New Perylene-Substituted Organotrialkynyltin Compounds for the Photosensitization of Tin Dioxide

G. Vilaça, K. Barathieu, B. Jousseaume, and T. Toupance*

Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS,
Université Bordeaux I, 351 Cours de la Libération, F33405 Talence Cedex, France

H. Allouchi

Laboratoire de Chimie Physique PIMIR, EA 2098, Faculté de Pharmacie, 31 Avenue Monge,
F37200 Tours, France

Received June 20, 2003

New perylene-substituted organotrialkynyltins $C_{10}H_{20}Sp{-}Sn(C{\equiv}CC_4H_9)_3$ (**1**; Sp = $-C_4H_8-$, $-C_6H_{12}-$, $-CH{=}CH-$) have been synthesized in two steps from the tricyclohexyltin analogues in fair to high yields (30−90%). Tricyclohexyltin derivatives were prepared in 50% yields either by coupling of 3-perylenyllithium with a (*ω*-iodoalkyl)tricyclohexyltin or by hydrostannation of 3-ethynylperylene by tricyclohexyltin hydride. Intermolecular $\pi-\pi$ contacts between the perylene units were found in the solid-state structure of 3-(4-(tricyclohexylstannyl)butyl)perylene. The presence of a (tricyclohexylstannyl)- or a (trialkynylstannyl)alkyl substituent does not affect the fluorescence emission properties of the perylene core, whereas an *ω*-(trichlorostannyl)alkyl or a 2-stannylethynyl group does. Molecules **1** are dye precursors for the photosensitization of nanocrystalline tin dioxide materials.

Introduction

Dye sensitization of wide-gap n-type semiconductors (TiO_2, SnO_2, ...) is a promising route for sunlight-to-electricity conversion.[1] At the beginning of the 1990s, Grätzel et al. accomplished a breakthrough in this field by depositing ruthenium polypyridine complexes, endowed with carboxylic acid groups, onto nanocrystalline porous titanium dioxide films with high surface area.[2] The corresponding devices exhibit yields of energy conversion comparable to those reported for silicon-based solar cells. As a result, various new photovoltaic systems based on nanocrystalline metal oxide have been described over the 10 past years. Most of them consist of titanium[2] or tin[3] dioxide colloidal particles modified with coordination complexes of ruthenium[2,4−6] or iron[7] or with organic dyes such as aromatic[8] and polyaromatic[9] compounds. The sensitizer is usually linked to the oxide surface via a spacer bearing carboxylic acid, ester,[10] catechol,[11] phosphonic acid,[9a,12] or *β*-diketone[13] functionalities. Up to now, the more successful systems were obtained with dye-bearing carboxylic acid groups, the latter reacting with the surface hydroxyl functionalities of the oxide. However, the weak sensitizer−oxide bond leads to unstable devices in neutral and basic media[13] which diminishes the light-to-electricity conversion yields and the stability of the device. To improve

---

* To whom correspondence should be addressed. E-mail: t.toupance@lcoo.u-bordeaux1.fr.

(1) (a) Anderson, S.; Constable, E. C.; Dare-Edwards, M. P.; Goodenough, J. B.; Hamnett, A.; Seddon, K. R.; Wright, R. D. *Nature* **1979**, *280*, 571.

(2) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.

(3) (a) Ford, W. E.; Rodgers, M. A. *J. Phys. Chem.* **1994**, *98*, 3822. (b) Bedja, I.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 4133. (c) Srivastava, D. N.; Chappel, S.; Palchik, O.; Zaban, A.; Gedanken, A. *Langmuir* **2002**, *18*, 4160.

(4) (a) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *J. Am. Chem. Soc.* **1995**, *117*, 11815. (b) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Meyer, G. J. *Inorg. Chem.* **1997**, *36*, 2. (c) Argazzi, R.; Bignozzi, C. A.; Hasselmann, G. M.; Meyer, G. J. *Inorg. Chem.* **1998**, *37*, 4533.

(5) (a) Kamat, P. V.; Bedja, I.; Hotchandani, S.; Patterson, L. K. *J. Phys. Chem.* **1996**, *100*, 4900. (b) Lees, A. C.; Evrard, B.; Keyes, T. E.; Vos, J. G.; Kleverlaan, C. J.; Alebbi, M.; Bignozzi, C. A. *Eur. J. Inorg. Chem.* **1999**, 2309.

(6) (a) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613. (b) Renouard, T.; Fallahpour, R.-A.; Nazeeruddin, M. K.; Humphry-Baker, R.; Gorelsky, S. I.; Lever, A. B. P.; Grätzel, M. *Inorg. Chem.* **2002**, *41*, 367.

(7) (a) Ferrere, S.; Gregg, B. A. *J. Am. Chem. Soc.* **1998**, *120*, 843. (b) Yang, M.; Thompson, D. W.; Meyer, G. J. *Inorg. Chem.* **2002**, *41*, 1254.

(8) (a) Sayama, K.; Hara, K.; Mori, N.; Satsuki, M.; Suga, S.; Tsukagoshi, S.; Abe, Y.; Sugihara, H.; Arakawa, H. *J. Chem. Soc., Chem. Commun.* **2000**, 1173. (b) Wang, Z.-S.; Li, F.-Y.; Huang, C.-H. *J. Chem. Soc., Chem. Commun.* **2000**, 2063. (c) Hara, K.; Horiguchi, T.; Kinoshita, T.; Sayama, K.; Sugihara, H.; Arakawa, H. *Solar Energy Mater. Solar Cells* **2000**, *64*, 115. (d) Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. *J. Chem. Soc., Chem. Commun.* **2001**, 569. (e) Tai, W.-P. *Mater. Lett.* **2001**, *51*, 451.

(9) (a) Burfeindt, B.; Hannappel, T.; Storck, W.; Willig, F. *J. Phys. Chem.* **1996**, *100*, 16463. (b) Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 4490.

(10) (a) Galoppini, E.; Guo, W., Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2001**, *123*, 4342. (b) Galoppini, E.; Guo, W.; Zhang, W.; Hoertz, P. G.; Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 7801.

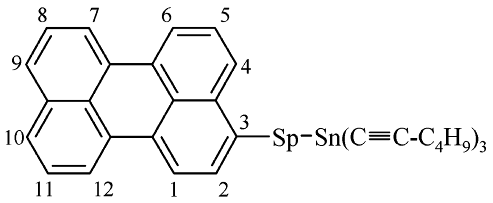
(11) (a) Rice, C. R.; Ward, M. D.; Nazeeruddin, M. K.; Grätzel, M. *New J. Chem.* **2000**, *24*, 651. (b) Dai, Q.; Rabani, J. *J. Chem. Soc., Chem. Commun.* **2001**, 2142.

(12) Péchy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1995**, 65.

(13) Heimer, T. A.; d'Arcangelis, S. T.; Farzad, F.; Stipkala, J. M.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 5319.

10.1021/om030478m CCC: $25.00
Publication on Web 10/03/2003

Chart 1



1a-c

Sp = -$(CH_2)_n$-,-(CH=CH)- n = 4,6

the stability of regenerative solar cells, it is therefore of great relevance to develop new chromophore−oxide linkages. For instance, it might be advantageous to exploit the more stable Sn(oxide)−O−Sn−C(alkyl) linkage in order to strongly attach a dye onto nanocrystalline tin dioxide powders.

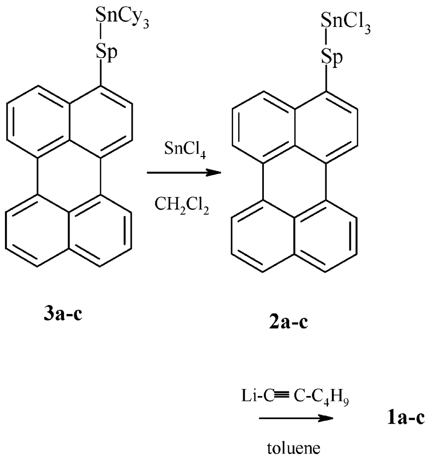
We have recently reported the preparation of nanocrystalline F-doped or undoped tin dioxide powders by the sol−gel route from β-diketonate-stabilized alkoxytins, which could be interesting oxide materials for photovoltaic applications.[14] To photosensitize these materials, our strategy was to prepare organotin compounds including an organic dye and three moisture-sensitive groups capable of reacting efficiently with the surface hydroxyl groups of the tin dioxide. Perylene dyes have been chosen for both fundamental and practical reasons. Indeed, they strongly absorb in the visible range ($\epsilon > 3 \times 10^4$ L mol^{-1} cm^{-1}) and the oxidation potential of their first excited singlet state lies very high above the lower edge of the conduction band of most oxide semiconductors with a wide band gap.[9a] Furthermore, alkynyl subsituents are good candidates as hydrolyzable groups since, on one hand, the corresponding organotins are easily prepared and purified from organotrichlorotins and, on the other hand, organotrialkynyltins smoothly react with alcohols or water to give alkoxides or oxides.[15] To the best of our knowledge, only one perylene-substituted organotin, namely *N*-(2,7-diisopropylphenyl)-1,7-bis(4-*tert*-butylphenoxy)-10-(tri-*n*-butyltin)perylene-3,4-dicarboximide, has been reported up to now and was used as a synthon in a Stille coupling reaction.[16] We have decided to introduce an alkylene or alkenylene bridging group between the tin atom and the perylenyl group in order to favor the grafting ability of the target molecules by reducing the bulk at the tin center.

Consequently, we report herein on the syntheses, characterization, and solution spectroscopic properties of perylene-substituted organotrialkynyltins **1** (Chart 1). While leading to stable sensitizer−oxide linkages, the nature (alkylene, alkenylene) of the spacer Sp should allow us to vary the electronic coupling between the dye and the oxide surface and/or surface state energetics.

Results and Discussion

Synthesis. It was recently shown that functional monoorganotrialkynyltins could be readily prepared in two steps from the corresponding tricyclohexyltin via a trichloride derivative.[15] A similar chemical pathway was followed to obtain the target molecules **1** (Scheme 1), the actual synthetic challenge lying in the preparation of the tricyclohexyltin derivatives **3**.

Scheme 1



Sp = -$(CH_2)_n$-, -(CH=CH)- n = 4,6
Cy = C_6H_{12}

Scheme 2

$$\underset{\mathbf{4}}{Cy_3Sn\text{-}(CH_2)_n\text{-}OH} \xrightarrow[\text{pyridine}]{p\text{-}CH_3C_6H_4SO_2Cl} \underset{\mathbf{5}}{Cy_3Sn\text{-}(CH_2)_n\text{-}OSO_2C_6H_4CH_3}$$

$$\xrightarrow[\text{acetone}]{\text{NaI}} \underset{\mathbf{6}}{Cy_3Sn\text{-}(CH_2)_n\text{-}I}$$

n = 4,6

Indeed, in the case of the alkylene bridging groups, two synthetic approaches could be followed to reach **3**: (i) hydrostannation of 3-(ω-alkenyl)perylenes with tricyclohexyltin hydride and (ii) displacement of halides in (ω-halogenoalkyl)tricyclohexyltins by using perylenyllithium. However, the synthesis of perylene-substituted α-olefins, which could be achieved by the coupling of a ω-alkenyl Grignard reagent with 3-(chloromethyl)perylene,[17] would require several steps involving purification difficulties, owing to the low solubility of the perylene unit. Furthermore, the second route, which is more convergent, is usually favored when delocalized carbanions and primary alkyl halides are used.[18] Consequently, the latter was preferred to prepare **3a**,**b**. The first key molecules were the (ω-iodoalkyl)tricyclohexyltin derivatives. These compounds were produced in a two-step synthesis from the suitable (ω-hydroxyalkyl)tricyclohexyltin species **4** (Scheme 2).[19]

The first reaction was an esterification with *p*-toluenesulfonyl chloride, which afforded the (ω-(tosyloxy)alkyl)tricyclohexyltin compound **5** in 75−90% yield.[20]

---

(14) (a) Gamard, A.; Jousseaume, B.; Toupance, T.; Campet, G. *Inorg. Chem.* **1999**, *38*, 4671. (b) Gamard, A.; Babot, O.; Jousseaume, B.; Rascle, M.-C.; Toupance, T.; Campet, G. *Chem. Mater.* **2000**, *12*, 3419.

(15) (a) Jaumier, P.; Jousseaume, B.; Lahcini, M.; Ribot, F.; Sanchez, C. *J. Chem. Soc., Chem. Commun.* **1998**, 369. (b) Franc, C.; Jousseaume, B.; Linker, M.; Toupance, T. *Chem. Mater.* **2000**, *12*, 3100.

(16) Schlichting, P.; Duchscherer, B.; Seinsenberger, G.; Bashé, T.; Bräuchle, C.; Müllen, K. *Chem. Eur. J.* **1999**, *5*, 2388.

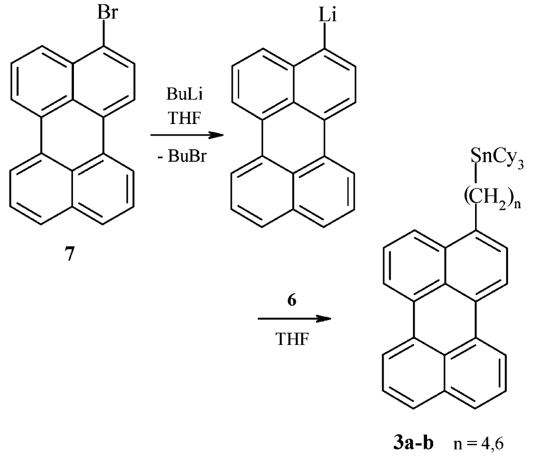
(17) (a) Buu-Hoï, N. P.; Long, C. T. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 1221. (b) Grechishnikova, I. V.; Johansson, B. A. L.; Molotkovsky, J. G. *Chem. Phys. Lip.* **1996**, *81*, 87.

(18) Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988; p 107.

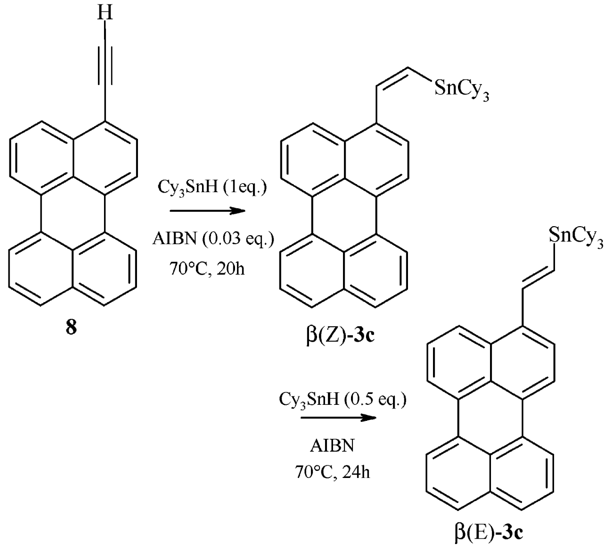
(19) Jousseaume, B.; Lahcini, M.; Rascle, M.-C.; Ribot, F.; Sanchez, C. *Organometallics* **1995**, *14*, 685.

(20) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman Scientific & Technical: London, p 654.

Scheme 3



Scheme 4



The latter was then converted into the iodide derivatives **6** by reaction with sodium iodide in acetone (yield: 85−95%).[21] Furthermore, we have chosen 3-bromoperylene **7**, which was isolated in 80% yield after NBS (*N*-bromosuccinimide) bromination of perylene in DMF,[16,22] as the starting material for perylenyllithium. The use of a slight excess of perylene has allowed us to avoid polybromination reactions. Then, metal−halogen exchange between 3-perylene and *n*-butyllithium at −78 °C furnished perylenyllithium, which was immediately reacted with **6** to give **3** in fair yields (50−60%) after purification (Scheme 3). Low temperature and an excess (1.4 equiv) of the iodide derivatives were essential to diminish both transmetalation and the competitive alkylation of the 1-bromobutane formed during the metal−halogen exchange stage.

For the alkenylene spacer, the synthesis of **3c** was achieved by an hydrostannation of 3-ethynylperylene **8** (Scheme 4), which was obtained in two steps from 3-bromoperylene.[23] As it was shown that metal-catalyzed hydrostannation of ethynylaryl compounds was used to give mixtures of α and $\beta(E/Z)$ isomers,[24] reactions under free-radical conditions were carried out.[25] The reaction of 3-ethynylperylene with tricyclohexyltin hydride in the presence of 0.03 equiv of AIBN in benzene at 70 °C gave the anti-hydrostannation product $\beta(Z)$-**3c** ((*Z*)-vinylstannane) regio- and stereoselectively. A 90% conversion rate was reached after 20 h, as monitored by ^{1}H NMR spectroscopy. Further additions of AIBN and Cy$_3$SnH led to the complete isomerization of $\beta(Z)$-**3c** into the (*E*)-vinylstannane $\beta(E)$-**3c** after 24 h, which was obtained in 50% yield after purification (Scheme 4).

Despite the addition of Et$_2$NH, partial decomposition of $\beta(E)$-**3c** over silica gel occurred during the purification step, which is at the origin of the discrepancy observed between the conversion rate and the isolated yield. The occurrence and the course of this reaction are consistent with experimental and theoretical results previously reported for hydrostannation of conjugated alkynes.[26] The stereoselectivity of the kinetic product, the $\beta(Z)$ isomer, would be a result of the intermediate vinyl radical, which exhibits an sp geometry at the radical carbon.[26b] Experimentally, the kinetic product then isomerizes and the thermodynamically more stable β-(*E*) isomer is obtained. It is also worth mentioning that the temperature had to be carefully controlled to obtain **3c**. Indeed, temperatures below 60 °C (or above 80 °C) have favored the α product (or decomposition of the vinylstannane). The formation of the α product can be rationalized by postulating an ionic mechanism,[27] the decomposition rate of AIBN being insufficient to be under pure free radical conditions.

Monoorganotrichlorotins **2a**,**b** were then conveniently synthesized in quantitative yields from **3a**,**b** and tin tetrachloride. These compounds were insoluble in alkanes and aromatic and aprotic polar solvents (CH$_3$CN, DMSO) and only sparingly soluble in dichloromethane and chloroform. Finally, alkynylation of the trichloride **2a**,**b** with hexynyllithium yielded the corresponding alkynides **1a**,**b** in very high yields (90−95%). A similar route was followed to prepare the target molecule including the alkenylene spacer. The chloride **2c** proved to be insoluble in organic solvents and was light sensitive (polymerization phenomenon), which has prevented its complete characterization in solution. It was therefore immediately reacted with an excess of hexynyllithium to give **1c** (30%).

Characterization. Compounds **1**−**3** have been thoroughly characterized in solution by multinuclear ^{1}H, ^{13}C and ^{119}Sn NMR and UV−visible absorption spectroscopies, high-resolution mass spectrometry and steady-state fluorescence emission spectroscopy.

---

[21] Kato, K.; Hirata, Y.; Yamamura, S. *Tetrahedron* **1971**, *27*, 5987.

[22] Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.

[23] (a) Vocanson, F.; Guo, Y. P.; Namy, J.-L.; Kagan, H. B. *Synth. Commun.* **1998**, *28*, 2571. (b) Crisp, G. T.; Jiang, Y. L. *Synth. Commun.* **1998**, *28*, 2571. (c) Inoue, M.; Hyodo, Y.; Nakazumi, H. *J. Org. Chem.* **1999**, *64*, 2704.

[24] For a recent review see: Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257. Only ZrCl$_4$ seems to give pure β-adduct. See: (a) Asao, N.; Liu, J. X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 2405. (b) Asao, N.; Liu, J. X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568.

[25] Cochran, J. C.; Phillips, H. K.; Tom, S.; Hurd, A. R.; Bronk, B. S. *Organometallics* **1994**, *13*, 947.

[26] (a) Cochran, J. C.; Leusink, A. J.; Noltes, R. J. *Organometallics* **1983**, *2*, 1099. (b) Petraco, N. D. K.; Modarelli, D. A.; Cochran, J. C. *Synth. React. Inorg. Met.-Org. Chem.* **2001**, *31*, 757.

[27] Kupchik, E. J. In *Organotin Compounds*; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1971; Vol. 1, pp 45−49, and references therein.

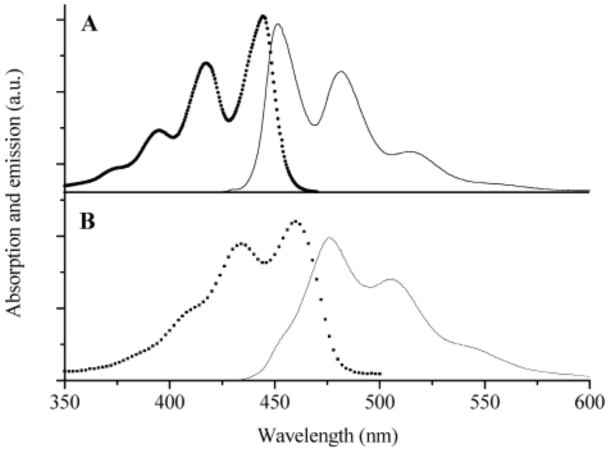


Figure 1. Absorption (dotted line) and emission (full line) spectra: (A) **1a**,**b**, **2a**,**b**, and **3a**,**b** (only one spectrum shown); (B) **3c** and **1c** (only one spectrum shown).

In the case of species with saturated spacers, the ^{119}Sn NMR chemical shifts of the tricyclohexyl-, trichloro-, and trihex-1-ynyltin compounds fall within the range of those reported for alkyltin analogues:[15b,19] i.e. −66 ppm for **3a**,**b**, +4 ppm for **2a**,**b**, and −250 ppm for **1a**,**b**. Interestingly, ^{1}H NMR data have allowed the identification of the three possible stereoisomers of the products endowed with an alkenylene spacer. For instance, isomer β(*E*)-**3c** (β(*Z*)-**3c**) shows two doublets at 6.86 and 7.58 ppm (6.39 and 8.07 ppm) with a $^{3}J_{HH}$ coupling constant of 19.5 Hz (13.8 Hz) in ^{1}H NMR spectroscopy. Furthermore, the *gem*-perylenyl group in the α byproduct shields the ^{1}H doublets to 5.67 and 5.97 ppm, the $^{2}J_{HH}$ coupling constant being equal to 3.5 Hz. ^{119}Sn NMR spectroscopy was also a suitable method to identify the different isomers. Indeed, ^{119}Sn NMR resonances are detected at −81, −98.5, and −100.1 ppm for α-**3c**, β(*E*)-**3c** and β(*Z*)-**3c**, respectively, which agree favorably with the trend of the correlation between the structure and the ^{119}Sn NMR chemical shift reported by Quintard et al.[28] and Cochran et al.[25] However, it must be noted that the chemical shift difference between the *Z* and *E* isomers is much smaller in our case. Furthermore, the vinylperylene group of β(*E*)-**1c** shields the ^{119}Sn resonance by 32 to −282 ppm when this value is compared to those found for **1a**,**b**. This is consistent with the shielding of the ^{119}Sn resonance as primary alkyl groups are replaced with vinyl or phenyl groups.[29]

The UV−visible absorption and fluorescence behaviors of the molecules synthesized have been investigated in solution so as to determine the influence of the tricyclo-, trichloro-, and trihex-1-ynylstannyl groups on the photophysical properties of the perylene unit. The UV−visible absorption spectra of **3a**,**b**, **2a**,**b**, and **1a**,**b** recorded in dichloromethane were similar to that of perylene (Figure 1A). The main absorption band in the visible range corresponds to the lowest energy $\pi-\pi^*$ transition, whose vibronic fine structure has maxima at 444, 417, 396 and 375 nm. The energy difference between each vibrational component is approximately equal to 1400 cm^{-1}, which is consistent with an interval of totally symmetric vibrational levels.[30] On the other hand, the absorptions of compounds **3c** and **1c** are slightly bathochromically shifted (∼15 nm) compared with molecules **3a**,**b** as a result of the extended π system, and the vibrational structure is not as well-resolved as in the previous cases.

Table 1. Quantum Yield of Fluorescence (Φ_{Em}) for 1−3

	3a	**3b**	**3c**	**2a**	**2b**	**1a**	**1b**	**1c**
Φ_{em}	0.72	0.75	0.17	0.19	0.23	0.68	0.66	0.12

As far as the fluorescence properties are concerned, the emission spectra recorded in dichloromethane of the dyes **3a**,**b**, **2a**,**b**, and **1a**,**b** exhibit maxima at 560, 515, 481, and 451 nm, close to those described for perylene.[31] For each compound, the absorption and excitation spectra overlap. The blue emission is attributed to $S_1 \rightarrow S_0$ fluorescence. In addition, these emission spectra show mirror image symmetry between the longest wavelength absorption band and the corresponding emission band, the Stokes shift between these two bands being remarkably small (∼400 cm^{-1}). Consequently, these features are consistent with S_0 and S_1 states of quite similar geometries, as previously reported for different perylene derivatives.[32] It is also worth mentioning that the spectra remain unchanged in the concentration range investigated: i.e., $1 \times 10^{-7}-5 \times 10^{-5}$ M. No eximer emission could be detected, therefore. Compounds β(*E*)-**3c** and β(*E*)-**1c** behave similarly, but Stokes shifts twice as large (∼775 cm^{-1}) were found (Figure 1B). To get a quantitative insight into the photophysical properties, the quantum yields of fluorescence were determined. Compounds **3a**,**b** and **1a**,**b** exhibit quantum yields near that measured under the same conditions for perylene, i.e., $\Phi_{em} = 0.75$ (Table 1). In contrast, the presence of a trichlorostannyl group strongly affects the quantum yields, which decrease to 0.23−0.19 for **2a**,**b**. Such a quenching was also noted for the alkenylene spacer series. The question arose about the origin of the quenching observed. While both absorption and emission spectra of **2a**,**b** are similar to those reported for perylene, the fact that those of **3c** and **1c** are very different indicates that the quenching processes are very likely different in origin. The behavior of the trichloride **2a**,**b** might be rationalized by considering that chlorine atoms are presumably responsible for the quenching observed. Indeed, heavy atoms and metal ions are known to be efficient quenchers of fluorescence.[33] In **3c** and **1c**, cis−trans isomerization of the double bond could take place and the emitting part is the 3-ethenylperylene group which is directly linked to the tin center. As a consequence, these processes might be invoked to explain the low quantum yields measured in these cases.

As mentioned in the Introduction, the dyes prepared will be used to sensitize nanoporous tin dioxide materials. Among all the possible effects governing the ef-

---

(28) Quintard, J.-P.; Degueil-Castaing, M.; Dumartin, G.; Barbe, B.; Petraud, M. *J. Organomet. Chem.* **1982**, *234*, 27.

(29) Smith, P. J.; Tupciauskas, A. *Annu. Rep. NMR Spectrosc.* **1978**, *8*, 291.

(30) Tanizaki, Y.; Yoshinaga, T.; Hiratsuka, H. *Spectrochim. Acta* **1978**, *34A*, 205.

(31) McKay, J. F.; Latham, D. R. *Anal. Chem.* **1972**, *44*, 2132.

(32) Koch, K.-H.; Müllen, K. *Chem. Ber.* **1991**, *124*, 2091.

(33) (a) Okamoto, M.; Teranishi, H. *J. Phys. Chem.* **1984**, *88*, 5644. (b) Sonoda, Y.; Kawanishi, Y.; Sakuragi, M. *Chem. Lett.* **1999**, 587. (c) Kanbara, T.; Takakusagi, H.; Kagaya, S.; Hasegawa, K. *Chem. Lett.* **1999**, 969.

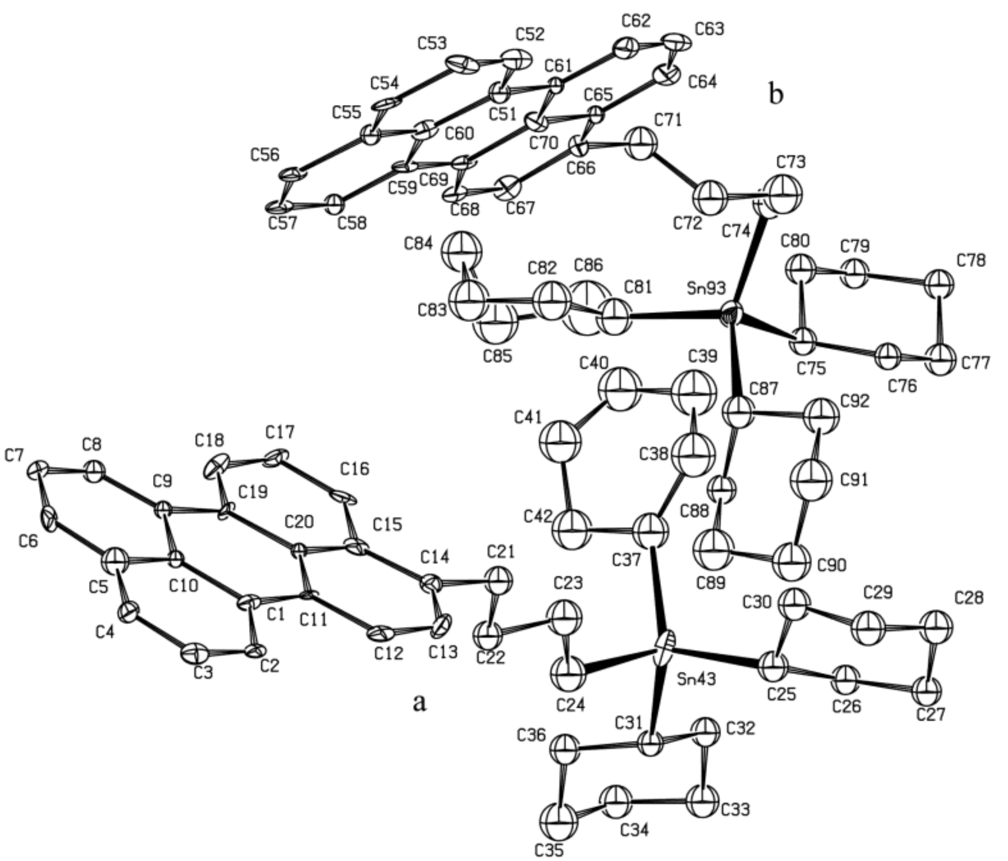


Figure 2. Molecular structure of $Cy_3Sn(CH_2)_4C_{10}H_{20}$ (**3a**) showing the 10% probability thermal ellipsoids for all non-hydrogen atoms.

Table 2. Selected Bond (Å) Lengths and Angles (deg) for 3a

Sn(43)−C(24)	2.19(4)	Sn(93)−C(74)	2.11(3)
Sn(43)−C(25)	2.11(3)	Sn(93)−C(75)	2.18(2)
Sn(43)−C(31)	2.14(2)	Sn(93)−C(81)	2.18(3)
Sn(43)−C(37)	2.15(4)	Sn(93)−C(87)	2.22(3)
C(14)−C(21)	1.52(2)	C(66)−C(71)	1.51(2)
C(21)−C(22)	1.50(2)	C(71)−C(72)	1.51(3)
C(22)−C(23)	1.58(2)	C(72)−C(73)	1.54(3)
C(23)−C(24)	1.51(3)	C(73)−C(74)	1.47(3)
C(25)−Sn(43)−C(31)	106.4(10)	C(87)−Sn(93)−C(75)	110.1(11)
C(25)−Sn(43)−C(24)	110.0(12)	C(87)−Sn(93)−C(81)	105.7(14)
C(31)−Sn(43)−C(24)	100.5(11)	C(75)−Sn(93)−C(81)	102.1(11)
C(25)−Sn(43)−C(37)	114.7(14)	C(87)−Sn(93)−C(74)	116.5(11)
C(31)−Sn(43)−C(37)	113.9(12)	C(75)−Sn(93)−C(74)	105.7(11)
C(24)−Sn(43)−C(37)	110.3(15)	C(81)−Sn(93)−C(74)	115.7(16)

ficiency of the electron transfer, the organization of the perylene units onto the surface should play an important part, since aggregation processes via $\pi-\pi$ stacking are known to strongly affect the photophysical properties of perylene derivatives.[34] It is therefore of interest to determine whether such interactions do exist in the solid state. All attempts to crystallize the tin trichlorides have unfortunately failed. However, X-ray diffraction quality crystals of **3a** were grown by slow evaporation of a chloroform solution. The molecular structures of the two independent molecules comprising the asymmetric unit of **3a** are depicted in Figure 2, and selected bond lengths and angles are shown in Table 2. The compound crystallizes in the monoclinic space group $P2_1$. The crystallographic unit cell comprises two sets of two independent entities arranged head to head, the perylene units of which exhibit a dihedral angle of ca. 69.3(1)°. The two independent molecules, labeled **a** and **b**, mainly differ in the conformation of their butylene spacer. Indeed, the butyl chain of the entity **a** adopts an anti conformation, whereas that of **b** exhibits a less stable gauche arrangement. The origin of this discrepancy remains unclear, but the influence of intermolecular packing effects may be important in these systems. The environments of the tin centers are best described in terms of a distorted-tetrahedral geometry defined by a $C'C_3$ donor set. The bond angles about tin convey the deviation from the ideal geometry. For instance, although the C(87)−Sn(93)−C(75) angle of 110.1(11)° was close to the ideal value, a closing of the C(75)−Sn(93)−C(81) and C(75)−Sn(93)−C(74) angles (102.1(11) and 105.7(11)°, respectively) and a concomitant opening of the C(87)−Sn(93)−C(74) and C(81)−Sn(93)−C(74) angles (116.5(11) and 115.7(16)°, respectively) were found. Furthermore, the $Sn-C_{alkyl}$ (2.19(4) and 2.11(3) Å) and $Sn-C_{Cy}$ (2.11(3)−2.22(4) Å) bond lengths were within the range of those reported for alkyl-,[35] halogeno-,[36] and carboxylatotricyclohexyltins.[37]

As a result, no intermolecular $\pi-\pi$ interaction between perylene cores could be detected in the asym-

---

(34) Sotero, P.; Arce, R. *Polycyclic Aromat. Compd.* **1999**, *14−15*, 295.

(35) (a) Cox, P. J.; Dodge-Harrison, S. M. S. V.; Nowell, I. W.; Howie, R. A.; Randall, A. P.; Wardell, J. L. *Inorg. Chim. Acta* **1990**, *172*, 225. (b) Glass, R. S.; Guo, Q.; Liu, Y. *Tetrahedron* **1997**, *53*, 12273.

(36) Calogero, S.; Ganis, P.; Peruzzo, V.; Tagliavini, G.; Valle, G. *J. Organomet. Chem.* **1981**, *220*, 11.

(37) (a) Molloy, K. C.; Purcell, T. G.; Hahn, E.; Schumann, H.; Zuckerman, J. J. *Organometallics* **1986**, *5*, 85. (b) Kamruddin, S. K.; Chattopadhyaya, T. K.; Roy, A.; Tiekink, E. R. T. *Appl. Organomet. Chem.* **1996**, *10*, 512.

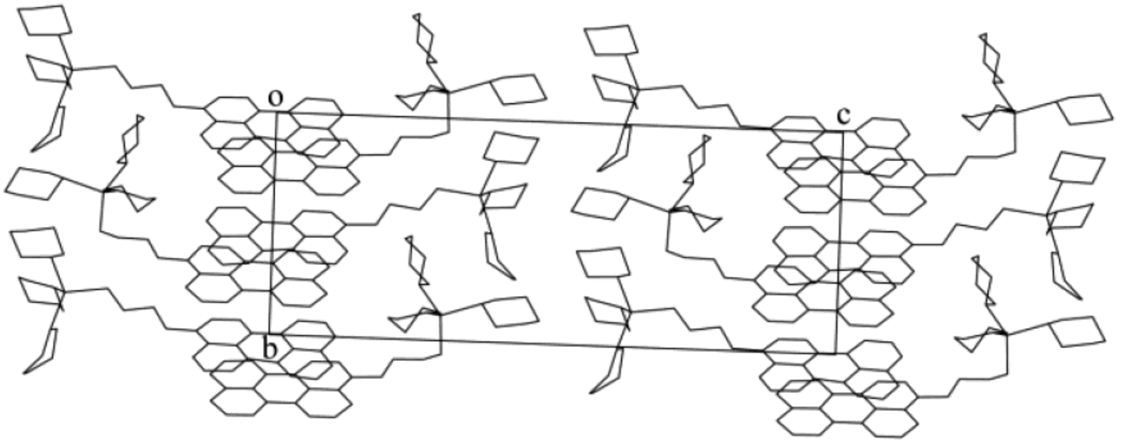


Figure 3. Side view along the (ox) axis of the unit cell (structure of **3a**).

metric unit. In contrast, $\pi-\pi$ contacts were found between the two aromatic rings of molecules belonging to two neighboring unit cells (Figure 3). Indeed, the distances C(6)−C(63)^i and C(13)−C(56)^i are 3.38 and 3.31 Å, respectively (symmetry operation i: $1 - x, -{}^1/_2 + y, -z$), values which are smaller than the sum of the van der Waals radii of two carbon atoms (3.40 Å).[38]

Conclusion

New perylene-substituted organotrialkynyltins have been synthesized in two steps from the corresponding tricyclohexyltins in very high yields. The crystal structure of 3-(4-(tricyclohexylstannyl)butyl)perylene reveals that $\pi-\pi$ contacts exist between the perylene units of molecules belonging to two neighboring unit cells. The absorption and fluorescence properties of the perylene core remain unaffected by the presence of a ω-(tricyclohexylstannyl)- or ω(-trihex-1-ynylstannyl)alkyl substituent but are strongly perturbed by a ω-(trichlorostannyl)-alkyl or a 2-stannylethynyl group.

Work is currently in progress to graft these new perylene-substituted organotrialkynyltins onto nanocrystalline tin dioxide powders. The corresponding results and the photoelectrochemical response of the materials obtained will be reported very shortly.

Experimental Section

General Procedures and Starting Materials. All manipulations of air and/or moisture-sensitive compounds were carried out using standard Schlenk line or drybox techniques under an atmosphere of nitrogen. THF and toluene were distilled from sodium benzophenone ketyl prior to use. Acetonitrile, chloroform, dichloromethane, and *n*-hexane were refluxed over CaH_2 and collected by distillation. All solvents were stored over activated 4 Å molecular sieves under an atmosphere of nitrogen. Perylene was purchased from Lancaster and used as received. The (ω-hydroxyalkyl)tricyclohexyltin species **4**,[19] 3-bromoperylene (**7**),[16,22] and 3-ethynylperylene (**8**)[23] were synthesized according to previously reported procedures.

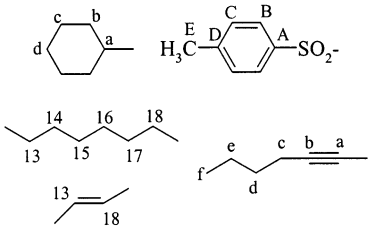
Instrumentation. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC-250, Bruker DPX-200, or Varian Unity Plus 500 spectrometers. ^1H and ^{13}C assignments were confirmed when necessary with the use of one-dimensional NOE experiments and of two-dimensional $^1H-^1H$ COSY, $^1H-^1H$ NOESY, and $^{13}C-^1H$ HMQC NMR experiments. All spectra were referenced internally to residual protio solvent (^1H) or solvent (^{13}C) resonances and are reported relative to trimethylsilane (δ 0 ppm). ^{119}Sn NMR spectra were recorded at 74.6 MHz (solvent $CDCl_3$, internal reference Me_4Sn). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz, while "s" stands for singlet, "d" for doublet, "dd" for doublet of doublets, "t" for triplet, and "m" for multiplet. Tin−carbon coupling constants (Hz) are given in brackets. Absorption UV−visible spectra were recorded with a Hewlett-Packard 8453 or a Hitachi U-3300 spectrophotometer. Fluorescence studies were carried out with a Spex Fluorolog 212 apparatus. The quantum yields of fluorescence Φ_{em} were measured in dichloromethane solution (10^{-7} M) by using quinine sulfate as a reference and were calculated according to the formula

$$\Phi_{em} = \frac{n_{CH_2Cl_2}[A(s)][Abs(ref)]}{n_{HClO_4}[A(ref)][Abs(s)]}\Phi_{em}(ref)$$

with $n_{CH_2Cl_2}$ and n_{HClO_4} = refractive indexes of dichloromethane and perchloric acid, A(s) and A(ref) = areas of the absorption spectra of the sample and the reference, Abs(s) and Abs(ref) = absorbances at 390 nm of the sample and the reference, and Φ_{em}(ref) = quantum yield of fluorescence of the reference in $HClO_4$ (10^{-7} M).

Mass spectrometry data were collected with a VG Autospec-Q working in the electronic impact mode. Elemental analyses were performed in the Center of Chemical Analysis of the CNRS (Vernaison, France).

Atom labeling used in NMR assignments is as follows:



(4-(Tosyloxy)butyl)tricyclohexyltin (5a). In a three-necked flask, tosyl chloride (4.8 g, 25.2 mmol) was added by portion to a solution of (4-hydroxybutyl)tricyclohexyltin (**4a**; 7.9 g, 17.9 mmol) in pyridine (17.3 mL) cooled to 0 °C. The mixture was warmed to room temperature and stirred for a further 8 h. After hydrolysis with HCl (10% v/v), the usual workup (extraction into ether, drying onto $MgSO_4$, evaporation of the solvent) gave a white powder which was stored at − 18 °C. Yield: 8.6 g (81%). mp 64 °C. ^1H NMR (250 MHz, $CDCl_3$, 293 K): δ 7.75 (d, 7.3, 2H, H_B), 7.3 (d, 7.3, 2H, H_C), 4.00 (t, 7.4, 2H, H_{21}), 2.42 (s, 3H, H_E), 1.80−1.10 (m, 37H, $H_{a,b,c,d}$ and $H_{22,23,24,25}$), 0.67 (m, [46], 2H, H_{26}). ^{13}C NMR (62.9 MHz, $CDCl_3$,

---

(38) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

293 K): δ 145.0 (C_A), 133.8 (C_D), 130.2 (C_B), 128.3 (C_C), 71.0 (C_{21}), 34.7 (C_{22}), 32.8 ([16], C_b), 29.7 ([52], C_c), 27.6 (C_d), 26.3 ([315], C_a), 25.3 ([17], C_{25}), 22.0 (C_E), 7.0 ([260], C_{26}). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −66.6. Anal. Found (calcd for $C_{29}H_{48}O_3SSn$): C, 58.6 (58.5); H, 8.1 (8.1); S, 5.8 (5.4).

(6-(Tosyloxy)hexyl)tricyclohexyltin (5b). 5b was formed by a procedure analogous to that for **5a** with tosyl chloride (1.9 g, 10 mmol) and (6-hydroxyhexyl)tricyclohexyltin (**4b**; 3.5 g, 7.5 mmol) in pyridine (7 mL). After hydrolysis, the standard workup yielded a white powder which was stored at −18 °C. Yield: 3.8 g (81%). mp 57 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 7.77 (d, 7.5, 2H, H_B), 7.32 (d, 7.5, 2H, H_C), 3.99 (t, 7.5, 2H, H_{21}), 2.42 (s, 3H, H_E), 1.80−1.10 (m, 41H, $H_{a,b,c,d}$ and $H_{22,23,24,25}$), 0.68 (m, [47], 2H, H_{26}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 146.0 (C_A), 133.0 (C_D), 129.8 (C_B), 127.9 (C_C), 70.8 (C_{21}), 34.4 (C_{22}), 32.4 ([17], C_b), 29.3 ([56], C_c), 28.9 (C_d), 27.3 ($C_{23,24}$), 26.0 ([16], C_{25}), 25.9 ([318], C_a), 22.0 (C_E), 7.0 ([255], C_{26}). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −65.9. Anal. Found (calcd for $C_{31}H_{52}O_3SSn$): C, 59.6 (59.7); H, 8.4 (8.4); S, 5.3 (5.1).

(4-Iodobutyl)tricyclohexyltin (6a). In a three-necked flask, sodium iodide (10.4 g, 69.4 mmol) was added to a solution of (4-(tosyloxy)butyl)tricyclohexyltin (**5a**; 7.9 g, 17.9 mmol) in anhydrous acetone (50 mL). The reaction mixture was refluxed for 12 h. The standard workup and column chromatography over silica gel (eluent *n*-pentane, $R_f = 0.95$) gave a colorless oil. Yield: 6.7 g (87%). ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 3.19 (t, 7.5, 2H, H_{21}), 1.90−1.10 (m, 37H, $H_{a,b,c,d}$ and $H_{22,25}$), 0.57 (m, [48], 2H, H_{26}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 39.0 (C_{22}), 32.1 ([18], C_b), 30.0 ([56], C_c), 28.7 (C_{25}), 27.9 ([6], C_d), 26.6 ([326], C_a), 7.2 (C_{21}), 5.5 ([270], C_{26}). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −64.5. Anal. Found (calcd for $C_{22}H_{41}ISn$): C, 47.5 (47.9); H, 7.3 (7.5); I, 23.0 (23.1).

(6-Iodohexyl)tricyclohexyltin (6b). 6b was formed by a procedure analogous to that for **6a** with tosyl chloride (7.2 g, 48.1 mmol) and (6-(tosyloxy)hexyl)tricyclohexyltin (**5b**; 6 g, 9.6 mmol) in anhydrous acetone (50 mL). The usual workup and column chromatography over silica gel (eluent *n*-pentane, $R_f = 0.95$) yielded a colorless oil. Yield: 5.4 g (96%). ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 3.17 (t, 7,5, 2H, H_{21}), 1.80−1.10 (m, 41H, $H_{b,c,d}$ and $H_{22,23,24,25}$), 0.74 ([47], 2H, H_{26}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 34.9 (C_{22}), 33.6 (C_{23}), 32.4 ([18], C_b), 30.1 (C_{24}), 29.7 ([52], C_c), 27.3 (C_d), 27.1 (C_{25}), 26.0 ([322], C_a), 7.4 (C_{21}), 6.7 ([269], C_{26}). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −65.7. Anal. Found (calcd for $C_{24}H_{45}ISn$): C, 50.1 (49.8); H, 8.0 (7.8); I, 21.2 (21.9).

3-(4-(Tricyclohexylstannyl)butyl)perylene (3a). In a Schlenk tube under a nitrogen atmosphere cooled to −78 °C, 2.7 mL (6.8 mmol) of *n*-butyllithium (2.5 M in hexanes) was added dropwise to a solution of 3-bromoperylene (**7**; 2.25 g, 6.8 mmol) in anhydrous THF. After 10 min, a solution of (4-iodobutyl)tricyclohexyltin (5.0 g, 9.1 mmol) in anhydrous THF (20 mL) was added. After it was stirred at −78 °C for 1 h, the mixture was warmed to room temperature and was stirred for a further 20 h. The solvent was then removed, and the residue was extracted into toluene. The resulting organic phase was washed, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was then purified by 10 successive column chromatographies over silica gel (elution gradient: *n*-pentane/dichloromethane 100/0 to 80/20 v/v; $R_f = 0.83$). Recrystallization from toluene gave analytically pure **3a** as yellow plates Yield: 2.5 g (54%). Mp: 169 °C. Crystals suitable for X-ray measurements were grown by slow evaporation of a concentrated solution of **3a** in chloroform. ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 8.18 (d, 7.8, 1H, H_6), 8.15 (d, 7.5, 1H, H_{12}), 8,13 (d, 7.5, 1H, H_7), 8.09 (d, 7.8, 1H, H_1), 7.89 (d, 8.3, 1H, H_4), 7.64 (d, 8.3, 1H, $H_{9\ \mathrm{or}\ 10}$), 7,62 (d, 7.5, 1H, $H_{9\ \mathrm{or}\ 10}$), 7.49 (dd, 8.3, 7.8, 1H, H_5), 7.45 (dd, 8.3, 7.5, 1H, $H_{8\ \mathrm{or}\ 11}$), 7.44 (dd, 8.3, 7.5, 1H, $H_{8\ \mathrm{or}\ 11}$), 7.32 (d, 7.8, 1H, H_2), 2.99 (m, 2H, H_{13}), 1.85−1.15 (m, 37H, $H_{a,b,c,d}$ and $H_{14,17}$), 0.82 (m, [46], 2H, H_{18}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 138.0 (C_3), 133.6, 132.0 (C_3−*C*−C_4), 130.7, 130.6, 130.5, 128.3, 128.0, 127.5, 126.6 ($C_{9\ \mathrm{or}\ 10}$), 126.2 ($C_{9\ \mathrm{or}\ 10}$), 125.7 (C_2), 125.7 ($C_{8\ \mathrm{or}\ 11}$), 125.5 ($C_{8\ \mathrm{or}\ 11}$), 125.1 (C_5), 122.9 (C_4), 119.0 ($C_{6\ \mathrm{and}\ 1\ \mathrm{and}\ (7\ \mathrm{or}\ 12)}$), 118.6 ($C_{7\ \mathrm{or}\ 12}$), 35.7 ($C_{14}$), 32.8 ($C_{13}$), 32.4 ([17], C_b), 29.2 ([53], C_c), 27.5 (C_{17}), 27.2 (C_d), 26.0 ([314], C_a), 6.7 ([245], C_{18}). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −65.7. UV−visible (CH_2Cl_2; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 228 (22 700), 256 (32 900), 396 (11 200), 417 (25 000), 445 (31 900). MS-EI (*m*/*z*): 676 (3%) [M^+], 593 (83%) [$M^+ - C_6H_{11}$], 511 (2%) [$M^+ - Sn(C_6H_{11})_2$], 426 (5%) [$M^+ - Sn(C_6H_{11})_3$], 309 (48%) [$M^+ - Sn(C_6H_{11})_3$], 265 (100%) [$M^+ - Sn(C_6H_{11})_3C_3H_6$]. HRMS-EI: found (calcd) 676.3057 (676.3091). Anal. Found (calcd for $C_{42}H_{52}Sn$): C, 74.3 (74.2); H, 7.7 (7.8).

3-(6-(Tricyclohexylstannyl)hexyl)perylene (3b). 3b was formed by a procedure analogous with that for **3a** with 3-bromoperylene (2.25 g, 6.8 mmol), *n*-butyllithium (2.7 mL, 6.8 mmol) 2.5 M in hexanes, and (6-iodohexyl)tricyclohexyltin (5.2 g, 9.0 mmol) in anhydrous THF (20 mL). The crude product was purified by 10 successive column chromatographies over silica gel (elution gradient: *n*-pentane/dichloromethane 100/0 to 80/20 v/v; $R_f = 0.83$). After recrystallization from toluene, yellow plates were isolated. Yield: 2.5 g (52%). Mp: 179 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 8.18 (d, 7.7, 1H, H_6), 8.16 (d, 7.7, 1H, H_{12}), 8.13 (d, 7.7, 1H, H_7), 8.09 (d, 7.7, 1H, H_1), 7.87 (d, 8.4, 1H, H_4), 7.64 (d, 8.1, 1H, $H_{9\ \mathrm{or}\ 10}$), 7.62 (d, 8.1, 1H, $H_{9\ \mathrm{or}\ 10}$), 7.49 (dd, 8.4, 7.7, 1H, H_5), 7.45 (dd, 8,1, 7.7, 1H, $H_{8\ \mathrm{or}\ 11}$), 7.44 (dd, 8.1 Hz 7.7, 1H, $H_{8\ \mathrm{or}\ 11}$), 7.32 (d, 7.7, 1H, H_2), 2.97 (m, 2H, H_{13}), 1.85−1.1 (m, 41H, $H_{a,b,c,d}$ and $H_{14,15,16,17}$), 0.74 (m, [46], 2H, H_{18}). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 139.3 (C_3), 134.9, 133.3 (C_3−*C*−C_4), 132.0, 131.7, 131.6, 129.6, 129.3, 128.8, 127.9 ($C_{9\ \mathrm{or}\ 10}$), 127.5 ($C_{9\ \mathrm{or}\ 10}$), 127.0 (C_2), 126.8 ($C_{11\ \mathrm{or}\ 8}$), 126.7 ($C_{11\ \mathrm{or}\ 8}$), 126.4 (C_5), 124.1 (C_4), 120.3 ($C_{6\ \mathrm{and}\ 1\ \mathrm{and}\ (7\ \mathrm{or}\ 12)}$), 119.8 ($C_{7\ \mathrm{or}\ 12}$), 34.9 ($C_{16}$), 33.4 ($C_{13}$), 32.4 ([17], C_b), 30.6 (C_{14}), 29.3 ([51], C_c), 29.3 (C_{15}), 27.3 (C_d), 27.3 (C_{17}), 25.9 ([314], C_a), 6.8 ([350], C_{18}). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −65.5. UV−visible (CH_2Cl_2; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 228 (23 200), 256 (33 500), 395 (12 800), 417 (28 000), 445 (35 700). MS-EI (*m*/*z*): 704 (9%) [M^+], 621 (46%) [$M^+ - C_6H_{11}$], 539 (13%) [$M^+ - Sn(C_6H_{11})_2$], 455 (6%) [$M^+ - Sn(C_6H_{11})_3$], 334 (59%) [$M^+ - Sn(C_6H_9)_3C_2H_4$], 265 (100%) [$M^+ - Sn(C_6H_{11})_3C_5H_{10}$]. HRMS-EI: Found (calcd) 704.3404 (704.3399). Anal. Found (calcd for $C_{44}H_{56}Sn$): C, 75.1 (75.0); H, 8.0 (8.0).

3-(2-(Tricyclohexylstannyl)ethenyl)perylene (3c). In a Schlenk tube under a nitrogen atmosphere, 0.6 g (1.63 mmol) of tricyclohexyltin hydride in benzene was added dropwise to a solution of 3-ethenylperylene (**8**; 0.5 g, 1.8 mmol) in benzene (90 mL). The mixture was heated to 70 °C, and a solution of AIBN (0.06 mmol) in benzene (10 mL) was then slowly added. The heating at 70 °C was continued for a further 4 h in order to obtain the pure β(*Z*) adduct. After addition of an excess of tricyclohexyltin hydride (0.95 g, 2.6 mmol) and AIBN (0.06 mmol), complete isomerization into the β(*E*) isomer was obtained after 24 h at 70 °C, as monitored by ^{1}H NMR spectroscopy. The solvent was then removed, and the residue was extracted into toluene. The resulting organic phase was washed with neutral water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (eluent: *n*-pentane/diethylamine 95/5 v/v; $R_f = 0.66$). Recrystallization from chloroform gave analytically pure β(*E*)-**3c** as orange plates. Yield: 0.57 g (49%). Mp: 185 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ 8.19 (d, 7.6, 1H, H_6), 8.17 (d, 7.8, 1H, H_{12}), 8,15 (d, 8.3, 1H, H_7), 8.14 (d, 7.8, 1H, H_1), 7.97 (d, 8.3, 1H, H_4), 7.65 (d, 7.8, 1H, H_2), 7.64 (d, 7.8, 1H, $H_{9\ \mathrm{or}\ 10}$), 7,63 (d, 8.3, 1H, $H_{9\ \mathrm{or}\ 10}$), 7.58 (d, 19.5, 1H, H_{18}), 7.50 (dd, 8.3, 7.6, 1H, H_5), 7.46 (dd, 8.1, 7.6, 1H, $H_{8\ \mathrm{or}\ 11}$), 7.44 (dd, 8.1, 7.6, 1H, $H_{8\ \mathrm{or}\ 11}$), 6.86 (d, 19.5, 1H, H_{13}), 1.98−1.27 (m, 37H, $H_{a,b,c,d}$). ^{13}C NMR (75.5 MHz, $CDCl_3$, 293 K): δ 144.0 ([9], C_{13}), 137.4 (C_3), 135.0, 133.7 ([305], C_{18}), 132.3, 131.9, 131.8, 130.9, 129.2, 128.9, 128.1 (C_5), 127.9 ($C_{9\ \mathrm{or}\ 10}$), 127.0 ($C_{9\ \mathrm{or}\ 10}$), 126.9 ($C_{8\ \mathrm{or}\ 11}$), 126.8 ($C_{8 \text{ or } 11}$), 124.7 (C_2), 124.0 (C_4), 120.7 ($C_{6 \text{ and } 1 \text{ and } (7 \text{ or } 12)}$), 120.4 ($C_{7 \text{ or } 12}$), 32.8 ([17], C_b), 29.7 ([56], C_c), 27.6 ([6], C_d), 26.4 ([330], C_a). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −98.5 (β), −100.1 (α). UV−visible (CH_2Cl_2; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 259 (39 600), 409 (14 500), 434 (29 300), 459 (34 400). MS-EI (*m*/*z*): 646 (5%) [M^+], 563 (32%) [$M^+ - C_6H_{11}$], 278 (100%) [$M^+ - Sn(C_6H_{11})_3$], 426 (5%) [$M^+ - Sn(C_6H_{11})_3$], 309 (48%) [$M^+ - Sn(C_6H_{11})_3$], 265 (100%) [$M^+ - Sn(C_6H_{11})_3C_3H_6$]. HRMS-EI: found (calcd) 646.2632 (646.2621). Anal. Found (calcd for $C_{42}H_{52}Sn$): C, 74.7 (74.4); H, 7.4 (7.2).

3-(4-(Trichlorostannyl)butyl)perylene (2a). In a Schlenk tube under a nitrogen atmosphere at room temperature, 1.61 g (6.2 mmol) of tin tetrachloride was added dropwise to a solution of **3a** (4.2 g, 6.2 mmol) in CH_2Cl_2 (100 mL). The stirring was then continued for a further 24 h. After evaporation of the solvent, the residue was washed with *n*-pentane (6 × 50 mL) in order to remove the tricyclohexyltin chloride formed. After drying under vacuum at 70 °C for 3 days, a yellow greenish powder of **2a** was isolated. Yield: 3.1 g (95%). This compound had to be stored under nitrogen with light exclusion. Mp: 120 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 8.21 (d, 7.9, 1H, H_6), 8.18 (d, 7.3, 1H, H_{12}), 8.15 (d, 7,9, 1H, H_7), 8.11 (d, 7.8, 1H, H_1), 7.81 (d, 7.9, 1H, H_4), 7.66 (d, 8.3, 1H, $H_{9 \text{ or } 10}$), 7.64 (d, 8,3, 1H, $H_{9 \text{ or } 10}$), 7.51 (dd, 7.9 and 7.9, 1H, H_5), 7.47 (dd, 8.3 and 7.9, 1H, $H_{8 \text{ or } 11}$), 7.44 (dd, 8.3 and 7.9, 1H, $H_{8 \text{ or } 11}$), 7.30 (d, 7.8, 1H, H_2), 3.08 (apparent triplet, 2H, H_{13}), 2.34 (apparent triplet, [84], H_{18}), 2.10−1.90 (m, 4H, $H_{14,17}$). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ +3.9. UV−visible (CH_2Cl_2; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 228 (33 200), 256 (37 000), 396 (12 100), 417 (25 700), 444 (33 100). MS-EI (*m*/*z*): 532 (16%) [M^+], 306 (65%) [$M^+ - SnCl_3$], 265 (100%) ($M^+ - SnCl_3C_3H_6$]. HRMS-EI: found (calcd) 531.9574 (531.9584). Anal. Found (calcd for $C_{24}H_{19}Cl_3Sn$): C, 54.5 (54.1); H, 3.6 (3.6); Cl, 19.8 (20.0).

3-(6-(Trichlorostannyl)hexyl)perylene (2b). **2b** was formed by a procedure analogous with that for **2a** with **3b** (1.9 g, 2.7 mmol) and tin tetrachloride (0.7 g, 2.7 mmol) in CH_2Cl_2 (60 mL). After evaporation of the solvent, washing with *n*-pentane, and drying under vacuum, a yellow greenish powder of **2b** was isolated. Yield: 1.5 g (98%). This compound had to be stored under nitrogen with light exclusion. Mp: 125 °C. ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 8.19 (d, 7.1, 1H, H_6), 8.16 (d, 7.1, 1H, H_{12}), 8.13 (d, 7.1, 1H, H_7), 8.09 (d, 7.8, 1H, H_1), 7.83 (d, 7.8 Hz, 1H, H_4), 7.65 (d, 8.3, 1H, $H_{9 \text{ or } 10}$), 7.64 (d, 7.1, 1H, $H_{9 \text{ or } 10}$), 7.49 (dd, 7.8 and 7.1, 1H, H_5), 7.45 (dd, 8.3 and 7.1, 1H, $H_{8 \text{ or } 11}$), 7.44 (dd, 8.3 and 7.1, 1H, $H_{8 \text{ or } 11}$), 7.30 (d, 7.8, 1H, H_2), 2.99 (apparent triplet, 2H, H_{13}), 2.33 (apparent triplet, [90], 2H, H_{18}), 1.83−1.68 (m, 2H, H_{17}), 1.60−1.40 (m, 4H, $H_{14,15,16}$). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 138.3, 134.6, 133.0, 132.9, 131.8, 131.4, 129.6, 128.5, 127.7, 127.4, 126.8, 126.6, 126.5, 126.3, 123.6, 120.2, 120.1, 120.0 (2C), 119.7, 30.5, 30.3, 29.7, 27.4, 26.2, 22.2. ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ +4.3. UV−visible (CH_2Cl_2; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 228 (24 600), 256 (29 100), 396 (8900), 417 (20 000), 444 (25 900). MS-EI (*m*/*z*): 560 (9%) [M^+], 336 (39%) [$M^+ - SnCl_3$], 265 (100%) [$M^+ - SnCl_3C_5H_{10}$]. HRMS-EI: found (calcd) 559.9887 (559.9865). Anal. Found (calcd for $C_{24}H_{19}Cl_3Sn$): C, 55.2 (55.7); H, 4.1 (4.1); Cl, 18.9 (20.0).

3-(4-(Trihex-1-ynylstannyl)butyl)perylene (1a). In a Schlenk tube under a nitrogen atmosphere cooled to −78 °C, 8.3 mL (20.8 mmol) of *n*-butyllithium (2.5 M in hexanes) was added dropwise to a solution of hex-1-yne (1.9 g, 23.1 mmol) in anhydrous THF (6 mL) at 0 °C. After it was stirred at room temperature for 30 min, the reaction mixture was cooled to −78 °C and a solution of **2a** (3.0 g, 5.6 mmol) in anhydrous THF (50 mL) was slowly added. After it was returned to room temperature, the mixture was stirred for a further 12 h. The solvent was then removed under reduced pressure, the resulting solids were extracted into CH_2Cl_2, and the solution obtained was filtered twice over anhydrous $MgSO_4$. Evaporation of the solvent and drying under vacuum at 50 °C gave an amber waxy solid. Yield: 3.6 g (95%). ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 8.18 (d, 7.8, 1H, H_6), 8.16 (d, 7.8, 1H, H_{12}), 8.12 (d, 7.8, 1H, H_7), 8.09 (d, 7.8, 1H, H_1), 7.86 (d, 8.3, 1H, H_4), 7.64 (d, 8.3, 1H, $H_{9 \text{ or } 10}$), 7.63 (d, 8.3, 1H, $H_{9 \text{ or } 10}$), 7.49 (dd, 8.3 and 7.8, 1H, H_5), 7.45 (dd, 8.3 and 7.8, 1H, $H_{8 \text{ or } 11}$), 7.44 (dd, 8.3 and 7.8, 1H, $H_{8 \text{ or } 11}$), 7.32 (d, 7.8, 1H, H_2), 3.00 (apparent triplet, 2H, H_{13}), 2.19 (m, [131], 6H, H_c), 1.82 (m, [96], 4H, $H_{14,17}$), 1.44 (m, 6H, H_d), 1.33 (m, 6H, H_e), 1.28 (t, 7.60, [72], 2H, H_{18}), 0.82 (t, 7.32, 9H, H_f). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 137.5 (C_3), 133.6, 132.3, 130.7, 130.5, 130.4, 128.4, 128.0, 127.5, 126.6 ($C_{9 \text{ or } 10}$), 126.3 ($C_{8 \text{ or } 10}$), 125.7 (C_2), 125.6 ($C_{11 \text{ or } 8}$), 126.5 ($C_{11 \text{ or } 8}$), 125.2 (C_5), 122.8 (C_4), 119.0 (3C, $C_{6 \text{ and } 1 \text{ et } (7 \text{ or } 12)}$), 118.6 ($C_{7 \text{ or } 12}$), 111.3 ([156], C_b), 76.3 ([804], C_a), 33.6 (C_{14}), 32.9 (C_{13}), 30.6 ([8], C_d), 25.8 ([29], C_{17}), 21.9 (C_e), 19.8 ([15], C_c), 15.2 ([601], C_{18}), 13.6 (C_f). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −249.8. UV−visible (CH_2Cl_2; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 228 (18 600), 256 (30 600), 395 (11 500), 417 (24 200), 445 (31 700). MS-EI (*m*/*z*): 670 (25%) [M^+], 614 (8%) [$M^+ - C_4H_9$], 588 (34%) [$M^+ - C_6H_9$], 278 (100%) [$M^+ - Sn(C_6H_9)_3C_2H_4$]. HRMS-EI: found (calcd) 670.2627 (670.2621). Anal. Found (calcd for $C_{42}H_{46}Sn$): C, 74.0 (75.3); H, 6.9 (6.9); Sn, 17.8 (17.7).

3-(6-(Trihex-1-ynylstannyl)hexyl)perylene (1b). **1b** was formed by a procedure analogous with that for **1a** with **2b** (3.1 g, 5.5 mmol), *n*-butyllithium 2.5 M in hexanes (8.1 mL, 20.2 mmol), and hex-1-yne (1.8 g, 21.9 mmol) in anhydrous THF (60 mL). After filtration over $MgSO_4$, evaporation of the solvent, and drying under vacuum, an amber waxy solid was isolated. Yield: 3.4 g (90%). ^{1}H NMR (250 MHz, $CDCl_3$, 293 K): δ 8.20 (d, 7.8, 1H, H_6), 8.17 (d, 7.8, 1H, H_{12}), 8.14 (d, 7.8, 1H, H_7), 8.10 (d, 7.8, 1H, H_1), 7.86 (d, 8.3, 1H, H_4), 7.65 (d, 8.3, 1H, $H_{9 \text{ or } 10}$), 7.63 (d, 8.3, 1H, $H_{9 \text{ or } 10}$), 7.49 (dd, 8.3 and 7.8, 1H, H_5), 7.45 (dd, 8.3 and 7.8, 1H, $H_{8 \text{ or } 11}$), 7.44 (dd, 8.3 and 7.8, 1H, $H_{8 \text{ or } 11}$), 7.32 (d, 7.8, 1H, H_2), 2.97 (apparent triplet, 2H, H_{13}), 2.18 (t, 7.10, [131], 6H, H_c), 1.72 (m, 2H, H_{14}), 1.66 (m, 2H, H_{17}), 1.44 (m, 10H, H_d $H_{15,16}$), 1.34 (m, 6H, H_e), 1.20 (t, 7.60, [76], 2H, H_{18}), 0.82 (m, 9H, H_f). ^{13}C NMR (62.9 MHz, $CDCl_3$, 293 K): δ 138.6 (C_3), 134.4, 132.8 ($C_3{-}C{-}C_4$), 131.5, 131.3, 131.2, 129.2, 128.9, 128.3, 127.5 ($C_{9 \text{ or } 10}$), 127.1 ($C_{9 \text{ or } 10}$), 126.5 (C_2), 126.4 ($C_{11 \text{ or } 8}$), 126.3 ($C_{11 \text{ or } 8}$), 126.0 (C_5), 123.6 (C_4), 119.9 (3C, $C_{6 \text{ and } 1 \text{ and } (7 \text{ or } 12)}$), 119.4 ($C_{7 \text{ or } 12}$), 112.0 ([150], C_b), 77.2 ([846], C_a), 33.5 (C_{13}), 33.0 ($C_{15 \text{ or } 16}$), 30.8 (C_d), 30.6 (C_{14}), 29.5 ($C_{15 \text{ or } 16}$), 25.7 ([31], C_{17}), 22.1 (C_e), 20.0 ([7], C_c), 15.7 ([655], C_{18}), 13.8 (C_f). ^{119}Sn NMR (74.6 MHz, $CDCl_3$, 293 K): δ −250.0. UV−visible (CH_2Cl_2; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 228 (15 500), 256 (28 000), 395 (10 000), 417 (21 000), 445 (27 000). MS-EI (*m*/*z*): 698 (25%) [M^+], 616 (15%) [$M^+ - C_4H_9$], 363 (5%) [$M^+ - Sn(C_4H_9)_3$], 334 (60%) [$M^+ - Sn(C_6H_9)_3C_2H_4$], 265 (100%) [$M^+ - Sn(C_6H_9)_3C_5H_{10}$]. HRMS-EI: found (calcd) 698.2978 (698.2934). Anal. Found (calcd for $C_{42}H_{46}Sn$): C, 74.5 (75.7); H, 7.2 (7.2); Sn, 17.6 (17.0).

3-(2-(Trihex-1-ynylstannyl)ethenyl)perylene (1c). First ol all, **2c** was formed by a procedure analogous with that for **2a** with **3c** (0.75 g, 1.16 mmol) and tin tetrachloride (1 mL, 1.16 M in CH_2Cl_2) in CH_2Cl_2 (30 mL). After evaporation of the solvent, washing with *n*-pentane, and drying under vacuum, a yellow greenish powder of **2c** was isolated. Yield: 0.56 g (96%). ^{1}H NMR (300 MHz, DMSO, 293 K): δ 7.61 (d, 7.9, 1H, H_6), 7.57 (d, 8.5, 1H, H_{12}), 7.54 (d, 8.5, 1H, H_7), 7.53 (d, 8.2, 1H, H_1), 7.13 (d, 8.5, 1H, H_4), 6.98 (d, 7.9, 1H, $H_{9 \text{ or } 10}$), 6.96 (d, 17.4, 1H, H_{18}), 6.95 (d, 7.6, 1H, $H_{9 \text{ or } 10}$), 6.86 (dd, 8.5, 7.9, 1H, H_5), 6.85 (dd, 8.5, 7.9, 1H, $H_{8 \text{ or } 11}$), 6.76 (dd, 8.5, 7.6, 1H, $H_{8 \text{ or } 11}$), 6.71 (d, 8.2, 1H, H_2), 6.11 (d, 17.4, 1H, H_{13}). This compound (0.5 g, 1 mmol), which is light and air sensitive, was immediately reacted with 3.6 equiv of hex-1-ynyllithium prepared from *n*-butyllithium 2.5 M in hexanes (1.46 mL, 3.6 mmol) and hex-1-yne (0.34 g, 4.1 mmol) in anhydrous THF (10 mL). After the mixture was stirred overnight at room temperature, a workup analogous with that for **1a**,**b** gave crude **1c** as an orange waxy solid. Final purification was achieved by washing with *n*-pentane. Yield: 0.2 g (30%). ^{1}H

Table 3. Crystal Data and Structure Refinement Details for 3a

empirical formula	$C_{84}H_{94}Sn_2$
formula wt	1340.97
cryst descripn	yellow plates
temp, K	120
cryst syst	monoclinic
space group	$P2_1$
a, Å	10.529(1)
b, Å	11.134(1)
c, Å	28,762(2)
α, deg	90
β, deg	96.820(2)
γ, deg	90
V, Å^3	3347.9(5)
Z	2
calcd density, Mg/m^3	1.33
F(000)	1396
μ, mm^{-1}	0.792
θ, deg	2−25
index ranges	$-12 \leq h \leq 12$ $-12 \leq k \leq 10$ $-34 \leq l \leq 23$
no. of data collected	10 543
no. of unique data	7908 (R(int) = 0.0452)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	7908/47/556
goodness of fit (F^2)	1.099
R1(F) ($I = 2\sigma(I)$)[a]	0.1139
wR2(F^2) ($I = 2\sigma(I)$)[a]	0.2470
extinction coeff	0.0026(8)
largest diff peak/hole, e/Å^3	1.435/−0.943

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

NMR (300 MHz, CDCl$_3$, 293 K): δ 8.22 (d, 7.2, 1H, H$_6$), 8.19 (d, 7.2, 1H, H$_{12}$), 8.17 (d, 7.2, 1H, H$_7$), 8.16 (d, 7.9, 1H, H$_1$), 8.02 (d, 8.7, 1H, H$_4$), 7.92 (d, 18.9, 1H, H$_{18}$), 7.76 (d, 8.3, 1H, H$_2$), 7.69 (d, 7.9, 1H, H$_{9\text{ or }10}$), 7.68 (d, 7.9, 1H, H$_{9\text{ or }10}$), 7.50 (dd, 8.7, 7.2, 1H, H$_5$), 7.49 (dd, 7.9, 7.2, 1H, H$_{8\text{ or }11}$), 7.48 (dd, 7.9, 7.2, 1H, H$_{8\text{ or }11}$), 6.75 (d, 18.9, 1H, H$_{13}$), 2.34 (m, 6H, H$_c$), 1.50 (m, 6H, H$_d$), 1.42 (m, 6H, H$_e$), 0.88 (t, 7.5, 9H, H$_f$). ^{13}C NMR (75.5 MHz, CDCl$_3$, 293 K): δ 144.5 ([11], C$_{13}$), 137.4 (C$_3$), 135.0, 134.5 ([290], C$_{18}$), 132.5, 132.2, 131.9, 131.2, 129.1, 128.5, 128.0 (C$_5$), 127.7 (C$_{9\text{ or }10}$), 127.2 (C$_{9\text{ or }10}$), 126.5 (C$_{8\text{ or }11}$), 126.7 (C$_{8\text{ or }11}$), 124.6 (C$_2$), 124.1 (C$_4$), 120.6 (C$_{6\text{ and }1\text{ and }(7\text{ or }12)}$), 120.4 (C$_{7\text{ or }12}$), 112.7 ([120], C$_b$), 76.4 ([630], C$_a$), 30.9 ([8], C$_d$), 22.2 (C$_e$), 20.1 ([8], C$_c$), 13.9 (C$_f$). ^{119}Sn NMR (111.9 MHz, CDCl$_3$, 293 K): δ −281.8. UV−visible (CH$_2$Cl$_2$; λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})): 229 (13 851), 260 (10 633), 434 (6967), 457 (7804). MS-EI (m/z): 363 (6%) [HSn(C$_6$H$_9$)$_3$], 278 (100%) [M$^+$ − HSn(C$_6$H$_9$)$_3$]. Anal. Found (calcd for C$_{40}$H$_{40}$Sn): C, 73.5 (75.1); H, 6.6 (6.3); Sn, 18.8 (18.6).

X-ray Crystallography. Crystal data collection and processing parameters are given in Table 3. Data were collected at 120 K using Mo Kα radiation with a Nonius Kappa-CCD[39] diffractometer equipped with an Oxford Cryosystems low-temperature device.[40] The images were processed, and equivalent reflections were merged; corrections for Lorentz−polarization and absorption were applied.[41] The structure was solved by direct methods, and subsequent Fourier difference syntheses revealed the position of all other non-hydrogen atoms. Structure refinement based on F^2 was carried out by extended block-diagonal matrix methods. Neutral-atom scattering factors were taken from ref 42. H atoms were placed in calculated positions and refined in a riding model. All crystallographic calculations were performed using SHELX97,[43] and illustrations were drawn with PLATON.[44] It is noteworthy to mention the very high vibration amplitudes found for some atoms of the cyclohexyl groups. The ellipsoid thermal parameters of these atoms could be rationalized in terms of either large librations of the cyclohexyl substituents or some conformational disorder.[45]

Acknowledgment. Drs. J-P. Desvergne and N. H. Rees are acknowledged for helpful discussions. Mrs. Belin, Mrs. Rascle, Mrs. Vitry, and Mr. Barbe are thanked for their valuable assistance. This work was supported by the Centre National de la Recherche Scientifique et the MENRT (fellowship and ACI Jeunes Chercheurs grant to G.V.).

Supporting Information Available: Tables of bond lengths, bond angles, atomic coordinates, and anisotropic displacement parameters for the structure of **3a**. This information is available free of charge via the Internet at http://pubs.acs.org.

OM030478M

---

(39) Nonius *Kappa CCD Reference Manual*; Nonius BV: Delft, The Netherlands, 1998.

(40) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105.

(41) Otwinowski, Z.; Minor, W. In *Macromolecular Crystallography Part A*; Methods in Enzymology 276; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; pp 307−326.

(42) *International Tables for Crystallography*; Wilson, A. J., Prince, E., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1999; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(43) Sheldrick, G. M. SHELX97 and SHELXL97; University of Göttingen, Göttingen, Germany, 1997.

(44) Spek, A. L. PLATON, Program for Drawing Crystal and Molecular Diagrams; University of Utrecht, Utrecht, The Netherlands, 2000.

(45) Calogero, S.; Ganis, P.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1979**, *179*, 145.