of the length of the spacer since medium-size spacers induce intramolecular cyclization reactions leading to soluble oligomers. This is not the case with aromatic, ethylenic, or acetylenic spacers, where the rigid rod-like spacer between the silicon atoms makes such cyclizations impossible and enables the preparation of gels even at very low concentrations of disilylated compounds.[3] These hybrid materials are often self-organized, which is detected either by birefringence studies or by X-ray data, when a spacer including an aromatic ring is used.[4] With more flexible alkylene chains as spacers, it is necessary to include functional groups able to increase the interchain interactions by formation of hydrogen bonds, such as urea groups.[5] Tin is a metal that forms carbon−metal bonds that are stable toward hydrolysis, which enables the preparation of hybrid materials.[6] However, due to the difficulty in obtaining the functional tin trialkoxides, which are the traditional starting materials for organosilicon hybrid materials, more accessible trialkynyltin derivatives were used instead.[7] Compounds containing two tin groups separated by short spacers can be prepared,[8] and they enable the synthesis

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[1] Gomez-Romero, P.; Sanchez, C. *Functional Hybrid Materials*; Wiley-VCM: Weinheim, Germany, 2003.

[2] (a) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306. (b) Shea, K. J.; Loy, D. A. *Acc. Chem. Res.* **2001**, *34*, 707. (c) Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431. (d) Cerveau, G.; Corriu, R. J. P.; Framery, E. *Chem. Mater.* **2001**, *13*, 3373. (e) Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1376.

[3] Chujo, Y.; Ihara, S.; Saegusa, T. *Macromolecules* **1993**, *26*, 5681.

[4] (a) Boury, B.; Corriu, R. J. P. *Chem. Commun.* **2002**, 795. (b) Boury, B.; Corriu, R. J. P.; Le Strat, V.; Delord, P.; Nobili, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3172. (c) Ben, F.; Boury, B.; Corriu, R. J. P. *Adv. Mater.* **2002**, *14*, 1081.

[5] (a) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C. *J. Am. Chem. Soc.* **2001**, *123*, 1509. (b) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C.; Bantignies, J.-L.; Dieudonné, P.; Sauvajol, J.-L. *J. Am. Chem. Soc.* **2001**, *123*, 7957.

[6] (a) Ribot, F.; Banse, F.; Sanchez, C.; Lahcini, M.; Jousseaume, B. *J. Sol-Gel Sci. Tech.* **1997**, *8*, 529. (b) Angiolini, L.; Caretti, D.; Carlini, C.; Jordens, F.; Jousseaume, B.; Niesel, T. *J. Inorg. Organomet. Polym.* **1998**, *8*, 48. (c) Jaumier, P. ; Jousseaume, B.; Riague, H.; Toupance, T.; Lahcini, M. In *Hybrid Organic/Inorganic Materials*; Laine, R. M., Sanchez, C., Giannelis, E., Brinker, C. J., Eds.; MRS, 2000; Vol. 628, p CC12.

[7] (a) Jousseaume, B.; Lahcini, M.; Rascle, M.-C.; Sanchez, C.; Ribot, F. *Organometallics* **1995**, *14*, 685. (b) Jousseaume, B.; Lahcini, M.; Fouquet, E.; Barbe, B. *J. Org. Chem.* **1994**, *59*, 8292. (c) Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1996**, *15*, 2237. (d) Jaumier, P.; Jousseaume, B.; Tiekink, E. R. T. Biesemans, M.; Willem, R. *Organometallics* **1997**, *16*, 5124. (e) Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Tiekink, E. R. T.; Lahcini, M.; Jaumier, P. ; Jousseaume, B. *Organometallics* **1998**, *17*, 90. (f) Jaumier, P.; Jousseaume, B.; Lahcini, M.; Ribot, F.; Sanchez, C. *J. Chem. Soc., Chem. Commun.* **1998**, 369. (g) Jaumier, P.; Jousseaume, B. *Main Group Met. Chem.* **1998**, *21*, 325. (h) Lahcini, M.; Jaumier, P.; Jousseaume, B. *Angew. Chem., Int. Ed.* **1999**, *32*, 402. (i) Willem, R.; Biesemans, M.; Jaumier, P.; Jousseaume, B. *J. Organomet. Chem.* **1999**, *572*, 233.

[8] Jousseaume, B.; Riague, H.; Toupance, T.; Lahcini, M.; Mountford, P.; Tyrrell, B. R. *Organometallics* **2002**, *21*, 4590.

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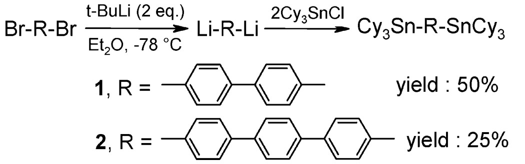
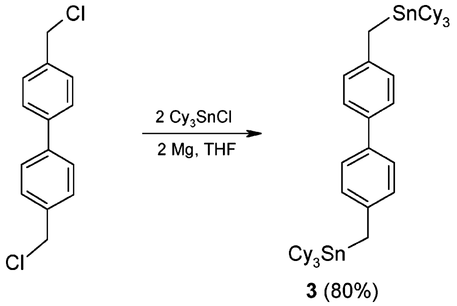
Scheme 1. Preparation of 4,4′-Bis(tricyclohexyltin)biphenyl (1) and 4,4″-Bis(tricyclohexyltin)-1,1′:4′,1″-terphenyl (2)



Scheme 2. Preparation of 4,4′-Bis(tricyclohexyltinmethyl)biphenyl (3)



of self-organized hybrid materials[9] in which layers of tin oxide are separated by the autoassembled organic spacers. However the starting materials used were limited to examples with short connected chains between the metals. In order to broaden the scope of the available precursors, we present here the synthesis of alkyl, aromatic, or benzylic α,ω-ditin hexaalkynyls in which the tin atoms are separated by two or three phenyl rings. Moreover, we report also the preparation and the structural characterization of cross-shaped aromatic α,ω-ditin hexaalkynyls with one or three benzene rings substituted by long alkoxy groups.

Results and Discussion

Many methods for the preparation of α,ω-ditin derivatives have been reported up to now. The first one involves the coupling of an α,ω-Grignard or an α,ω-dilithium reagent with a triorganotin halide or the coupling of a triorganotinmetal with an α,ω-dihalide. It can be successfully used when the chain separating the tin atoms is either of aliphatic[10,11] or aromatic type.[12,13] The second method, which is useful when dimetallic species are not available, is conducted under milder conditions, as it involves the palladium-catalyzed[14] or uncatalyzed[15] addition of hexaorganoditins to unsaturated compounds. Finally, the hydrostannation of unsaturated compounds is also very convenient to prepare compounds containing two separated tin atoms, as this addition reaction is highly regiospecific and thus leads to linear compounds.[16]

To prepare hexaalkynylditins where the tin atoms are separated by two or three aromatic rings, we employed the method that led successfully to simpler compounds. This strategy consists of the preparation of hexacyclohexylditins via di-Grignard reagents and their cleavage with tin tetrachloride to obtain the corresponding hexachlorides, followed by the alkynylation of these polychlorides with alkynyllithiums. However the previously described way was not very satisfactory since the coupling of 4,4′-di(bromomagnesio)biphenyl or 4,4″-di-(bromomagnesio)-1,1′:4′,1″-terphenyl with tricyclohexyltin chloride led to very poor yields of the corresponding ditin derivatives. Fortunately, the corresponding dilithio reagents were more soluble and enabled the isolation of the ditin compounds in satisfactory yields. In order to measure the distance between the tin atoms, necessary for the study of the derived hybrid materials, a structural study of 4,4″-bis(tricyclohexyltin)-1,1′:4′,1″-terphenyl (**2**) was conducted. Suitable crystals were grown from a toluene solution of **2**. The asymmetric unit of the crystal structure is illustrated in Figure 1. The molecule in the solid state is characterized by non-coplanar phenyl rings, with the central one twisted by about 30° relative to each of the other rings. In the case of *p*-terphenyl, crystallographic studies reveal a similar coplanar relationship between the remote rings, with the central ring twisted by about 13°.[17] In the case of substituted *p*-terphenyl the central ring can be twisted up to about 31°.[18] The cyclohexyl rings are nearly staggered with respect to the Sn−Sn axis, the dihedral angles $C_{Cyclohexyl}-Sn-Sn-C_{Cyclohexyl}$ varying from 50° to 78°. Each tin atom is in a tetrahedral environment and is slightly outside of the plane formed by the

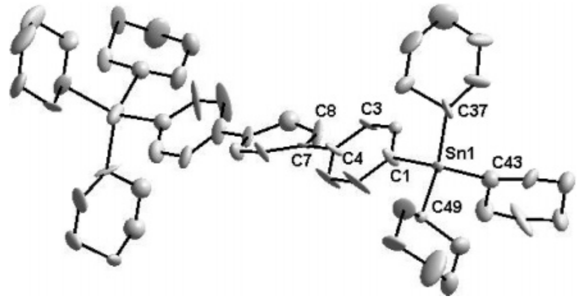


Figure 1. Molecular structure of **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C1 2.147(12), Sn1−C43 2.161(13), Sn1−C49 2.166(9), Sn1−C37 2.169(14), C1−Sn1−C43 101.6(5), C1−Sn1−C49 109.3(4), C43−Sn1−C49 112.7(5), C1−Sn1−C37 107.5(6), C43−Sn1−C37 109.1(5), C49−Sn1−C37 115.6(5), C3−C4−C7−C8 30.1(1).

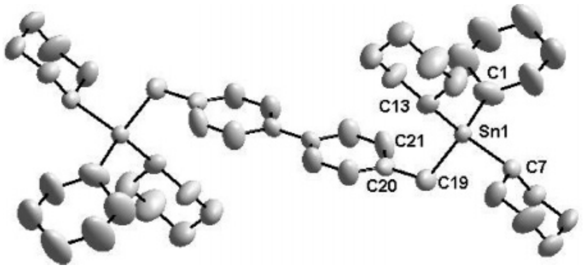


Figure 2. Molecular structure of **3**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C1 2.147(12), Sn1−C7 2.182(7), Sn1−C19 2.156(9), Sn1−C13 2.180(9), C1−Sn1−C19 110.2(5), C1−Sn1−C13 115.1(4), C13−Sn1−C19 110.5(4), C1−Sn1−C7 109.0(4), C7−Sn1−C19 103.3(3), C7−Sn1−C13 108.1(3), Sn1−C19−C20 117.5(6), Sn1−C19−C20−C21 77.0(1).

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[9] Elhamzaoui, H.; Jousseaume, B.; Riague, H.; Toupance, T.; Dieudonne, P.; Zakri, C.; Maugey, M.; Allouchi, H. *J. Am. Chem. Soc.* **2004**, *126*, 8130.

[10] Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1976**, *110*, 167.

[11] Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651.

[12] (a) Boue, S.; Gielen, M.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1967**, *76*, 559. (b) Juara, K. L.; Hundal, H. S.; Handa, R. D. *Indian J. Chem.* **1967**, *5*, 211.

[13] Wursthorn, K. R.; Kuivila, H. G.; Smith, G. F. *J. Am. Chem. Soc.* **1977**, *100*, 2779.

[14] Mitchell, T. M.; Amamria, A.; Killing, H.; Rutshow, D. *J. Organomet. Chem.* **1986**, *304*, 257.

[15] Beg, M. A. A.; Clark, H. C. *Chem. Ind.* **1962**, 140.

[16] Van der Kerk, G. J. M.; Noltes, J. G. *J. Appl. Chem.* **1957**, *7*, 366.

[17] Baudour, J. L. *Acta Crystallogr.* **1991**, *B47*, 935.

[18] Xu, J.; Côté, A. P.; Chen, B. *Acta Crystallogr.* **2004**, *E60*, 1697.

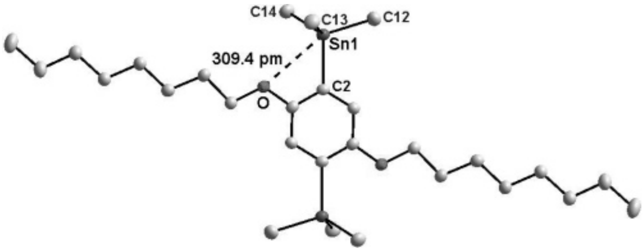


Figure 3. Molecular structure of **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C12 2.1509(27), Sn1−C13 2.1378(28), Sn1−C14 2.1408(30), Sn1−C2 2.1461(20), C12−Sn1−C13 111.52(10), C12−Sn1−C14 109.38(11), C13−Sn1−C14 110.36(11), C2−Sn1−C12 109.92(9), C2−Sn1−C13 106.14(9), C2−Sn1−C14 113.44(9).

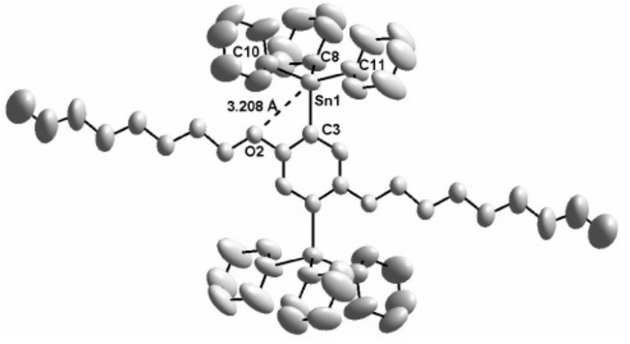
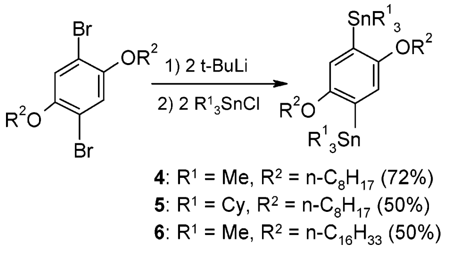


Figure 4. Molecular structure of **5**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C10 2.142(5), Sn1−C3 2.148(4), Sn1−C8 2.172(4), Sn1−C11 2.180(5), C10−Sn1−C3 111.51(18), C10−Sn1−C8 109.66(19), C3−Sn1−C8 107.96(16), C10−Sn1−C11 113.2(2), C3−Sn1−C11 103.91(17), C8−Sn1−C11 110.40(19).

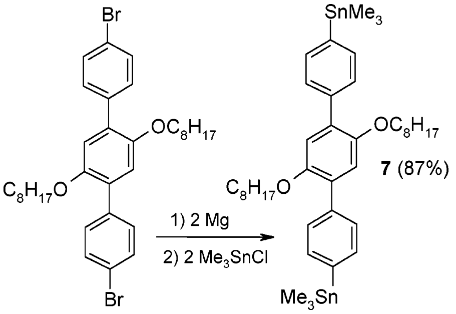
Scheme 3. Preparation of 2,5-Dialkyloxy-1,4-bis(trialkyltin)benzenes (4−6)



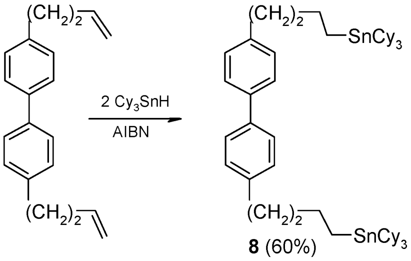
terminal rings (aromatic plane−C1−Sn: 5.6°). The distance between the tins is 15.77 Å.

4,4′-Bis(tricyclohexyltinmethyl)biphenyl (**3**) was successfully prepared by a Barbier reaction, since lithium or magnesium reagents derived from 4,4′-bis(chloromethyl)biphenyl are not stable. Thus, the treatment of a THF solution of 4,4′-bis(chloromethyl)biphenyl and tricyclohexyltin chloride with magnesium led to **3** in good yield. The X-ray diffraction study of a monocrystal of **3** revealed a centrosymmetric structure with coplanar aromatic rings (Figure 2). The tricyclohexyltin groups are in the anti position, in contrast to that observed in its hexaphenyl analogue with one aromatic ring, where the triphenyltin groups are in the syn position, probably because of a more favorable crystal packing.[19] The tin environment is normal for a tricyclohexyl derivative, and the distance between the tins is 12.78 Å.

Scheme 4. Preparation of 2′,5′-Dioctyloxy-4,4″-bis(trimethyltin)-1,1′:4′,1″-terphenyl (7)



Scheme 5. Preparation of 4,4′-Bis(4-tricyclohexyltinbutyl)biphenyl (8)



We encountered the same difficulty for the preparation of aromatic ditin compounds substituted with long side arms as for the preparation of **1** and **2**, the use of a di-Grignard reagent leading only to poor results. However, the coupling of the corresponding dilithium reagents with tricyclohexyl- and trimethyltin chloride enabled the isolation of the ditin derivatives in satisfactory yields. The crystal structures of compounds **4** (Figure 3), **5** (Figure 4), and **6** (Figure 5) were determined. **5** shows a center of symmetry and the tins are in the same slightly distorted tetrahedral environment as in **3**. They lie in the plane of the aromatic ring. The long tin−oxygen distance, 3.21 Å, forbids any eventual coordination of the metals by the oxygen atoms. The cyclohexyl groups are in an almost perfect staggered position with respect to the Sn−Sn axis, the dihedral angles $C_{Cyclohexyl}$−Sn−Sn−$C_{Cyclohexyl}$ varying from 59° to 63°. The alkoxyl chains present an all-trans conformation and are close to being coplanar with the plane of the aromatic ring (dihedral angle: 3.8°). The crystal structures of **5** and **6** are nearly the same, except that the steric release around the tin atoms introduced by changing bulky cyclohexyl groups by smaller methyl groups allows a closer contact between tin and oxygen atoms, 3.09 Å in **4** and 3.06 Å in **5** instead of 3.21 Å in the case of **6**. The side chains are in an all-trans conformation. They are slightly more twisted (6.5°) in **6** than in **5**, but the terminal methyl groups lie out of the chain plane, probably to avoid too close contacts with the methyl groups linked to the tin atom of another molecule. The distance between the tins in **4** and **6** is 7.11 Å (7.14 Å in **5**), and the distance between the terminal carbon atoms of the chains is 25.22 Å in **4**, 24.51 Å in **5**, and 44.07 Å in **6**.

When the spacer between the tin atoms was of a *p*-terphenyl type, with the central ring substituted with two alkoxyl chains, the use of the corresponding di-Grignard reagent was shown to be more advantageous than that of the corresponding dilithium reagent. The Grignard route led to the ditin compound **7** with an 87% yield. It is a centrosymmetric molecule in the solid state

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(19) Thodupunoori, S. K.; Alamudun, I. A.; Cervantes-Lee, F.; Gomez, F. D.; Carrasco, Y. P.; Pannell, K. *J. Organomet. Chem.* **2006**, *691*, 1790.

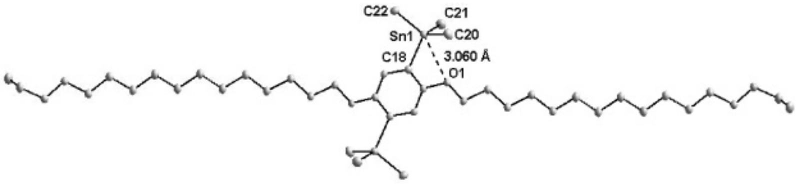


Figure 5. Molecular structure of **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C20 2.135(2), Sn1−C21 2.138(2), Sn1−C18 2.1466(18), Sn1−C22 2.147(2), C20−Sn1−C21 110.75(9), C20−Sn1−C18 109.92(8), C21−Sn1−C18 110.46(8), C20−Sn1−C22 109.18(9), C21−Sn1−C22 110.08(9), C18−Sn1−C22 106.35(8).

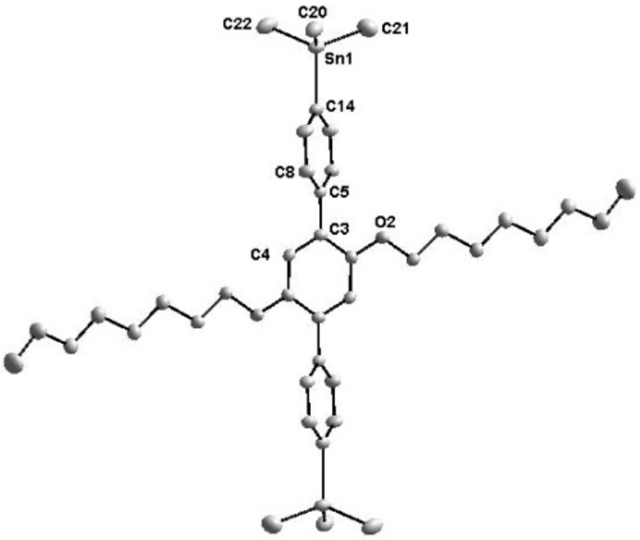


Figure 6. Molecular structure of **7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C20 2.128(2), Sn1−C21 2.139(2), Sn1−C22 2.143(2), Sn1−C14 2.1483(17), C20−Sn1−C21 113.05(9), C20−Sn1−C22 110.94(9), C21−Sn1−C22 107.73(10), C20−Sn1−C14 107.08(8), C21−Sn1−C14 107.80(8), C22−Sn1−C14 110.19(8), C8−C5−C3−C4 39.4(2).

Figure 7. Molecular structure of **12**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−Cl1 2.518(3), Sn1−Cl2 2.218(2), Sn1−Cl3 2.179(3), Sn1−C4 2.221(5), Cl3−Sn1−Cl2 111.56(11), Cl3−Sn1−C4 120.1(3), Cl2−Sn1−C4 109.9(2), Cl3−Sn1−Cl1 85.85(12), Cl2−Sn1−Cl1 95.02(12), C4−Sn1−Cl1 130.8(3).

(Figure 6). The aromatic rings are much more twisted (39.4°) than in **2**, and the side chains are almost coplanar. In the crystal, the molecules are arranged in such a manner that all the corresponding planes are parallel. The distance between the tins is 15.77 Å, and the distance between the terminal carbon atoms of the chains is 25.09 Å.

As 4,4′-di(but-3-enyl)biphenyl was found readily available from the dimerization of 1-bromo-4-(but-3-enyl)benzenyl magnesium in the presence of titanium tetrachloride,[20] the radical addition of tricyclohexylstannane to the α,*ω*-diene was used to obtain the corresponding ditin compound. Thus, treatment of the diene with an excess of stannane at 130 °C for 7 days in the presence of AIBN (portionwise added during the reaction) led to **8** in a good yield (60%). Then the bis(tricyclohexylated) compounds **1**−**3**, **5**, and **8** were treated with 1 equiv of tin tetrachloride at 70 °C (20 °C for **8**) for 1 day (3 days for **8**), which resulted in the complete replacement of the tricyclohexyltin groups by trichlorotin groups. Extraction with a mixture pentane/acetonitrile or washing with pentane both led to the bis(trichlorotin) compounds in high yields, except in the case of **5**, where the hexachloride was very soluble in pentane and could not be separated from tricyclohexyltin chloride. We thus had to find another way to prepare the very lipophilic ditin hexachlorides. It was anticipated that a secondary product with a very low boiling point could be separated from the heavy hexachlorides in conditions mild enough not to decompose them. We thus treated the hexamethylated ditins with an excess of tin tetrachloride (4 equiv/Sn) at 120 °C for a few hours and then distilled the mixture of unreacted tin tetrachloride and methyltin chlorides under high vacuum. The crude hexachlorides were pure enough to be used in the next step without further purification. The crystal structure of **12** was determined by X-ray diffraction (Figure 7). The molecule has a center of symmetry and the tin atoms are in a slightly distorted tetrahedral environment, which is normal for an alkyltin trichloride. The

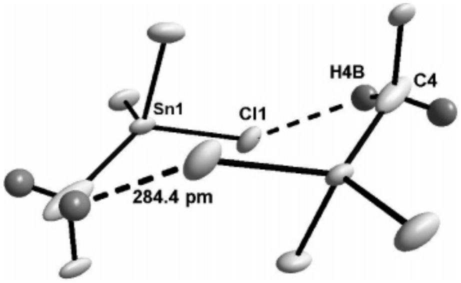
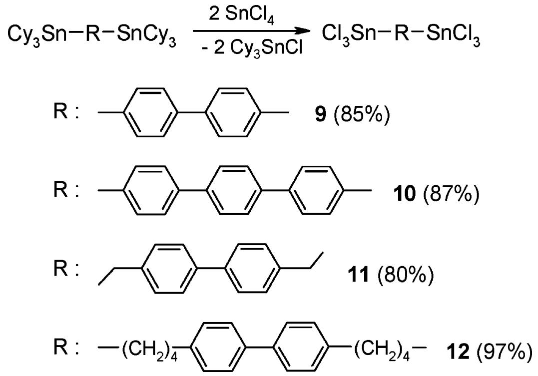


Figure 8. Intermolecular bonding in **12**.

Scheme 6. Preparation of Linear Ditin Hexachlorides (9−12)



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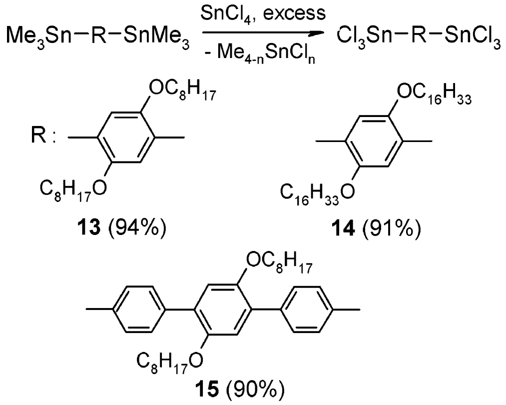
[20] Inoue, A.; Kitagawa, K.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2000**, *56*, 9601.

Scheme 7. Preparation of Cross-Shaped Ditin Hexachlorides (13−15)



more prominent feature of this structure is the folded conformation of the butylene chains, which are not completely extended, whereas the structures of ditin hexachlorides with the metal atoms separated by an alkylene chain are linear. However, the tin atoms and the last carbon of the chains are in the plane of the aromatic rings. The tin−tin distance is shorter (16.41 Å) than expected (21.21 Å) if the chains were completely extended, which results from this folding. Such an arrangement could be explained by the existence of stabilizing interactions between the Cl1 and the H4B of a neighboring molecule, as the distance between these atoms is 2.84 Å and the angle C4−H4B−Cl1 is 140° (Figure 8). These atoms are part of an eight-membered ring[21] in a pseudochair conformation formed with two chlorine, two hydrogen, two carbon, and two tin atoms. Such close contacts are shorter than OH−Cl[22] (3.40 Å) or NH−Cl[23] (3.12 Å) interactions in titanium complexes but longer than CH−Cl interactions in chloroform-solvated platinum[24] (2.76 Å) or than charge-assisted CH−Cl interactions in gold[25] (2.59 Å) complexes. The value of the C4−H4B−Cl1 angle (140°) shows that this interaction can be described as a hydrogen bond rather than as a van der Waals contact.[26] As a consequence, the Sn1−Cl1 bond is considerably lengthened. It measures 2.51 Å, whereas the length of other Sn−Cl bonds are 2.18 and 2.22 Å, respectively.

The molecular structure of **13** is shown in Figure 9. It differs from the corresponding trialkylated compounds **4** and **5** by a shorter tin−oxygen distance, 2.86 Å instead of 3.09 and 3.21 Å, respectively, indicating the existence of a weak coordination bond between both atoms, disfavored by the formation of a sterically demanding four-bond ring. The difference between the sum of the angles formed by the equatorial bonds and the sum of the angles formed by the axial bonds is 22.6° (0° for a tetrahedron, 90° for a trigonal bipyramid).[27] The tin lies 0.60 Å above the C2−Cl1−Cl2 plane. The geometry of the tin can thus be considered as that of a distorted tetrahedron. The structure of **13** also differs by a significantly different orientation of the side chains. The angle between the Sn−Sn axis and the side chain ranges from 80° and 81° in **4** and **5**, respectively, to 28.6° in **13**. This different behavior could be due to the angle made by the Sn−C2 bond and the O4−C3 bond, which is smaller in **13** than in its methylated analogue **6**, which thus brings closer the chain from the tin atom. Another possible reason could be the existence of weak interactions between the chlorine atom Cl2 and the hydrogen atom H7A, which are separated by 3.08 Å. The distance between the terminal carbon atoms of the chains is 23.52 Å.

The molecular structure of **14** is roughly identical to that of **13**, with fully extended side arms and a distorted tetrahedral environment of tin atoms. Then alkynylation of the hexachlorides was performed with a stoichiometric amount of propynyllithium at low temperature to form the corresponding hexaalkynylditins in a good yield as crystalline solids.

The molecular structure of **20** is depicted in Figures 11 and 12. It shows a center of symmetry. The tin atoms are in a slightly distorted tetrahedral environment, not so different from what has been observed in **4**, with a shorter Sn−O distance, 2.96 Å instead of 3.09 Å, which can be explained by the higher electrophilic character of the tin due to the electroattractive propynyl groups. However, this distance is longer than when the tin is substituted by chlorine atoms as in **13**, 2.86 Å. It is worth noting the regular variation of the tin−oxygen bond distance and of the $Sn^1-C^2-C^3$ and $O^4-C^5-C^6$ angles (see Table 1) with the electronegativity of the substituents of the tin atoms in **5**, **6**, **13**, **14**, and **20**. ^{119}Sn NMR proved to be a very powerful tool to study weak coordination of tin in solution. [7] The ^{119}Sn chemical shifts of **5**, **6**, **13**, **14**, and **20** were thus compared to the ^{119}Sn chemical shifts of their unsubstituted analogues. However, while upfield shifts were expected, only inconclusive differences were found. The side chains are not coplanar with the aromatic ring, as they are in the hexamethylated **4**. From C5, the plane of the chain is almost perpendicular to the aromatic ring. Moreover, the axis of the chain is out of the aromatic plane, almost parallel to an alkynyl group, and forms an angle of 64° with the aromatic ring. This position of the chain could be explained by the existence of a favorable interaction between the hydrogen atom H8B with the π electrons of one of the triple bonds. The distance between H8B and the triple bond is 3.24 Å, and the angle C8−H8B−triple bond is 141°. Such weak bonds have already been described in alkynylmetallic compounds where the metal makes the triple bond more nucleophilic.[28] It usually involves acidic hydrogen atoms, like those of chloroform,[29] cyclopentadienes,[30] or alkynes,[31] with distances varying from 2.33 to 2.61 Å.

Compounds **16**−**22** were subsequently hydrolyzed in THF, yielding transparent or opaque gels, depending on the hydrolysis conditions, which were then thermolyzed, forming high surface area mesoporous tin oxide.[32]

In conclusion, we have developed synthetic methods for the preparation of ditin compounds where the organic groups

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(21) Baldovino-Pantaleon, O.; Morales-Morales, D.; Hernandez-Ortega, S.; Toscano, R. A.; Valdes-Martinez, J. *Cryst. Growth Des.* **2007**, *7*, 117.

(22) Bastiansen, O.; Fernholt, L.; Hedberg, K.; Seip, R. *J. Am. Chem. Soc.* **1985**, *107*, 7836.

(23) Guzei, I. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 4415.

(24) Jones, P. G.; Schmutzler, R.; Vogt, R. *Acta Crystallogr.* **2002**, *E58*, m476.

(25) Freytag, M.; Jones, P. G. *Chem. Commun.* **2000**, 277.

(26) (a) Aullon, G.; Bellamy, D.; Guy Orpen, A.; Brammer, L.; Bruton, E. A. *Chem. Commun.* **1998**, 653. (b) Thallapally, P. K.; Nangia, A. *CrystEngComm* **2001**, *3*, 114.

(27) Kolb, U.; Dräger, M.; Jousseaume, B. *Organometallics* **1991**, *10*, 2737.

(28) Fan, M.-F.; Lin, Z.; McGrady, J. E.; Mingos, M. P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 563.

(29) Müller, T. E.; Mingos, M. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1787.

(30) Steiner, T.; Tamm, M. *J. Organomet. Chem.* **1998**, *570*, 235.

(31) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1995**, 95.

(32) (a) Toupance, T.; El Hamzaoui, H.; Jousseaume, B.; Riague, H.; Saadeddin, I.; Campet, G.; Brötz, J. *Chem. Mater.* **2006**, *18*, 6364. (b) Boutet, S.; Jousseaume, B.; Toupance, T.; Biesemans, M.; Willem, R.; Labrugere, C.; Delattre, L. *Chem. Mater.* **2005**, *17*, 1803. (c) Vilaca, G.; Jousseaume, B.; Mahieux, C.; Toupance, T.; Belin, C.; Cachet, H.; Bernard, M.-C.; Vivier, V. *Adv. Mater.* **2006**, *18*, 1073. (d) Elhamzaoui, H.; Jousseaume, B.; Toupance, T.; Zakri, C.; Maugey, M. *Langmuir* **2007**, *23*, 785.

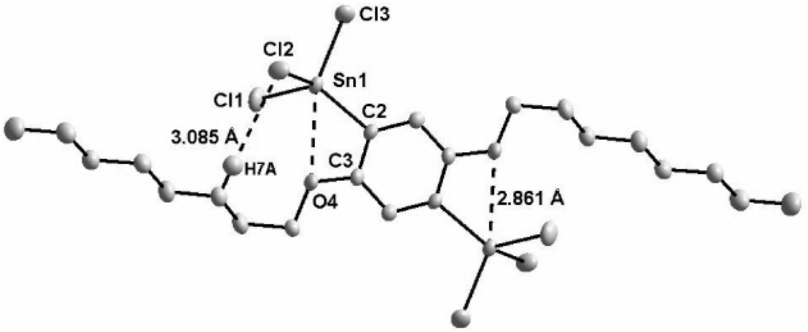


Figure 9. Molecular structure of **13**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C2 2.091(3), Sn1−Cl1 2.2978(11), Sn1−Cl2 2.3055(10), Sn1−Cl3 2.3225(10), C2−Sn1−Cl1 116.64(10), C2−Sn1−Cl2 118.26(11), Cl1−Sn1−Cl2 104.06(4), C2−Sn1−Cl3 107.57(10), Cl1−Sn1−Cl3 104.13(4), Cl2−Sn1−Cl3 104,75(4).

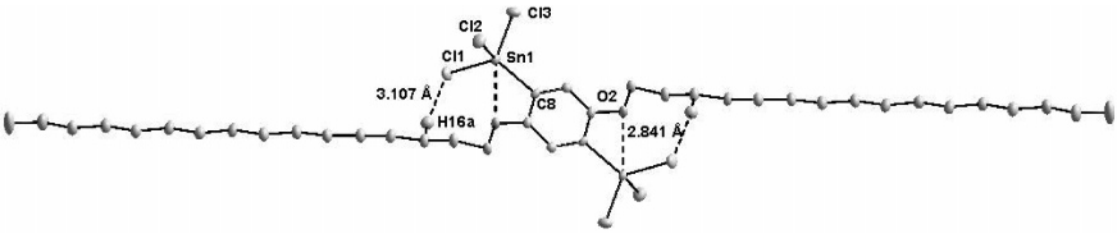


Figure 10. Molecular structure of **14**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C8 2.096(3), Sn1−Cl2 2.2962(10), Sn1−Cl1 2.3011(10), Sn1−Cl3 2.3242(10), C8−Sn1−Cl2 114.59(10), C8−Sn1−Cl1 119.21(10), Cl2−Sn1−Cl1 104.96(4), C8−Sn1−Cl3 108.04(10), Cl2−Sn1−Cl3 105.65(4), Cl1−Sn1−Cl3 103.06(4).

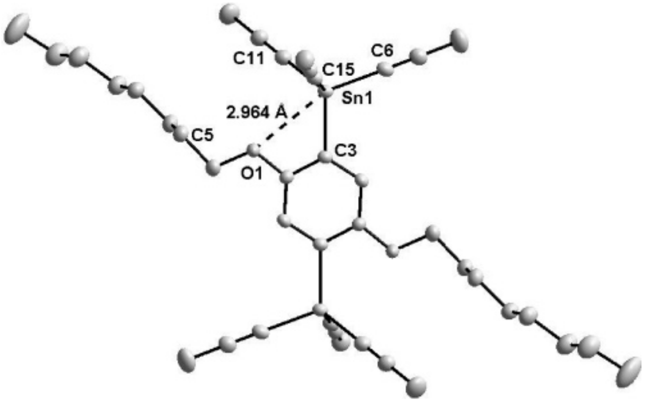
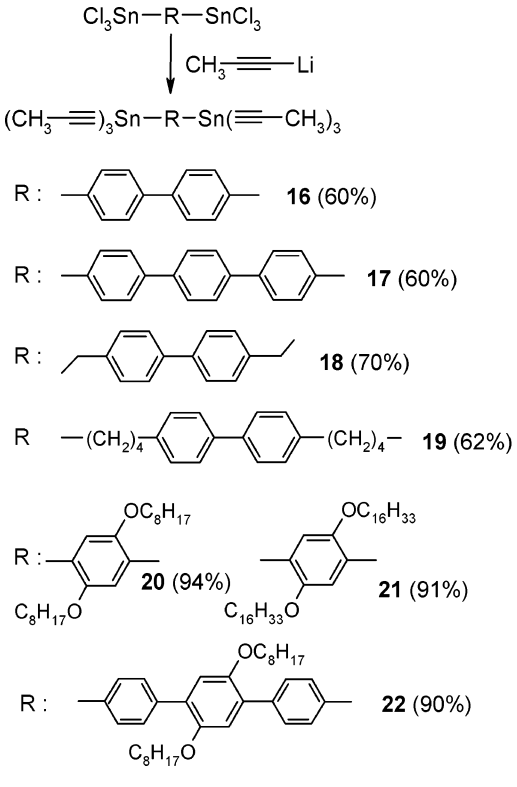


Figure 11. Molecular structure of **20**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Sn1−C11 2.073(2), Sn1−C6 2.081(2), Sn1−C15 2.082(2), Sn1−C3 2.1068(19), C11−Sn1−C6 106.49(9), C11−Sn1−C15 108.65(8), C6−Sn1−C15 108.07(8), C11−Sn1−C3 116.28(8), C6−Sn1−C3 107.96(8), C15−Sn1−C3 109.10(8).

Scheme 8. Preparation of Hexapropynylditins (16−22)



separating the tin atoms can be substituted or not with long aliphatic chains. X-ray diffraction studies showed that weak tin−oxygen interactions exist in the ditin derivatives with an oxygen atom in the *β*-position from the tin atom, which results in the formation of an unfavorable four-membered ring.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Pentane, THF, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Acetonitrile was distilled over CaH_2. Tin tetrachloride was distilled before use. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker AC 200, AC 250, or DPX 300 spectrometer (solvent $CDCl_3$). Tin−hydrogen and tin−carbon coupling constants are given in square brackets. Elemental analyses were performed by the “Service d’analyse du CNRS” at Vernaison, France.

4,4′-Bis(tricyclohexyltin)biphenyl (1). A solution of 4,4′-dibromobiphenyl (4 g, 12.8 mmol) in diethyl ether (400 mL) was cooled to −78 °C with an ethanol/liquid N_2 bath. With the addition

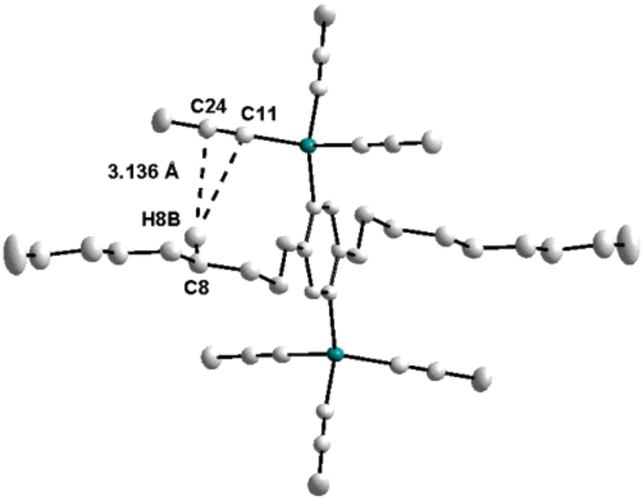
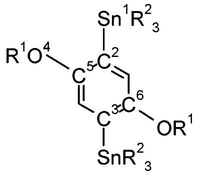


Figure 12. Another view of **20**.

Table 1. Tin−Oxygen Distances and O−C and Sn−C Alignment in the Ditin Compounds 4, 5, 6, 13, 14, and 20



compound	R^1	R^2	d_{Sn-O} (Å)	Sn^1−C^2−C^3 (deg)	O^4−C^5−C^6 (deg)
4	*n*-C_8H_{17}	Me	3.094	175.8	175.9
5	*n*-C_8H_{17}	Cy	3.208	177.9	177.4
6	*n*-$C_{16}H_{33}$	Me	3.060	177.6	175.9
13	*n*-C_8H_{17}	Cl	2.861	172.8	173.2
14	*n*-$C_{16}H_{33}$	Cl	2.841	172.2	172.2
20	*n*-C_8H_{17}	propynyl	2.964	172.8	174.0

of *tert*-butyllithium (34.2 mL, 1.5 M in pentane, 4 equiv) the white suspension turned slightly orange after 4 h under stirring. The mixture was warmed to room temperature for 2 h, and the suspension turned yellow. It was cooled to −78 °C again, before adding a solution of tricyclohexyltin chloride (13.0 g, 32.2 mmol) in THF (100 mL). After 30 min, the reaction was allowed to warm to room temperature. After stirring for 72 h, the mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted. The solvents were removed in vacuo. The resulting product was recrystallized from 2-methylbutan-2-ol to give **1** (5.71 g) in a 50% yield. Mp: 227 °C. ^{1}H NMR: δ 1.1−1.2 (m, 66H), 7.5−7.65 (m, 8H). ^{13}C NMR: δ 27.2 [334], 27.4, 29.6 [56], 32.6 [16], 126.6 [36], 137.8 [26], 140, 140.8. ^{119}Sn NMR: δ −101.7. Anal. Calcd for $C_{48}H_{74}Sn_2$: C, 64.88; H, 8.39; Sn, 26.72. Found: C, 65.13; H, 8.31; Sn, 26.84.

4,4′-Bis(trichlorotin)biphenyl (9). $SnCl_4$ (2.5 mL, 21.3 mmol) was slowly added to a solution of 4,4′-bis(tricyclohexyltin)biphenyl (7 g, 7.9 mmol) in toluene (100 mL). After stirring at room temperature for 3 h, the mixture was warmed to 70 °C for 12 h. Then the solvent was evaporated under reduced pressure. Acetonitrile (100 mL) was added. The solution was extracted with pentane (5 × 50 mL) to remove the tricyclohexyltin chloride. To displace acetonitrile, a washing with THF (2 × 300 mL) was performed. Mp: 85 °C. Yield: 5 g (85%). ^{1}H NMR: δ 7.18 (s, 8H) [125, 108, 44, 31] with coordinated acetonitrile (or 7.70−7.9 (m, 8H) with coordinated THF). ^{13}C NMR: δ 129.1 [128, 4], 134.9 [80], 136.5, 144.3. ^{119}Sn NMR: δ −68.1 (with coordinated acetonitrile), −163.3 (with coordinated THF). Anal. Calcd for $C_{12}H_8Cl_6Sn_2 \cdot 2THF$: C, 32.17; H, 3.24; O, 4.28; Cl, 28.49; Sn, 31.80. Found: C, 30.81; H, 3.10; O, 5.23; Cl, 28.16; Sn, 31.45.

4,4′-Bis(triprop-1-ynyltin)biphenyl (16). A solution of *n*-butyllithium (23.9 mL, 59.7 mmol) in hexane (2.5 M) was slowly added to a solution of propyne (87.4 mmol) in toluene (55 mL) at −78 °C. After 15 min stirring at room temperature, a solution of 4,4′-bis(trichlorotin)biphenyl (5 g, 8.3 mmol) in toluene (100 mL) was added at −78 °C. The suspension was stirred at room temperature for 12 h and then filtered on dry $MgSO_4$ under dry N_2, and the toluene was evaporated to give **16** (3.1 g) as a white solid. Mp: 250 °C dec. Yield: 60%. ^{1}H NMR: δ 1.97 (s, 18H, [15]), 7.6−7.8 (m, 8H, [73]). ^{13}C NMR: δ 5.3 [16], 76.0 [934], 108.5 [193], 127.6 [80], 134.3, 136.1 [59], 142.6. ^{119}Sn NMR: δ −285.2 [931, 193]. Anal. Calcd for $C_{30}H_{24}Sn_2$: C, 57.75; H, 4.20; Sn, 38.05. Found: C, 57.08; H, 4.57; Sn, 38.22.

4,4′′-Bis(tricyclohexyltin)-1,1′:4′,1′′-terphenyl (2). A suspension of 4,4′′-dibromo-1,1′:4′,1′′-terphenyl[33] (10 g, 25.7 mmol) in diethyl ether (425 mL) was cooled to −78 °C with an ethanol/liquid N_2 bath. With the addition of *tert*-butyllithium (68.75 mL, 1.5 M in pentane, 4 equiv) the white suspension turned yellow after 4 h under stirring.[34] The mixture was warmed to room temperature for 1 h. It was cooled to −78 °C again, before adding a solution of tricyclohexyltin chloride (20 g, 49.5 mmol) in THF (100 mL). After 30 min, the reaction was allowed to warm to room temperature. After stirring for 72 h, the mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted. The solvent was removed in vacuo, and the resulting product was recrystallized from 2-methylbutan-2-ol to give **2** (6.2 g) as a white solid. Mp: 250 °C dec. Yield: 25%. ^{1}H NMR: δ 1.1−2 (m, 66H), 7.5−7.65 (m, 8H), 7.69 (s, 4H). ^{13}C NMR: δ 27.2 [344], 27.4, 29.5 [57], 32.5 [17], 126.5 [37], 127.5, 137.9 [26], 140.2, 140.24, 140.3. ^{119}Sn NMR: δ −101.5. Anal. Calcd for $C_{54}H_{78}Sn_2$: C, 67.24; H, 8.15; Sn, 24.61. Found: C, 67.99; H, 8.31; Sn, 22.71.

4,4′′-Bis(trichlorotin)-1,1′:4′,1′′-terphenyl (10). $SnCl_4$ (2 mL, 17 mmol) was slowly added to a solution of 4,4′′-bis(tricyclohexyltin)-1,1′:4′,1′′-terphenyl (6.5 g, 6.7 mmol) in toluene (200 mL). After stirring at room temperature for 3 h, the mixture was warmed to 70 °C under stirring for 24 h, and the solvent was evaporated under reduced pressure. The solid was extracted with petroleum ether (4 × 30 mL) to remove the tricyclohexyltin chloride. The solvent was evaporated to give **10** (3.95 g) as a white solid. Mp: 200 °C. Yield: 87%. ^{1}H NMR: δ 7.74 (s, 4H), 7.75−7.90 (m, 8H). ^{13}C NMR: δ 128.2, 128.9, 134.7, 135.3, 139.7, 145.4. ^{119}Sn NMR: δ −58.4. Anal. Calcd for $C_{18}H_{12}Cl_6Sn_2$: C, 31.87; H, 1.78; Cl, 31.35; Sn, 35.00. Found: C, 31.66; H, 2.02; Cl, 31.09; Sn, 31.30.

4,4′′-Bis(triprop-1-ynyltin)-1,1′:4′,1′′-terphenyl (17). 17 was prepared as **16**. Mp: 250 °C (dec). Yield: 60%. ^{1}H NMR: δ 1.96 (s, 18H, [15]), 7.6−7.8 (m, 12H). ^{13}C NMR: δ 5.4 [16], 76.1 [931], 108.6 [193], 127.6 [80], 127.8 [72], 134.1, 136.2 [58], 140.2, 142.5 [15]. ^{119}Sn NMR: δ −285.2 [931, 193, 80]. Anal. Calcd for $C_{24}H_{30}Sn_2$: C, 61.77; H, 4.32; Sn, 33.92. Found: C, 51.64; H, 4.56; Sn, 32.56.

4,4′-Bis(tricyclohexyltinmethyl)biphenyl (3). A solution of 4,4′-bis(chloromethyl)biphenyl (7.77 g, 30.9 mmol) and chlorotricyclohexyltin (25 g, 61.9 mmol) in 100 mL of THF was added dropwise to a suspension of magnesium (5 g, 206 mmol) in 50 mL of THF. The mixture was then refluxed for 2 h. After hydrolysis, extraction with pentane (200 mL), and drying, the solvents were evaporated. The resulting product was recrystallized from 2-methylbutan-2-ol to give **3** (22.6. g) as a white solid. Mp: 158 °C. Yield: 80%. ^{1}H NMR: δ 1−2 (m, 66H), 2.34 (s, 4H [52]), 7.08 (d, 4H [8]), 7.40 (d, 4H [8]). ^{13}C NMR: δ 15.6 [201], 27.2 [320], 27.4, 29.5 [55], 32.4 [16], 126.6, 127.9 [18], 136.1 [12], 142.7 [32].

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(33) Wang, Z.; Heising, J. M.; Clearfield, A. *J. Am. Chem. Soc.* **2003**, *125*, 10375.

(34) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.

^{119}Sn NMR: −74.4. Anal. Calcd for $C_{50}H_{78}Sn_2$: C, 65.52; H, 8.58; Sn, 25.90. Found: C, 65.22; H, 8.87; Sn, 24.74.

4,4′-Bis(trichlorotinmethyl)biphenyl (11). $SnCl_4$ (6 mL, 51,1 mmol) was slowly added to a solution of **3** (17.59 g, 19.2 mmol) in 60 mL of toluene at 0 °C. After stirring overnight, toluene and excess $SnCl_4$ were evaporated. The residue was taken up in acetonitrile (250 mL) and extracted with pentane (5 × 60 mL). Evaporation of acetonitrile gave a green oil, which was washed with THF (2 × 300 mL). **11** (9.68 g) was obtained as a solid after evaporation of THF. Yield: 80%. Mp: 125 °C dec. ^{1}H NMR: δ 3.72 (s, 4H [107]), 7.36 (d, 4H [8]), 7.60 (d, 4H [8]). ^{119}Sn NMR: δ −63.5.

4,4′-Bis(triprop-1-ynyltinmethyl)biphenyl (18). **18** was prepared as **16**. Mp: 178 °C. Yield: 70%. ^{1}H NMR: δ 1.88 (s, 18H [15]), 2.71 (s, 4H [96]), 7.22 (d, 4H), 7.48 (d, 4H). ^{13}C NMR: δ 5.3 [16], 23.0 [575], 76.2 [851], 108.5 [174], 126.9 [21, 7], 128.5 [39], 136.7 [60], 137.8 [26, 11]. ^{119}Sn NMR: δ −262.5 [852, 173, 54]. Anal. Calcd for $C_{32}H_{30}Sn_2$: C, 58.95; H, 4.64; Sn, 36.41. Found: C, 59.12; H, 4.59; Sn, 36.31.

4,4′-Bis(4-but-3-enyl)biphenyl. A solution of allyl chloride (19.13 g, 250 mmol) in 120 mL of ether was slowly added to a suspension of magnesium (6 g, 250 mmol) in 20 mL of ether. After refluxing for 2 h, the Grignard reagent solution was transferred via a cannula to a solution of 1-bromo-4-(bromomethyl)benzene (7.49 g, 30 mmol) in THF (100 mL). After refluxing for 30 min, the mixture was hydrolyzed with a saturated NH_4Cl solution. After extraction, washing with water, drying, and evaporation of the solvents, 1-bromo-4-(but-3-enyl)benzene was purified by distillation. Bp: 130 °C/20 mmHg. To a 1 M solution of 4-(but-3-enyl)-benzylmagnesium in THF (50 mL 50 mmol) at −80 °C was slowly added $TiCl_4$ (14.25 g, 75 mmol).[35] After stirring for 30 min at 0 °C, the mixture was hydrolyzed with a NH_4Cl-saturated solution. After extraction, drying, and evaporation of the solvents 4,4′-bis-(4-but-3-enyl)biphenyl (8.0 g) was purified by Kugelrohr distillation. Bp: 140 °C/0.001 mmHg. Yield: 61%. ^{1}H NMR: δ 2.40−2.60 (m, 4H), 2.87 (t, 4H), 5.05−5.30 (m, 4H), 5.90−6.10 (m, 2H), 7.36 (d, 4H), 7.63 (d, 4H). ^{13}C NMR: δ 35.1, 35.6, 115.1, 127.0, 128.9, 138.2, 138.8, 140.8.

4,4′-Bis(4-(tricyclohexyltin)butyl)biphenyl (8). A solution of 4,4′-bis(4-but-3-enyl)biphenyl (6 g, 22.9 mmol), tricyclohexyltin hydride (15.2 g, 41,2 mmol), and AIBN (0.6 g, 3.6 mmol) was heated at 110 °C for 4 days and then at 130 °C for 3 more days. During that period, small portions of AIBN (100 mg) were added about every 6 h. The crude mixture was purified by chromatography on silica gel (eluent: chloroform) to give **8** (12.36 g) as a white solid. Yield: 60%. Mp: 143 °C. ^{1}H NMR: δ 0.80−0.92 (m, 4H), 1.27−1.87 (m, 74H), 2.68 (t, 4H), 7.27 (d, 4H), 7.57 (d, 4H). ^{13}C NMR: δ 6.7, 26.2[321]) 27.1 [18], 27.4, 29.5, [52], 32.6 [16], 35.2, 36.8 [51], 126.9, 128.9, 138.7, 141.8. ^{119}Sn NMR: δ −64.5. Anal. Calcd for $C_{56}H_{90}Sn_2$: C, 67.21; H, 9.06; Sn, 23.72. Found: C, 66.45; H, 8.93; Sn, 23.076.

4,4′-Bis(4-(trichlorotin)butyl)biphenyl (12). $SnCl_4$ (1.79 mL, 15,3 mmol) was added to a solution of **8** (4.2 g, 5.9 mmol) in 150 mL of toluene. After stirring for 72 h at room temperature, the solvent and the excess $SnCl_4$ were evaporated. The residue was taken up in acetonitrile (150 mL) and the solution extracted with pentane (7 × 100 mL). After evaporation of acetonitrile, the solid was solubilized in THF (100 mL). Evaporation of the solvent gave **12** (4.1 g) as a white solid. Mp: 107 °C. Yield: 97%. ^{1}H NMR: δ 1.74−1.79 (m, 4H), 1.89−1.94 (m, 4H), 2.31 (t, 4H [79]), 2.65 (t, 4H), 7.16 (d, 4H), 7.44 (d, 4H). ^{13}C NMR: δ 24.6 [58], 32.8 [657], 34.1 [106], 34.8, 127.3, 129.0, 139.0, 140.1. ^{119}Sn NMR: δ 7.8. Anal. Calcd for $C_{20}H_{24}Cl_6Sn_2$: C, 33.62; H, 3.39; Cl, 29.77; Sn, 33.23. Found: C, 33.77; H, 3.48; Cl, 28.44; Sn, 32.23.

4,4′-Bis(4-(triprop-1-ynyltin)butyl)biphenyl (19). **19** was prepared as **16**. Mp: 107 °C. Yield: 62%. ^{1}H NMR: δ 1.25 (t, 4H [76]), 1.68 (m, 8H), 1.83 (s, 18H [14]), 2.60 (t, 4H), 7.17 (d, 4H), 7.41 (d, 4H). ^{13}C NMR: δ 5.3 [15], 15.0 [633], 25.3 [30], 34.7 [84], 35.0, 76.8 [802], 107.9 [168], 126.9, 128.9, 138.6, 141.3. ^{119}Sn NMR: δ −252, 0 [802, 167]. Anal. Calcd for $C_{38}H_{42}Sn_2$: C, 60.00; H, 5.75; Sn, 32.25. Found: C, 60.79; H, 5.88; Sn, 32.08.

2,5-Dibromo-1,4-dialkoxybenzenes. To a solution of 1,4-dialkoxybenzene[36] (67.0 mmol) in dichloromethane (500 mL) was added dropwise bromine (26.8 g, 168 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at room temperature for 72 h. An aqueous solution of potassium hydroxide (300 mL) was then added, extracted with dichloromethane, and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo. Recrystallization from ethanol gave pure 2,5-dibromo-1,4-dialkoxybenzenes. 2,5-Dibromo-1,4-dioctyloxy benzene: mp 73 °C, 88% yield. ^{1}H NMR: δ 0.90 (t, 6H), 1.2−1.6 (m, 20H), 1.8 (q, 4H), 3.94 (t, 4H), 7.08 (s, 4H). ^{13}C NMR: δ 14.2, 22.8, 26.1, 29.3, 29.40, 29.45, 31.9, 70.4, 111.3, 118.5, 150.2. 2,5-Dibromo-1,4-di(hexadecyloxy)-benzene: mp 89 °C, 76% yield. ^{1}H NMR: δ 0.88 (t, 6H), 1.15−1.6 (m, 56H), 1.80 (q, 4H), 3.95 (t, 4H), 7.01 (s, 4H). ^{13}C NMR: δ 14.3, 22.9, 26.1, 29.3, 29.51, 29.58, 29.77, 29.8, 29.87, 29.92, 32.1, 70.5, 113.3, 118.6, 150.2.

2,5-Bis(tricyclohexyltin)-1,4-dioctyloxybenzene (5). A solution of 2,5-dibromo-1,4-dioctyloxybenzene (10 g, 20.3 mmol) in diethyl ether (400 mL) was cooled to −78 °C. With the addition of *tert*-butyllithium (54.18 mL, 1.5 M in pentane, 4 equiv) a white suspension was obtained, which turned to greenish-yellow after 4 h under stirring.[37] The mixture was warmed to room temperature for 2 h. It was cooled again to −78 °C, and a solution of tricyclohexyltin chloride (20.6 g, 51 mmol) in THF (120 mL) was added. After 30 min, the reaction was allowed to warm to room temperature. After stirring for 72 h, the mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted. The organic layer was dried over anhydrous $MgSO_4$. The solvents were removed in vacuo. The resulting solid was recrystallized from chloroform to give **5** (6.85 g). Mp: 176.4 °C. Yield: 50%. ^{1}H NMR: δ 0.91 (t, 6H), 1.1−2.1 (m, 90H), 3.89 (t, 4H), 6.84 (s, 2H, [19, 41]). ^{13}C NMR: δ 14.3, 22.9, 26.5, 27.5, 27.8 [350], 29.7 [58], 32.1, 32.5 [15], 68.2, 118.4 [23], 129.6 [334], 157.4. ^{119}Sn NMR: δ −92.3. Anal. Calcd for $C_{58}H_{102}O_2Sn_2$: C, 65.17; H, 9.62; O, 2.99; Sn, 22.21. Found: C, 64.46; H, 9.58; O, 2.99; Sn, 20.31.

2,5-Bis(trimethyltin)-1,4-dioctyloxybenzene (4). A solution of 2,5-dibromo-1,4-dioctyloxybenzene (13.5 g, 27.4 mmol) in diethyl ether (600 mL) was cooled to −78 °C. With the addition of *tert*-butyllithium (73.2 mL, 1.5 M in pentane, 4 equiv) a white suspension was obtained, which turned to greenish-yellow after 4 h under stirring. The mixture was warmed to room temperature for 2 h. It was cooled again to −78 °C, and a solution of tricyclohexyltin chloride (13.71 g, 68.8 mmol) in THF (120 mL) was added. After 30 min, the reaction was allowed to warm to room temperature. After stirring for 72 h, the mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted. The organic layer was dried over anhydrous $MgSO_4$. The solvents were removed in vacuo. The resulting solid was recrystallized from ethanol to give **4** (13.0 g). Mp: 93 °C. Yield: 72%. ^{1}H NMR: δ 0.29 (s, 18H, [56]), 0.92 (t, 6H), 1.3−1.55 (m, 20H), 1.77 (q, 4H), 3.93 (t, 4H), 6,87 (s, 2H, [22, 52]), ^{13}C NMR: δ −8.7 [359], 14.3, 22.9, 26.4, 29.5, 29.6, 29.9, 32.0, 68.4, 117.3 [30], 132.0 [453], 157.8 [22, 52]. ^{119}Sn NMR: δ −32.2. Anal. Calcd for $C_{28}H_{54}O_2Sn_2$: C, 50.94; H, 8.24; O, 4.85; Sn, 35.96. Found: C, 50.85; H, 8.10; O, 4.57; Sn, 32.60.

2,5-Bis(trichlorotin)-1,4-dioctyloxybenzene (13). $SnCl_4$ (8.55 mL, 72.8 mmol) was slowly added to a solution of **4** (6 g, 9.1

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[35] Inoue, A.; Kitagawa, K.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2000**, *56*, 9601.

[36] Tamura, H.; Watanabe, T.; Imanishi, K.; Sawada, M. *Synth. Met.* **1999**, *107*, 19.

[37] Lightowler, S.; Hird, M. *Chem. Mater.* **2004**, *16*, 3963.

Table 2. Crystal Data and Structure Refinements for Ditin Compounds

	2	3	4	5	6	7	12	13	14	20
empirical formula	$C_{54}H_{78}Sn_2$	$C_{50}H_{78}Sn_2$	$C_{28}H_{54}O_2Sn_2$	$C_{58}H_{102}O_2Sn_2$	$C_{44}H_{86}O_2Sn_2$	$C_{40}H_{62}O_2Sn_2$	$C_{20}H_{24}Cl_6Sn_2$	$C_{22}H_{36}Cl_6O_2Sn_2$	$C_{38}H_{68}Cl_6O_2Sn_2$	$C_{40}H_{54}O_2Sn_2$
fw	964.64	916.5	330.05	1068.78	884.50	812.28	714.48	782.58	1007.00	804.21
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	*C*121 (5:b1)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P12_1/a1$ (14:b3)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a (Å)	14.834(3)	8.548(2)	6.6057(2)	10.696	7.4280(3)	7.7368(3)	6.665(3)	8.4073(4)	8.4028(1)	8.1292(5)
b (Å)	17.700(4)	10.347(4)	10.4017(3)	11.584	9.8610(4)	10.8683(5)	8.907(11)	10.5641(8)	10.4973(1)	11.3297(6)
c (Å)	18.80.9(4)	14.667(3)	12.4606(4)	1263.7	16.7050(4)	12.8803(6)	10.679(8)	17.6320(9)	26.7764(3)	11.9733(7)
α (deg)	90.00	96.19(2)	99.56(0)	77.07	83.790(2)	110.247(4)	90.05(4)	90.00	80.0327(7)	114.029(6)
β (deg)	101.74(3)	102.92(1)	91.47(0)	71.12	89.035(3)	102.111(4)	89.12(5)	90.688(4)	81.3864(8)	92.593(5)
γ (deg)	90.00	110.07(2)	107.79(0)°	87.88	72.043(2)	89.552(4)	81.93(5)	90.00	83.1463(8)	96.610(5)
V (Å^3)	4835.2(18)	1163.2(6)	801.23(64)	1442.9	1156.99(7)	991.03(8)	627.6(9)	1565.88(16)	2289.37(4)	995.33(10)
Z	4	2	2	2	1	2	2	4	2	1
D_{calcd} (Mg/m^3)	1.325	1.308	1.36797	1.230	1.269	1.361	1.890	1.660	1.461	1.342
R_{int}	0.0641	0.0246	0.0247	0.0371	0.0232	0.023	0.0898	0.0224	0.0224	0.026
R1 ($I > 2\sigma(I)$)	0.0814	0.0797	0.0270	0.0485	0.0230	0.0287	0.0621	0.0345	0.0371	0.0327
wR2	0.1892	0.1838	0.0622	0.1028	0.0535	0.0693	0.1493	0.0820	0.0936	0.0646

mmol). The mixture was warmed to 120 °C under stirring for 4.5 h. The excess $SnCl_4$ and the secondary products were then evaporated under reduced pressure at 120 °C to give **13** (6.7 g). Mp: 133 °C. Yield: 94%. ^{1}H NMR: δ 0.91 (t, 6H), 1.25−1.6 (m, 20H), 1.88 (q, 4H), 4.15 (t, 4H), 7.21 (s, 2H, [145, 72]). ^{13}C NMR: δ 14.3, 22.8, 25.9, 28.9, 29.32, 29.36, 31.9, 71.1, 116.9, 132.6 [22, 133], 156.0 [157]. ^{119}Sn NMR: δ −83.5. Anal. Calcd for $C_{22}H_{36}O_2Cl_6Sn_2$: C, 33.76; H, 4.64; O, 4.09; Cl, 27.18; Sn, 30.34. Found: C, 34.22; H, 4.55; O, 4.40; Cl, 26.71; Sn, 27.06.

2,5-Bis(triprop-1-ynyltin)-1,4-dioctyloxybenzene (20). To a solution of propyne (87.3 mmol) in toluene (76 mL) at −78 °C was slowly added a solution of *n*-butyllithium (31.56 mL, 48 mmol) in hexane (2.0 M). After 2 h stirring at room temperature, a solution of 2,5-bis(trichlorotin)-1,4-dioctyloxybenzene (6.5 g, 8.3 mmol) in toluene (100 mL) was added at −78 °C. The suspension was stirred at room temperature for 12 h and then filtered on dry $MgSO_4$. After evaporation of the solvents, **20** (5.0 g) was recovered as a white solid. Mp: 165 °C. Yield: 75%. ^{1}H NMR: δ 0.88 (t, 6H), 1.20−1.60 (m, 20H), 1.80 (q, 4H), 1.92 (s, 18H, [15]), 4.00 (t, 4H), 7.10 (s, 2H, [40, 94]). ^{13}C NMR: δ 5.3 [16], 14.2, 22.8, 26.1, 29.3, 29.4, 29.6, 32.0, 69.4, 71.1 [956], 107.1 [196], 118.2 [51], 128.0 [13, 885], 157.2 [98]. ^{119}Sn NMR: δ −296.5 [957, 197, 37]. Anal. Calcd for $C_{40}H_{54}O_2Sn_2$: C, 59.73; H, 6.97; O, 3.58; Sn, 29.52. Found: C, 59.87; H, 6.87; O, 3.75; Sn, 29.93.

2,5-Bis(trimethyltin)-1,4-di(*n*-hexadecyloxy)benzene (6). 6 was prepared in the same way as **4**. Mp: 88 °C. Yield: 50%. ^{1}H NMR: δ 0.29 (s, 18H, [55]), 0.89 (t, 6H), 1.15−1.6 (m, 56H), 1.75 (q, 4H), 3.91 (t,4H), 6,85 (s, 2H, [22, 53]). ^{13}C NMR: δ −8.7 [359], 14.3, 22.9, 26.3, 29.5, 29.6, 29.8, 29.9, 32.1, 68.4, 117.3 [7, 30], 131.9, 157.7. ^{119}Sn NMR: δ −32.2. Anal. Calcd for $C_{44}H_{86}O_2Sn_2$: C, 59.74; H, 9.81; O, 3.61; Sn, 26.83. Found: C, 60.68; H, 9.95; O, 3.82; Sn, 24.60.

2,5-Bis(trichlorotin)-1,4-di(*n*-hexadecyloxy)benzene (14). 14 was prepared as **13**. Mp: 111 °C. Yield: 91%. ^{1}H NMR: δ 0.88 (t, 6H), 1.15−1.6 (m, 56H), 1.83 (q, 4H), 4.13 (t, 4H), 7.19 (s, 2H, [72, 145]). ^{13}C NMR: δ 14.3, 22.9, 25.9, 28.9, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.1, 71.1, 116.9, 132.6, 156.0. ^{119}Sn NMR: δ −83.3. Anal. Calcd for $C_{38}H_{68}Cl_6O_2Sn_2$: C, 45.32; H, 6.81; O, 3.18; Cl, 21.12; Sn, 23.97. Found: C, 47.00; H, 6.99; O, 3.85; Cl, 19.88; Sn, 21.31.

2,5-Bis(triprop-1-ynyltin)-1,4-di(*n*-hexadecyloxy)benzene (21). 21 was prepared in the same way as **20**. Mp: 90 °C. Yield: 78%. ^{1}H NMR: δ 0.88 (t, 6H), 1.15−1.60 (m, 56H), 1.83 (q, 4H), 1.93 (s, 18H, [15]), 4.01 (t, 4H), 7,11 (s, 2H, [41, 94]). ^{13}C NMR: δ 5.4 [16], 14.3, 22.8, 26.2, 29.4, 29.5, 29.81, 29.85, 29.9, 32.1, 69.5, 71.1 [955], 107.2 [196], 118.3 [52], 128.0, 157.3. ^{119}Sn NMR: δ −296.6 [37]. Anal. Calcd for $C_{56}H_{86}O_2Sn_2$: C, 65.39; H, 8.43; O, 3.11; Sn, 23.08. Found: C, 65.98; H, 8.58; O, 3.32; Sn, 21.10.

4,4′′-Bis(trimethyltin)-2′,5′-dioctyloxy-1,1′:4′,1′′-terphenyl (7). A 30 mL portion of a solution of 20 mL of 4,4′′-dibromo-2′,5′-dioctyloxy-1,1′:4′,1′′-terphenyl[37] (10.08 g, 15.6 mmol) in dry THF (300 mL) was slowly added to magnesium (1.6 g, 60 mmol) in THF (40 mL). The mixture was heated to initiate the reaction. The rest of the solution was slowly added under reflux, and the mixture was refluxed for 2 h. After cooling to 0 °C, a solution of trimethyltin chloride (48.60 g, 120 mmol) in dry THF (200 mL) was slowly added. The mixture was stirred at room temperature overnight and then hydrolyzed with a saturated solution of NH_4Cl and extracted with pentane. The organic phase washed with water and dried with $MgSO_4$, and the solvents were evaporated. Recrystallization from toluene gave **7** (11.0 g) as a white solid. Mp: 104 °C. Yield: 87%. ^{1}H NMR: δ 0.43 (s, 18H, [55]), 0.98 (t, 6H), 1.3−1.6 (m, 20H), 1.79 (q, 4H), 4.01 (t, 4H), 7.09 (s,2H), 7.62−7.75 (m, 8H). ^{13}C NMR: δ −9.3 [350], 14.3, 22.8, 26.3, 29.4, 29.5, 32.0, 69.7, 116.4, 129.3 [46], 130.9, 135.6 [11], 138.5, 140.8 [465], 150.4. ^{119}Sn

NMR: δ −27.0 [349]. Anal. Calcd for $C_{40}H_{62}O_2Sn_2$: C, 59.14; H, 7.69; O, 3.94; Sn, 29.22. Found: C, 59.12; H, 7.72; O, 4.12; Sn, 28.21.

4,4″-Bis(trichlorotin)-2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl (15). **15** was prepared as **13**. Mp: 125 °C. Yield: 90%. ^{1}H NMR: δ 0.89 (t, 6H), 1.15−1.65 (m, 20H), 1.72 (q, 4H), 3.96 (t, 4H), 6.98 (s, 2H), 7.72 (d, 4H), 7.85 (m, 4H). ^{13}C NMR: δ 14.3, 22.8, 26.2, 29.39, 29.41, 31.9, 69.8, 115.9, 130.0 [12], 131.5 [126], 133.7 [81], 134.7, 143.5, 150.4. ^{119}Sn NMR: δ −59.3. Anal. Calcd for $C_{36}H_{44}O_2Sn_2$: C, 43.69; H, 4.74; O, 3.42; Cl, 22.75; Sn, 25.39. Found: C, 44.67; H, 4.94; O, 3.88; Sn, 24.86.

4,4″-Bis(triprop-1-ynyltin)-2′,5′-dioctyloxy-1,1′:4′,1″-terphenyl (22). **22** was prepared as **20**. Mp: 180 °C (dec). Yield: 65%. ^{1}H NMR: δ 0.89 (t, 6H), 1.15−1.45 (m, 20H), 1.71 (q, 4H), 1.97 (s, 18, [15]), 3.92 (t, 4H), 6.97 (s, 2H), 7.69 (m, 8H). ^{13}C NMR: δ 5.4 [15], 14.3, 22.8, 26.2, 29.40, 29.48, 31.9, 69.7, 76.3 [924], 108.4 [191], 116.3, 130.0 [78], 130.7, 133.4 [81], 135.3 [58], 140.4, 150.4. ^{119}Sn NMR: δ −285.7. Anal. Calcd for $C_{56}H_{86}O_2Sn_2$: C, 65.30; H, 6.53; O, 3.35; Sn, 24.82. Found: C, 65.84; H, 6.52; O, 3.43; Sn, 23.72.

X-ray Crystallography. Crystal data collection and processing parameters are given in Table 2. Suitable crystals were covered with mineral oil (Aldrich), mounted onto glass fibers, and transferred directly to the 150 K N_2 stream of a Nonius Kappa CCD diffractometer, or were mounted onto a 1.0 mm glass capillary at room temperature. Structures were solved by direct methods (SHELXS97)[38] and refined by full-matrix least-squares against F^2 using SHELXL97.[39] All non-H atoms were refined anisotropically with the exception of disordered atoms. H atoms were fixed in calculated positions at parent C atoms. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

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Supporting Information Available: Tables with bond lengths, bond angles, atomic coordinates, and anisotropic displacement parameters for the structures of **2**−**7**, **12**−**14**, and **20**. This information is available free of charge via the Internet at http://pubs.acs.org.

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(38) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

(39) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Universität von Göttingen: Göttingen, Germany, 1997.