Synthesis, characterization and nonlinear optical properties in a series of new chiral organotin(IV) Schiff base complexes

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Abstract

Four new chiral organotin derivatives are reported with their crystal structure. They were synthesized by reaction of diphenyltin oxide and four different ligands obtained from the Schiff base condensation of 4-(diethylamino)salicylaldehyde and (1R,2S)-(+)-norephedrine, (R)-(−)-phenylglycinol, (R)-(−)-1-amino-2-propanol and (1S,2R)-2-amino-1,2-diphenylethanol. Their nonlinear optical properties were investigated experimentally in solid state and with the electric field induced second harmonic (EFISH) technique. In particular, the compound obtained with (R)-(−)-phenylglycinol exhibits an efficiency 11 times that of urea in second harmonic generation at 1.907 μm. The properties are discussed in relation with computational studies conducted within the framework of the DFT theory.
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1. Introduction

An important class of diorganotin(IV) complexes are those derived from Schiff bases. Their investigation has initially been encouraged by the discovery of in vitro and in vivo antitumour activity in organotin(IV) derivatives [1–3]. These types of compounds have also found application in homogeneous catalysis [4], and medicinal chemistry [5]. By contrast, very few investigations have focused on Schiff base tin complexes as molecular materials, although numerous reports have been devoted to Schiff bases metal complexes exhibiting magnetic [6], or nonlinear optical (NLO) properties [7,8].

Certainly, diorganotin(IV) derivatives do not deserve any interest as magnetic complexes, in relation to the close-shell electronic structure of Sn^{IV}. More surprisingly, the investigation of NLO properties in organotin derivatives is a rather unexplored topic, despite the fact that optical nonlinearities have been reported since the late eighties in molecules containing metal [9] and organometallic [10] fragments. One reason, which may have hampered the investigation of these systems may be the fact that tin is not parametrized in the ZINDO (Zerner intermediate neglect of differential overlap) formalism [11]. Indeed, since the early nineties, the science of chromophore design has deeply been influenced by the computational chemistry procedures. In particular, the proven INDO-SOS [12,13] approach has successfully been used to predict, and moreover to provide a precise description of the NLO response at the microscopic level. This has oriented synthetic chemists towards the most promising candidates, for which the chemical intuition could have led at best to qualitative prediction of the NLO response.

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Few years ago, we have reported on quadratic nonlinear optical (NLO) properties in a series of "push–pull" boronate derivatives built up from the Schiff base condensation of salicylideneiminophenols and phenylboronic acids [14]. The observation that the NLO skeleton is invariably deeply bent in these molecules, which reduces the charge transfers and hence the NLO properties, encouraged us to extend our investigation to diorganotin derivatives [15], in which a better planarity was expected. Finally, a molecular NLO response enhancement of about 50% was evidenced in solution for the tin derivatives, versus the related boron derivatives.

In the present contribution, we wish to further investigate the potential of organotin derivatives with the report of both solid state and solution NLO measurements, in a series of four new derivatives, presented in Scheme 1. The synthesis and the X-ray crystal structures will be reported first, then the nonlinear optical properties will be discussed, in relation to a computational approach, to rationalize the origin of the effect.

2. Experimental

2.1. Starting materials and equipments

All starting materials were purchased from Aldrich Chemical Co. Solvents were used without further purification. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Infrared spectra were measured on a Perkin–Elmer spectrum GX spectrophotometer using KBr pellets. ^{1}H, ^{119}Sn and ^{13}C NMR spectra were recorded on Bruker Avance DPX 300 Jeol FX 270 and Jeol Eclipse + 400 spectrometers. Chemical shifts (ppm) are relative to $(CH_3)_4Si$ for ^{1}H and ^{13}C and to $Sn(CH_3)_4$, for ^{119}Sn. Mass spectra were recorded on a HP 5989 A spectrometer. UV–Vis spectra were recorded on a Varian Cary 4000 spectrophotometer, and optical rotations
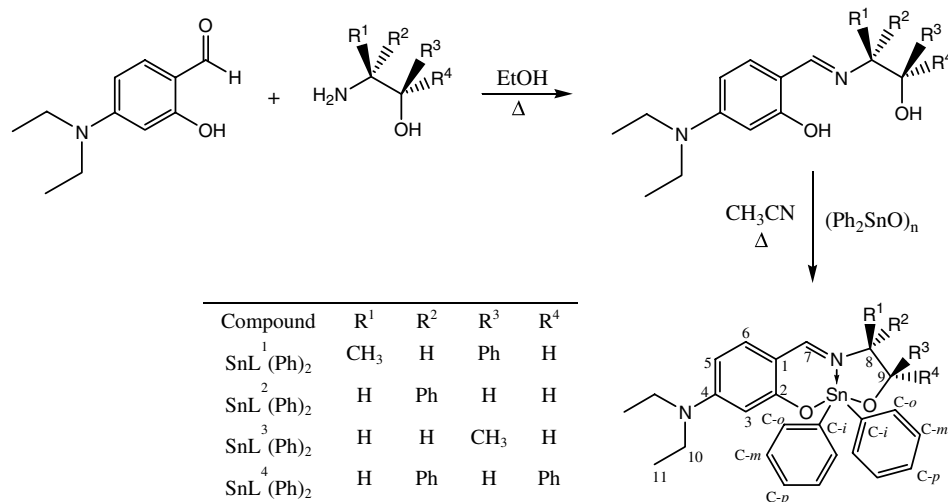
on a polarimeter Perkin–Elmer 241 polarimeter. Elemental analyses were carried out on a Thermo Finnigan Flash 1112 elemental analyzer.

2.2. Syntheses

2.2.1. Compound $SnL^1(Ph)_2$

5-Diethylamino-2-[(2-hydroxy-1-methyl-2-phenyl-ethyl-imino)-methyl]-phenol (H_2L^1) was synthesized from 1.00 g (5.17 mmol) of 4-(diethylamino)-salicylaldehyde and 0.78 g (5.17 mmol) of (1S,2R)-(+)-Norephedrine. The reaction was refluxed in ethanol for 1 h using a Dean-Stark trap. The product was obtained as an orange solid 1.51 g (4.62 mmol), Yield: 89%. M.p: 148–150 °C. IR v_{max} (KBr): 3432 (OH) 3061, 2972, 2930, 2888, 2689, 1638, 1607 (C=N), 1506, 1375, 1351, 1256, 1218, 1136, 1073, 1013, 793, 748, 701, 555 cm^{-1}. NMR (400 MHz, CDCl$_3$) [δ, ppm]: 1.14 (t, 6H, $J = 7.0$ Hz, CH$_3$), 1.21 (d, 3H, $J = 6.6$ Hz, CH$_3$-8), 3.31 (q, 4H, $J = 7.0$ Hz, CH$_2$), 3.62 (dq, 1H, $J = 4.8$ Hz, $J = 6.6$ Hz, H-8), 4.80 (d, 1H, $J = 4.8$ Hz, H-9), 6.02 (d, 1H, $J = 2.6$ Hz, H-3), 6.10 (dd, 1H, $J = 2.6$ Hz, $J = 8.8$ Hz, H-5), 6.91 (d, 1H, $J = 8.8$ Hz, H-6), 7.24-7.37 (m, 5H, H-*ortho*, H-*meta*, H-*para*), 7.87 (s, 1H, H-7). ^{13}C NMR (100.5 MHz, CDCl$_3$), [δ, ppm]: 12.8 (CH$_3$-11), 17.2(CH$_3$-8), 44.5 (CH$_2$-10), 67.0 (C-8), 77.1 (C-9), 98.5 (C-3), 103.2 (C-5), 108.1 (C-1), 126.9 (C-*meta*), 127.7 (C-6), 128.2 (C-*ortho*), 133.6 (C-*para*), 141.2 (C-*ipso*), 152.3 (C-4), 162.5 (C-7), 168.6 (C-2). MS (*m/z*, %): 326 (M$^+$, 9), 219 (100), 202 (10), 175 (8), 147 (4). Anal. Calc for C$_{20}$H$_{26}$N$_2$O$_2$: C, 73.59; H, 8.03; N,8.58. Found: C, 73.29; H, 8.37; N, 8.10%.

2,2,4-Triphenyl-5-methyl-(4'diethylaminobenzo[h])-6-aza-1,3-dioxa-6-en-2-stannacyclononene ($SnL^1(Ph)_2$) was synthesized from 0.50 g (1.53 mmol) of H_2L^1 and 0.44 g (1.53 mmol) of diphenyltin oxide. The reaction was carried out refluxing in acetonitrile for 36 h, using a Dean-Stark trap. The product was obtained as a yellow

Compound	R^1	R^2	R^3	R^4
SnL^1(Ph)$_2$	CH$_3$	H	Ph	H
SnL^2(Ph)$_2$	H	Ph	H	H
SnL^3(Ph)$_2$	H	H	CH$_3$	H
SnL^4(Ph)$_2$	H	Ph	H	Ph

Scheme 1.

solid 0.77 g (1.29 mmol), Yield: 84%. M.p: 222–225 °C. IR ν_{max} (KBr): 3050, 2970, 2925, 2781, 1595 (C=N), 1504, 1430, 1388, 1349, 1312, 1248, 1140, 1120, 1076, 1006, 826, 781, 732, 700, 657, 579, 544, 441 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [δ, ppm]: 0.91 (d, 3H, $J = 6.5$ Hz, CH$_3$-8), 1.28 (t, 6H, $J = 7.0$ Hz, CH$_3$-11), 3.46 (q, 4H, $J = 7.0$ Hz, CH$_2$-10), 3.68 (dq, 1H, $J = 6.5$ Hz, $J = 3.5$ Hz, H-8), 5.23 (d, 1H, $J = 3.5$ Hz, H-9), 6.14 (dd, 1H, $J = 2.2$ Hz, $J = 8.8$ Hz, H-5), 6.25 (d, 1H, $J = 2.2$ Hz, H-3), 6.91 (d, 1H, $J = 8.8$ Hz, H-6), 7.30–7.48 (m, 9H, H-*meta*, H-*para*), 7.60 (d, 2H, $J = 7.5$ Hz, H-*ortho* 9-Ph), 7.95 (dd, 2H, $J = 2.4$ Hz, $J = 7.5$ Hz, J ^{1}H, ^{119}Sn = 82.2 Hz, H-*ortho* Ph–Sn), 8.08 (s, 1H, H-7), 8.27 [dd, 2H, $J = 1.1$ Hz, $J = 7.9$ Hz, J (^{1}H, ^{119}Sn) = 83.2 Hz, H-*ortho* Ph–Sn]. ^{13}C NMR (100.52 MHz, CDCl$_3$) [δ, ppm]: 13.0 (CH$_3$-11), 17.0 (8-CH$_3$), 44.8 (CH$_2$-10), 67.3 [C-8, ^2J (^{13}C, ^{119}Sn) = 34.8 Hz], 76.4 [C-9, ^2J (^{13}C, ^{119}Sn) = 13 Hz], 101.0 (C-3), 103.6 (C-5), 108.9 [C-1, ^3J (^{13}C, ^{119}Sn) = 28.4H], 126.3 (C-*meta* 9-Ph), 126.8 (C-*para* 9-Ph), 128.2 (C-*ortho* 9-Ph), 128.4 [C-*meta* Ph–Sn, ^3J (^{13}C, $^{117/119}$Sn) = 73.3 Hz, 76.5 Hz], 128.5 [C-*meta* Ph–Sn, ^3J (^{13}C, $^{117/119}$Sn) = 78.1 Hz, 81.1 Hz], 129.6 [C-*para* Ph–Sn, ^4J (^{13}C, ^{119}Sn) = 16 Hz], 129.7 [C-*para* Ph–Sn, ^4J (^{13}C, ^{119}Sn) = 16 Hz], 136.9 (C-6), 137.0 [C-*ortho* Ph-Sn, ^3J (^{13}C, ^{119}Sn) = 41.6 Hz], 137.2 [C-*ortho* Ph–Sn, ^3J (^{13}C, ^{119}Sn) = 65.3 Hz], 141.4 [SnC-*ipso*, ^1J (^{13}C, $^{117/119}$Sn) = 921 Hz, 963 Hz], 142.1 [SnC-*ipso*, ^1J (^{13}C, ^{119}Sn) = 977 Hz, 1022 Hz], 144.7 [C-*ipso*, ^3J (^{13}C, ^{119}Sn) = 24.8 Hz], 154.6 (C-4), 167.1 [C-7, ^2J (^{13}C, ^{119}Sn) = 10.8 Hz], 171.7 [C-2, ^3J (^{13}C, ^{119}Sn) = 29.6 Hz]. ^{119}Sn NMR (111.88 MHz, CDCl$_3$), [δ, ppm]: −334.3. MS (m/z, %): (^{120}Sn M$^+$, 8), 492 (100), 450 (6), 415 (5), 374 (72), 337 (2), 296 (12), 238 (42), 218 (12). Anal. Calc. for C$_{32}$H$_{34}$SnN$_2$O$_2$: C, 64.34; H, 5.74; N, 4.69. Found: C, 64.28; H, 5.63; N, 4.72%.

2.2.2. Compound SnL^2(Ph)$_2$

5-Diethylamino-2-[(2-hydroxy-1-phenyl-ethylimino)-methyl]-phenol (H_2L^2) was synthesize from 1.00 g (5.17 mmol) of 4-(diethylamino)salicylaldehyde and 0.71 g (5.17 mmol) of R-(−)-2-phenylglycinol. The reaction was carried out under reflux of ethanol using a Dean-Stark trap for 1 h. The product was obtained as an orange solid 1.54 g (4.93 mmol), Yield: 95%. M.p: 111–113 °C IR ν_{max} (KBr): 3226, 2973, 2967, 2916, 1615(C=N), 1558, 1523, 1423, 1378, 1351, 1300, 1242, 1132, 1067, 1040, 909, 855, 824, 788, 755, 695, 538, 457 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) [δ, ppm]: 1.19 (t, 6H, $J = 7.0$ Hz, CH$_3$-11), 3.38 (q, 4H, $J = 7.0$ Hz, CH$_2$-10), 3.83-3.93 (m, 2H, H-9), 4.43 (dd, 1H, $J = 5.4$ Hz, $J = 7.5$ Hz, H-8), 6.13 (d, 1H, $J = 2.0$ Hz H-3), 6.16 (dd, 1H, $J = 2.0$ Hz, $J = 8.5$ Hz, H-5), 6.99 (d, 1H, $J = 8.5$ Hz, H-6), 7.28–7.38 (m, 5H, H-*ortho*, H-*meta*, H-*para*), 8.14 (s, 1H, H-7). ^{13}C NMR (75.47 MHz, CDCl$_3$), [δ, ppm]: 12.9 (CH$_3$-11), 44.7 (CH$_2$-10), 67.9 (C-9), 73.7 (C-8), 98.6 (C-3), 103.2 (C-5), 108.3 (C-1), 127.2 (C-*meta*), 127.8 (C-*para*), 128.8 (C-*ortho*), 133.6 (C-6), 139.9 (C-*ipso*), 152.3 (C-4), 164.5 (C-7), 165.97(2). MS (m/z, %): 312(M$^+$, 31), 313 (M$^+$ + 1, 9), 282 (40), 281(100), 237(7), 209(8), 91

(6). Anal. Calc. for C$_{19}$H$_{24}$N$_2$O$_2$: C, 73.05; H, 7.74; N,8.97. Found: C, 73.22; H, 7.83; N, 9.07%.

2,2,5-Triphenyl-(4′-diethylaminobenzo[h])-6-aza-1,3-dioxa-6-en-2-stannacyclononene (SnL^2(Ph)$_2$) was synthesized from 0.50 g (1.60 mmol) of H$_2$L^2 and 0.46 g (1.60 mmol) of diphenyltin oxide. The reaction was carried out refluxing 36 h in acetonitrile reflux, using a Dean-Stark trap. The product was obtained as a yellow solid 0.63 g (1.07 mmol), Yield: 67%. M.p: 216–219 °C. IR ν_{max} (KBr): 3036, 2979, 2936, 2886, 2818, 1590 (C=N), 1500, 1428, 1384, 1352, 1306, 1249, 1168, 1135, 1063, 932, 819, 781, 742, 695, 659, 585, 521, 439 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [δ, ppm]: 1.24 (t, 6H, $J = 7.0$ Hz, CH$_3$-11), 3.42 (q, 4H, $J = 7.0$ Hz, CH$_2$-10), 4.04 (dd, 1H, $J = 8.1$ Hz, $J = 10.3$ Hz, H-9a), 4.42 (dd, 1H, $J = 5.7$ Hz, $J = 10.3$ Hz, H9b), 4.60 (dd, 1H, $J = 8.1$ Hz, 5.7 Hz, H-8) 6.07 (dd, 1H, $J = 2.2$ Hz, $J = 9.0$ Hz, H-5), 6.23 (d, 1H, $J = 2.2$ Hz, H-3), 6.72 (d, 1H, $J = 9.0$ Hz, H-6), 7.21–7.36 and 7.36–7.50 (m, 11H, H-*meta* Ph–Sn and 8-Ph, H-*para* Ph-Sn and 8-Ph, H-ortho 8-Ph), 7.88 (s, 1H, H-7), 8.00 (dd, 2H, $J = 1.1$ Hz, $J = 7.5$ Hz, H-*o* Ph–Sn), 8.04 (dd, 2H, $J = 1.6$ Hz, $J = 7.7$ Hz, H-*ortho* Ph–Sn). ^{13}C NMR (100.52 MHz, CDCl$_3$) [δ, ppm]: 13.0 (CH$_3$-11), 44.8 (CH$_2$-10), 69.4 [C-8, ^2J (^{13}C, ^{119}Sn) = 44 Hz], 69.7 (C-9), 100.7 (C-3), 103.8 (C-5), 109.0 [C-1, ^3J (^{13}C, ^{119}Sn) = 28 Hz], 128.0 (C-*para* 8-Ph), 128.4 and 128.5 (C-*meta*), 128.9 (C-*ortho* 8-Ph), 129.7 [C-*para*, ^4J (^{13}C, ^{119}Sn) = 17 Hz], 136.9 (C-*ortho*, ^2J (^{13}C, ^{119}Sn) $J =$ 52 Hz), 137.4 (C-6), 140.3 (C-*ipso*), 141.4 [C-*ipso*, ^1J (^{13}C, $^{117/119}$Sn) = 913 Hz, 957 Hz], 141.8 [C-*ipso*, ^1J (^{13}C, $^{117/119}$Sn) = 977 Hz, 1020 Hz], 154.9 (C-4), 169.1 (C-7), 172.0 [C-2, ^2J (^{13}C, ^{119}Sn) = 29 Hz]. ^{19}Sn NMR (111.88 MHz, CDCl$_3$), [δ, ppm]: −327.0; MS (m/z, %): (^{120}Sn M$^+$, 9), 554 (100), 555 (32), 556 (17), 558 (16), 552 (77), 550 (41), 477 (4), 450 (4), 374 (93), 375 (16), 376 (15), 373 (38), 372 (79), 296 (17), 254 (28), 238 (55), 167 (14). Anal. Calc. for C$_{31}$H$_{32}$SnN$_2$O$_2$: C, 63.83; H, 5.53; N, 4.80. Found: C, 63.62; H, 5.47; N, 4.69%.

2.2.3. Compound SnL^3(Ph)$_2$

5-Diethylamino-2-[(2-hydroxy-propylimino)-methyl]-phenol (H_2L^3) was synthesized from 1.00 g (5.17 mmol) of 4-(diethylamino)-salicylaldehyde and 0.39 g (5.17 mmol) of R-(−)-1-amino-2-propanol. The reaction was carried out under reflux of ethanol, using a Dean-Stark trap for 1 h. The product was obtained as a brown solid 1.12 g (4.47 mmol), Yield: 86%. M.p: 61–64 °C. IR ν_{max} (KBr): 3075, 2969, 2929, 1646 (C=N), 1608, 1515, 1414, 1350, 1285, 1259, 1220, 1140, 1076, 1006, 825, 780, 692 cm^{-1}. ^{1}H NMR (270 MHz, CDCl$_3$) [δ, ppm]: 1.15 (t, 6H, $J = 7.1$ Hz, CH$_3$-11), 1.21 (d, 3H, $J = 6.5$ Hz, 9-CH$_3$), 3.32 (dd, H8a), 3.33 (q, 4H, CH$_2$-10), 3.53 (dd, 1H, $J = 3.7$ Hz, $J = 12.6$ Hz, H8b), 3.99 (m, 1H, H-9), 6.00 (d, 1H, $J = 2.2$ Hz, H-3), 6.08 (dd, 1H, $J = 2.2$ Hz, $J = 8.9$ Hz, H-5), 6.91 (d, 1H, $J = 8.9$ Hz, H-6), 7.89 (s, 1H, H-7). ^{13}C NMR (67.94 MHz, CDCl$_3$) [δ, ppm]: 2.8 (CH$_3$-11), 20.6 (9-CH$_3$), 44.6 (CH$_2$-10), 63.5 (C-8), 67.2

(C-9), 98.6 (C-3), 103.3 (C-5), 108.1 (C-1), 133.6 (C-6), 152.4 (C-4), 164.0 (C-7), 168.7 (C-2). MS (m/z, %): 250 (M$^+$, 64), 251 (M$^+$ + 1, 13), 235 (11), 205 (100), 191 (6), 178 (8), 162 (8), 133 (7). Anal. Calc. for C$_{14}$H$_{22}$N$_2$O$_2$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.22; H, 8.58; N, 11.21%.

2,2-Diphenyl-4-methyl-(4'diethylaminobenzo[h])-6-aza-1,3-dioxa-6-en-2-stannacyclononene (SnL^3(Ph)$_2$) was synthesized from 0.50 g (2.00 mmol) of H$_2$L^3 and 0.58 g (2.00 mmol) of diphenyltin oxide. The reaction was carried out refluxing 36 h in acetonitrile, using a Dean-Stark trap. The product was obtained as a yellow solid 0.78 g (1.49 mmol), Yield: 75%. M.p: 167–170 °C. IR ν_{max} (KBr): 3048, 2970, 2893, 1598 (C=N), 1508, 1430, 1389, 1349, 1311, 1248, 1227, 1138, 1074, 1048, 861, 826, 781, 732, 701, 661, 637, 583, 448 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) [δ, ppm]: 1.23 (t, 6H, J = 6.9 Hz, CH$_3$-11), 1.35 (d, 3H, J = 6.0 Hz, 9-CH$_3$), 3.21 (dd, 1H, J = 9.4 Hz, J = 15.9 Hz, H8a), 3.39–3.58 (m, 5H, H-8b, 10-CH$_2$), 4.13 (m, 1H, H-9), 6.09 (dd, 1H, J = 2.3 Hz, J = 8.9 Hz, H-5), 6.18 (d, 1H, J = 2.3 Hz, H-3), 6.86 (d, 1H, J = 8.9 Hz, H-6), 7.34–7.46 (m, 6H, H-meta, H-para), 7.93 (dd, 2H, J = 1.7 Hz, J = 7.7 Hz, H-o Ph–Sn), 8.01 (s, 1H, H-7), 8.02 (dd, 1H, J = 1.7 Hz, 7.2 Hz, H-ortho). ^{13}C NMR (75.47 MHz, CDCl$_3$) [δ, ppm]: 13.0 (CH$_3$-11), 23.11 [9-CH$_3$, ^3J (^{13}C, ^{119}Sn) = 18.7 Hz], 44.8 (CH$_2$-10), 64.6 [C-8, ^2J (^{13}C, ^{119}Sn) = 44.4 Hz], 67.7 [C-9, ^2J (^{13}C, ^{119}Sn) = 16.4 Hz], 100.9 (C-3), 103.5 (C-5), 108.7 [C-1, ^3J (^{13}C, ^{119}Sn) = 28.3 Hz], 128.4 [C-meta, ^3J (^{13}C, $^{117/119}$Sn) = 80.5 Hz, 83.9 Hz], 128.5 [C-meta, ^3J (^{13}C, $^{117/119}$Sn) = 58.5 Hz, 61.8 Hz], 129.6 [C-para, ^4J (^{13}C, ^{119}Sn) = 16.3 Hz, 136.8 (C6), 136.9 [C-orto, ^2J (^{13}C, ^{119}Sn) = 52 Hz], 137.1 [C-ortho, ^2J (^{13}C, ^{119}Sn) = 51 Hz], 141.7 [C-ipso, ^1J (^{13}C, $^{117/119}$Sn) = 923 Hz, 966 Hz], 142.2 [C-ipso, ^1J (^{13}C, $^{117/119}$Sn) = 965 Hz, 1009 Hz], 154.6 (C-4), 167.8 [C-7, ^2J (^{13}C, ^{119}Sn) = 11.4 Hz], 171.7 [C-2, ^2J (^{13}C, ^{119}Sn) = 29.5 Hz]. ^{119}Sn NMR (111.88 MHz, CDCl$_3$), [δ, ppm]: −329.0; MS (m/z, %): (^{120}Sn M$^+$, 15), 521 (2), 522 (1), 478 (100), 479 (25), 477 (48), 476 (76), 475 (35), 474 (42), 450 (11), 401 (22), 374 (62), 375 (11), 376 (10), 373 (26), 372 (24), 296 (19), 254 (18), 238 (39), 204 (33), 162 (9). Anal. Calc. for C$_{26}$H$_{30}$SnN$_2$O$_2$: C, 59.91; H, 5.80; N, 5.37. Found: C, 59.98; H, 5.92; N, 5.43%.

2.2.4. Compound SnL^4(Ph)$_2$

5-Diethylamino-2-[(2-hydroxy-1,2-diphenyl-ethylimino)-methyl]-phenol (H$_2$L^4) was synthesized from 1.00 g (5.17 mmol) of 4-(diethylamino)-salicylaldehyde and 1.10 g (5.17 mmol) of (1S,2R)-(+)-2-amino-1,2-diphenyl-ethanol. The reaction was carried out under reflux of ethanol, using a Dean-Stark trap for 1 h. The product was obtained as a yellow solid 1.93 g (4.97 mmol), Yield: 96%. M.p: 138–141 °C. IR ν_{max} (KBr): 3435, 3062, 2975, 2928, 2894, 2687, 1604 (C=N), 1512, 1450, 1391, 1345, 1261, 1226, 1143, 1094, 829, 777, 758, 594 cm^{-1}. ^{1}H NMR (270 MHz, CDCl$_3$) [δ, ppm]: 1.13 (t, 6H, J = 7.2 Hz, CH$_3$-11), 3.32 (q, 4H, J = 7.2 Hz, CH$_2$-10),

4.46 (d, 1H, J = 6.7 Hz, H-8), 5.00 (d, 1H, J = 6.7 Hz, H-9), 6.07-6.09 (m, 2H, H-3, H-5), 6.84 (d, 1H, J = 9.1 Hz, H-6), 7.19–7.33 (m, 10H, H-ortho, H-meta, H-para) 7.83 (s, 1H, H-7). ^{13}C NMR (67.94 MHz, CDCl$_3$) [δ, ppm]: 12.8 (CH$_3$-11), 44.6 (CH$_2$-10), 78.3 and 78.2 (C-8, C-9), 97.9 (C-3), 103.2 (C-5), 108.3 (C-1), 127.3 (C-meta), 127.9 (C-para), 127.8 (C-para), 128.1 (C-ortho), (C-meta), 128.6 (C- ortho), 133.3 (C-6), 139.9 (C-ipso), 140.5 (C-ipso), 151.6 (C-4), 164.2 (C-7), 164.8 (C-2). MS (m/z, %): 281 (M$^+$ − C$_6$H$_5$CHOH, 100), 237 (5), 209 (4). Anal. Calc. for C$_{25}$H$_{28}$N$_2$O$_2$: C, 77.29; H, 7.26; N,7.21. Found: C, 77.54; H, 7.38; N, 7.28%.

2,2,4,5-Tetraphenyl-(4'-diethylaminobenzo[h])-6-aza-1,3-dioxa-6-en-2-stannacyclononene (SnL^4(Ph)$_2$) was synthesized from 0.50 g (1.29 mmol) of H$_2$L^4 and 0.37 g (1.29 mmol) of diphenyltin oxide. The reaction was carried out refluxing 36 hr in acetonitrile, using a Dean-Stark trap during. The product was obtained as a yellow solid 0.68 g (1.03 mmol), Yield: 80%. M.p: 270-273 °C. IR ν_{max} (KBr): 3056, 2977, 2891, 2784, 1607 (C=N), 1591, 1499, 1450, 1428, 1380, 1350, 1307, 1248, 1186, 1143, 1072, 1049, 1025, 830, 779, 729, 697, 659, 629, 590, 549, 508, 449 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) [δ, ppm]: 1.30 (t, 6H, J = 7.0 Hz, CH$_3$-11), 3.48 (q, 4H, J = 7.7 Hz, CH$_2$-10), 4.67 (d, 2H, J = 4.4 Hz, J ^{1}H ^{119}Sn = 45 Hz, H-8), 5.49 (d, 1H, J = 4.4 Hz, H-9), 6.12 (dd, 1H, J = 2.2 Hz, J = 9.1 Hz, H-5), 6.30 (d, 1H, J = 2.2 Hz, H-3), 6.81 (d, 1H, J = 9.1 Hz, H-6), 6.88 (d, 2H, J = 7.3 Hz, H-ortho), 6.95 (t, 2H, J = 7.7 Hz, H-meta), 7.07 (t, 1H, J = 7.3 Hz, H-para), 7.20–7.26 and 7.40–7.54 (m, 11H, H-meta, H-para, H-ortho), 8.03 (dd, 2H, J = 1.5 Hz, J = 7.0 Hz, H-ortho Sn), 8.07 (s, 1H, H-7), 8.31 (dd, 2H, J = 1.4 Hz, J = 7.7 Hz, J ^{1}(H, ^{119}Sn) = 83.5 Hz, H-ortho) ^{13}C NMR (100.52 MHz, CDCl$_3$) [δ, ppm]: 13.0 (CH$_3$-11), 44.8 (CH$_2$-10), 74.1 [C-8, ^2J (^{13}C, ^{119}Sn) = 31 Hz], 77.8 (C-9), 100.9 (C-3), 104.0 (C-5), 109.1 [C-1, ^3J (^{13}C, ^{119}Sn) = 28 Hz], 126.5 (C-para), 126.7 (C-meta), 126.9 (C-para), 127.4 (C-meta), 127.7 (C-ortho), 128.5 (C-meta), 128.6 (C-meta), 128.8 (C-ortho), 129.7 (C-para Sn), 129.8 [C-para Sn, ^4J (^{13}C, ^{119}Sn) = 16.6 Hz], 136.9 (C-ortho), 137.3 (C-6), 137.6 (C-ortho), 139.7 (C-ipso), 141.1 (C-ipso), 142.11 [C-ipso, ^1J (^{13}C, $^{117/119}$Sn) = 916 Hz, 960 Hz], 144.0 [C-ipso, ^1J (^{13}C, $^{117/119}$Sn) = 976 Hz, 1021 Hz], 155.0 (C-4), 169.5 (C-7), 172.1 [C-2, ^2J (^{13}C, ^{119}Sn) = 30 Hz] . ^{119}Sn NMR (111.88 MHz, CDCl$_3$), [δ, ppm]: −329.0; MS (m/z, %): (^{120}Sn M$^+$, 2), 556 (15), 555 (27), 554 (87), 553 (22), 552 (66) 551 (10), 550 (36), 477 (3), 450 (4), 400 (1), 376 (16), 375 (18), 374 (100), 373 (41), 372 (85), 371 (35), 370 (50), 296 (14), 238 (53), 176 (3), 167 (13) 105 (1). Anal. Calc. for C$_{37}$H$_{36}$SnN$_2$O$_2$: C, 67.39; H, 5.50; N, 4.25. Found: C, 67.22; H, 5.39; N, 4.29%.

2.3. Structure analysis and refinement

The single crystals suitable for X-ray structural studies were obtained by slow evaporation in a mixture of CH$_2$Cl$_2$ and hexane for the four derivatives. The crystal data were

recorded on an Enraf Nonius-Fr590 Kappa-CCD (λ Mo Kα = 0.71073 Å, graphite monochromator, T = 293 K, CCD rotating images scan mode). The crystals were mounted on a Lindeman tube. Absorption corrections were performed within the SHELX-A [16] program or by the semi empirical correction through MULTISCAN procedure (PLATON) [17]. All reflection data set were corrected for Lorentz and polarization effects. The first structure solution was obtained using the SHELXS-97 program and then SHELXL-97 ver. 34 program [16] was applied for refinement and output data. All software manipulations were done under the WINGX [18] environment program set. Molecular perspectives were drawn under ORTEP 3 [19] drawing application. All heavier atoms were found by Fourier map difference and refined anisotropically. Some hydrogen atoms were refined isotropically. The remaining hydrogen atoms were geometrically modeled and not refined. Crystal data are summarized in Table 1.

2.4. Computational details

The gas phase geometries for the four tin derivatives were fully optimized within the framework of DFT at the B3PW91/6-31+G*/LANL2DZ(Sn) level [20] using the finite field (FF) procedure included in the Gaussian98 package [21]. The use of a pseudo-potential allows the description of relativistic effects for Sn. Metrical parameters used for the starting geometries were those of the present crystal structures. Vibrational analysis was performed at the same level in order to establish the presence of a minimum on the potential energy surface. The molecular hyperpolarizability (β) was computed, with the default value of Field strength of 0.001 atomic units. In this approach, β is obtained as the numerical partial derivative of the energy (W) with respect to the electric field (E), evaluated at zero field according to the following equation:

$$\beta_{ijk} = -\left(\frac{\partial^3 W}{\partial E_i \partial E_j \partial E_k}\right)_{E=0} \tag{1}$$

An expression which is only valid for the static field limit ($E = 0$). Following this approach, β is the magnitude of the vectorial hyperpolarizability $\beta = \sqrt{(\beta_x)^2 + (\beta_y)^2 + (\beta_z)^2}$ with $\beta_i = \beta_{ixx} + \beta_{iyy} + \beta_{izz}$, after assumption of the Kleinman symmetry conditions [22]. For the sake of simplification, dimethylamino groups (instead of diethylamino) were introduced in the calculations.

Table 1
Crystal data for the four organotin(IV) complexes

	SnL^1(Ph)$_2$	SnL^2(Ph)$_2$	SnL^3(Ph)$_2$	SnL^4(Ph)$_2$
Crystal data				
Chemical formula	C$_{32}$H$_{34}$N$_2$O$_2$Sn	C$_{31}$H$_{32}$N$_2$O$_2$Sn	C$_{26}$H$_{30}$N$_2$O$_2$Sn	C$_{37}$H$_{36}$N$_2$O$_2$Sn
Mol. wt.	597.30	584.15	521.21	660.18
Crystal size (mm)	0.1 × 0.2 × 0.1	0.2 × 0.2 × 0.2	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_1$
a (Å)	9.6646(2)	9.6852(2)	13.9367(2)	9.00120(10)
b (Å)	13.2648(2)	11.0095(2)	9.5321(1)	10.43280(10)
c (Å)	22.3780(5)	25.5677(5)	19.0348(3)	34.0273(3)
β (°)	90	90	109.221(1)	92.88
V (Å^3)	2868.84(10)	2726.26(9)	2387.74(6)	3191.38(5)
ρ_{calc} (Mg/m^3)	1.383	1.387	1.450	2.745
μ (Mo Kα) (mm^{-1})	0.921	0.964	0.935	1.670
Data collection				
Radiation (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	293(2)	293(2)	293(2)	293(2)
Scan mode	θ and ϕ	θ and ϕ	θ and ϕ	θ and ϕ
θ Range (°)	1.78–27.48	2.25–27.49	3.62–27.49	2.31–27.52
No. of reflections				
Measured	6493	6033	9566	28869
Unique	6493	6033	9402	12989
Used	5921	5545	7478	11474
Refinement				
Refinement on	F^2	F^2	F^2	F^2
No. of variables	435	390	488	638
H-atom treatment	Observed	Observed	Calculated	Calculated
R^a [$I > 2\sigma(I)$]	0.0421	0.0355	0.0352	0.0732
wR^b	0.0754	0.0778	0.0657	0.1921
$\Delta\rho_{max}$ (e Å^{-3})	0.572	0.380	0.661	2.757
$\Delta\rho_{min}$ (e Å^{-3})	−0.453	−0.376	−0.428	−1.193
GOF	1.114	1.023	1.023	1.148
Flack parameter	−0.03(2)	−0.02(2)	0.19(9)	−0.03(4)

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$.
[b] $wR = [\sum w(|F_o| - |F_c|)^2/\sum(wF_o)^2]^{1/2}$.

Additionally, the all-valence INDO (intermediate neglect of differential overlap) method [11], was employed for the calculation of the optical spectra of the representative H_2L^1 ligand, which was first optimized by DFT, as previously described. Calculations were performed using the INDO/1 Hamiltonian incorporated in the commercially available MSI software package ZINDO [23]. The monoexcited configuration interaction (MECI) approximation was employed to describe the excited states. The 100 lowest energy transitions between the 10 highest occupied molecular orbitals and the 10 lowest unoccupied ones were chosen to undergo CI mixing. Tin being not parametrized within ZINDO, the calculated spectra are not available for the complexes.

2.5. NLO measurements

The experimental hyperpolarizabilities (β) were investigated by the electric field induced second harmonic (EFISH) technique [24,25]. The data were recorded using a picosecond Nd:YAG pulsed (10 Hz) laser operating at 1.064 μm. The outcoming Stokes-shifted radiation at 1.907 μm generated by Raman effect in a hydrogen cell (1 m long, 50 bar) was used as the fundamental beam for second harmonic generation (SHG). The centrosymmetry of the solution was broken by dipolar orientation of the chromophores with a high voltage pulse (5 kV) synchronized with the laser pulse. The SHG signal was selected through a suitable interference filter, detected by a photomultiplier, and recorded on an ultrafast Tektronic TDS 620 B oscilloscope.

Additionally, the solid state SHG efficiency was evaluated by the Kurtz–Perry powder test [26]. The samples were uncalibrated powders put between two glass plates. The efficiencies were quantified versus a sample of powdered urea used as a reference.

3. Results and discussion

3.1. Design and spectral characterization of organotin (IV) derivatives

Pyridoxal (Vitamin B_6 aldehyde)-amino-acid Schiff bases are believed to be intermediate in biologically important amination processes [27]. Furthermore, metal ions catalyse transamination reactions involving vitamin B_6 [28,29]. These concurrent results seem to indicate that metal complexes of Schiff bases are formed as intermediates in transamination reactions involving vitamin B_6 [30]. Most of the work has dealt with transition-metal complexes of salicylideneamino-acid Schiff bases [31–35].

The syntheses of compounds $SnL^1(Ph)_2$, $SnL^2(Ph)_2$, $SnL^3(Ph)_2$, and $SnL^4(Ph)_2$ towards push–pull Schiff bases built up from diphenyltin oxide [15], follow the synthesis of the Schiff bases H_2L^1, H_2L^2, H_2L^3, and H_2L^4, respectively, and finally their reaction with diphenyltin oxide. They imply the synthesis of optically active Schiff bases starting from 4-diethylaminosalicylaldehyde and: (1R,2S)-

(+)-norephedrine, (R)-(−)-phenylglycinol, (R)-(−)-1-amino-2-propanol and (1S,2R)-2-amino-1,2-diphenylethanol for H_2L^1, H_2L^2, H_2L^3, and H_2L^4, respectively (Scheme 1). The reactions were carried out by refluxing in ethanol during 1 h. In the synthesis of the tin complexes, equimolecular quantities of Schiff bases and, diphenyltin oxide were reacted in acetonitrile during 36 h. The compounds were fully characterized by spectroscopic techniques.

The ^{13}C NMR spectra of Schiff bases show the iminic signal between 162 and 165 ppm, the corresponding iminic proton (H-7) appears between 7.83 and 8.14 ppm in the ^1H NMR spectra. For the tin complexes the ^{13}C NMR spectra show the iminic signal between 167 and 169 ppm, the corresponding iminic proton (H-7) appears between 7.88 and 8.09 ppm in the ^1H NMR spectra. The ^{119}Sn NMR spectra show the tin signal in the range between −337 and −334 ppm, which is characteristic for this type of pentacoordinate tin derivatives containing nitrogen coordination [3c,36,37]. The infrared spectra of the ligands show the band assigned to the imine bond between 1604 and 1646 cm^{-1}, for tin complexes the infrared band for the imine bond appears between 1590 and 1607 cm^{-1} which is present in all compounds. Mass spectra show the molecular ion in low abundance, the main fragment ion is $M^+ - RCHO$. The presence of the tin atom is easily detected due to the isotopic abundances of tin [38].

3.2. Crystal structure description

The molecular structures of the four organotin derivatives, $SnL^1(Ph)_2$, $SnL^2(Ph)_2$, $SnL^3(Ph)_2$, and $SnL^4(Ph)_2$ are presented in Fig. 1, with the atom labelling scheme. $SnL^1(Ph)_2$ crystallizes in the $P2_12_12_1$ orthorhombic space group, with one isolated molecule in the asymmetric unit cell. Similarly, $SnL^2(Ph)_2$ crystallizes in the same $P2_12_12_1$ space group. However, the examination of the lattice reveals that the compound exhibits slight intermolecular interactions between atoms O(2) and H(18), with an oxygen to hydrogen distance equal to 2.548 Å and an O(2)–H(18)–C(18) angle of 153.9°. This is illustrated in Fig. 2.

Compounds $SnL^3(Ph)_2$, and $SnL^4(Ph)_2$ crystallize in the $P2_1$ monoclinic space group. Two molecules are present in the asymmetric unit cell in both cases.

The coordination spheres around the tin atoms are described in Table 2, and appear roughly similar to those observed in other tin complexes [39]. The bond angles around the tin atom for compounds $SnL^1(Ph)_2$, $SnL^2(Ph)_2$, $SnL^3(Ph)_2$, and $SnL^4(Ph)_2$ are in the range from 76.22(10)° to 162.60(9)°, where the smaller angles are those of tin bonded to oxygen. The tin atom in compounds $SnL^1(Ph)_2$, $SnL^2(Ph)_2$, $SnL^3(Ph)_2$, and $SnL^4(Ph)_2$ has a distorted trigonal bipyramid geometry, where the axial positions are occupied by the oxygen atoms with bond angles values of 161.6°, 161.4°, 161.3°, and 159.4 for O(1)–Sn(1)–O(2), respectively, the atoms occupying equatorial positions are C(10), C(16) and N(1). The average values for the bond
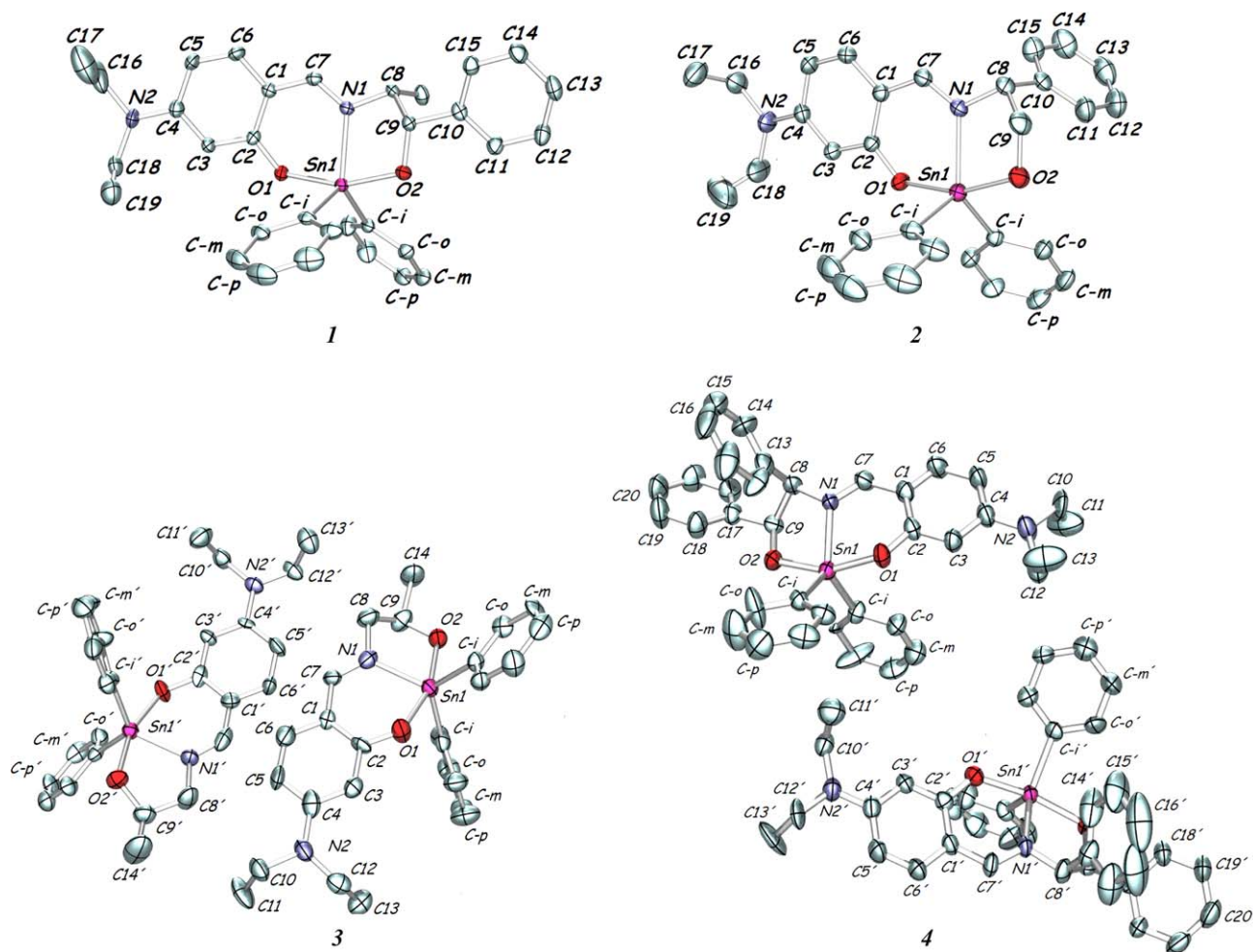
Fig. 1. Molecular structures of SnL^1(Ph)$_2$ (**1**), SnL^2(Ph)$_2$ (**2**), SnL^3(Ph)$_2$ (**3**), and SnL^4(Ph)$_2$ (**4**), with the atom labelling scheme (thermal ellipsoids at 30%).
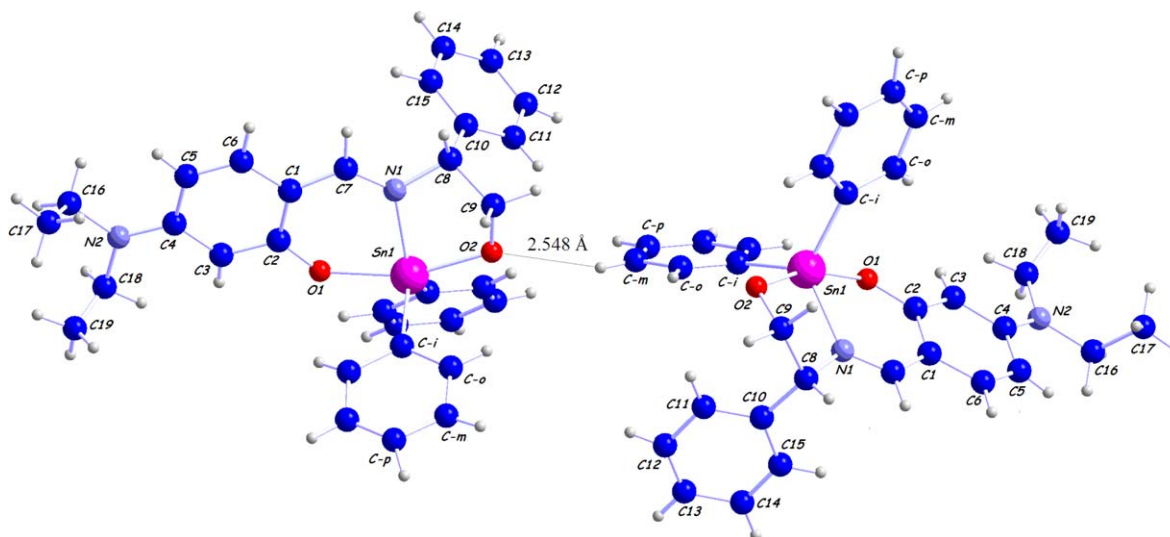

Fig. 2. Intermolecular hydrogen bonding in compound SnL^2(phen)$_2$, with O(2)–H(18) distance of 2.548 Å.

angles in the five-membered rings are 103.35°, 103.77°, 103.79°/104.84 and 103.83°/104.43°, for SnL^1(Ph)$_2$, SnL^2(Ph)$_2$, SnL^3(Ph)$_2$, and SnL^4(Ph)$_2$, respectively. These results are indicative of a high ring strain in the five-mem-

bered rings. The largest deviations from the mean plane formed by C(2)–C(1)–C(7)–N(1)–Sn(1)–O(1) in SnL^1(Ph)$_2$, SnL^2(Ph)$_2$, SnL^3(Ph)$_2$, and SnL^4(Ph)$_2$ are observed at O(1) (−0.263 Å), Sn(1) (−0.152 Å), O(1) (0.222 Å), O(3)

Table 2
Selected bond lengths (Å) and angle (°) in the coordination sphere of the tin atom in the four organotin(IV) complexes

	$SnL^1(Ph)_2$	$SnL^2(Ph)_2$	$SnL^3(Ph)_2$		$SnL^4(Ph)_2$	
			Molecule 1	Molecule 2	Molecule 1	Molecule 2
N(1)–Sn(1)	2.143(3)	2.152(3)	2.157(6)	2.154(5)	2.153(8)	2.153(8)
Sn(1)–C(i)	2.129(4)	2.133(4)	2.137(4)	2.128(4)	2.146(5)	2.131(5)
Sn(1)–C(i)	2.124(4)	2.127(4)	2.144(3)	2.142(4)	2.160(5)	2.182(4)
Sn(1)–O(1)	2.121(3)	2.115(3)	2.123(5)	2.113(5)	2.107(7)	2.112(7)
Sn(1)–O(2)	2.072(3)	2.045(3)	2.043(4)	2.046(4)	2.065(6)	2.053(7)
N(1)–Sn(1)–O(1)	82.85(12)	82.83(11)	83.1(2)	82.5(2)	82.1(3)	82.5(3)
N(1)–Sn(1)–C(i)	117.71(16)	116.53(14)	118.3(3)	118.0(3)	112.7(3)	114.4(3)
N(1)–Sn(1)–C(i)	120.37(14)	123.63(13)	119.5(2)	119.1(2)	128.04(3)	126.9(4)
N(1)–Sn(1)–O(2)	78.86(12)	78.86(12)	78.1(2)	78.7(2)	78.0(3)	77.7(3)
O(1)–Sn(1)–C(i)	93.17(16)	94.31(15)	94.3(2)	92.8(2)	95.4(3)	96.1(3)
O(1)–Sn(1)–C(i)	91.98(14)	90.78(13)	90.5(2)	91.8(2)	91.1(3)	91.0(3)
O(1)–Sn(1)–O(2)	161.70(11)	161.43(10)	161.12(19)	161.09(19)	158.5(3)	158.7(3)
C(i)–Sn(1)–C(i)	121.89(15)	119.73(14)	122.2(2)	122.8(2)	119.3(3)	118.7(3)
C(i)–Sn(1)–O(2)	95.93(16)	96.56(16)	95.9(2)	94.8(2)	94.9(3)	94.9(3)
C(i)–Sn(1)–O(2)	96.60(14)	96.79(13)	97.4(3)	98.5(2)	99.6(3)	98.9(3)
O(1)–Sn(1)–C(i)–C(o)	−173.1(4)	179.1(4)	174.9(2)	143.8(3)	−169.6(5)	−174.2(5)
O(1)–Sn(1)–C(i)–C(o)	12.8(3)	1.1(4)	−5.1(2)	−38.9(3)	15.3(5)	10.4(4)
O(2)–Sn(1)–C(i)–C(o)	27.7(4)	2.5(3)	12.1(2)	−20.4(4)	−5.0(5)	−9.3(5)
O(2)–Sn(1)–C(i)–C(o)	−150.9(4)	179.0(3)	−167.9(2)	157.0(3)	179.8(5)	175.3(4)

(0.227 Å), Sn(2) (−0.227 Å) and O(3) (0.287 Å), respectively.

The dihedral angles for the O1–Sn1–Ci–Co fragment in compounds $SnL^1(Ph)_2$, $SnL^2(Ph)_2$, $SnL^3(Ph)_2$, and $SnL^4(Ph)_2$ are 12.8° (3), 1.1°(4), −5.1 °(2), −38.9° (3), 15.3° (5) and 10.4° (4) which correspond to a nearly eclipsed conformation for that fragment. Fig. 3 shows the envelope conformations in the five membered-rings of compounds $SnL^1(Ph)_2$ and $SnL^4(Ph)_2$, in the crystalline state, where the atom which is out of the plane is, in all cases, C9 (atom bonded to O2). The six-membered rings are almost planar. Fig. 4 shows that C9 in $SnL^3(Ph)_2$ is the most deviated atom from the five member ring plane (0.296 Å).

3.3. Nonlinear optical properties

When a molecule is subjected to the intense electric field (E) of a laser light, the molecular polarization is expressed as follows:

$$\mu(E) = \mu_0 + \alpha E + \beta E^2 + \cdots \tag{2}$$

In this expression, μ_0 is the permanent dipole moment, α is the linear polarizability, and β the quadratic hyperpolarizability (origin of the NLO response). In most cases, β can be expressed in term of a set of a few low energy electronic transitions with charge transfer character and is related to the transition energies (E_i), their oscillator strengths (f_i) and the differences between the ground and excited state dipole moments ($\Delta\mu_i$) occurring during the transitions, according to Eq. (3) [40]:

$$\beta = \sum_i \frac{3e^2\hbar f_i \Delta\mu_i}{2mE_i^3} \times \frac{E_i^4}{(E_i^2 - (2\hbar\omega)^2)(E_i^2 - (\hbar\omega)^2)} \tag{3}$$

Relation in which the second part of the term on the right is a dimensionless dispersion factor, accounting for the relationship between β and the energy of the laser beam ($\hbar\omega$). Chromophores are NLO active when they possess π-electronic systems and charge asymmetry, a situation obtained with the use of donor–acceptor substituents linked
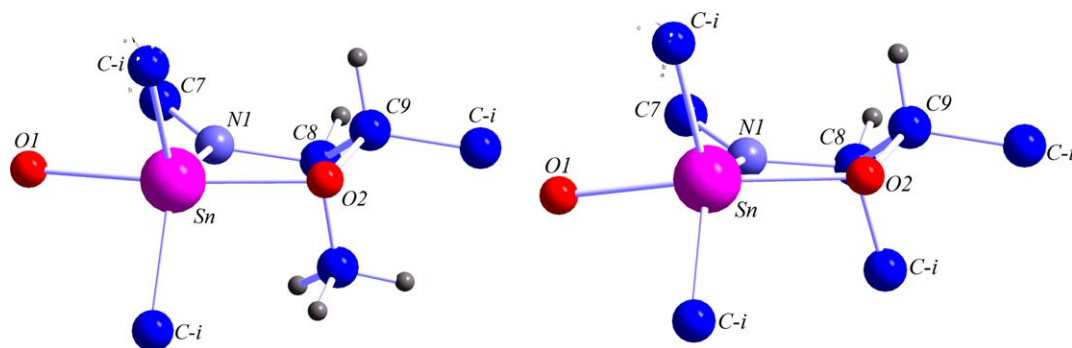

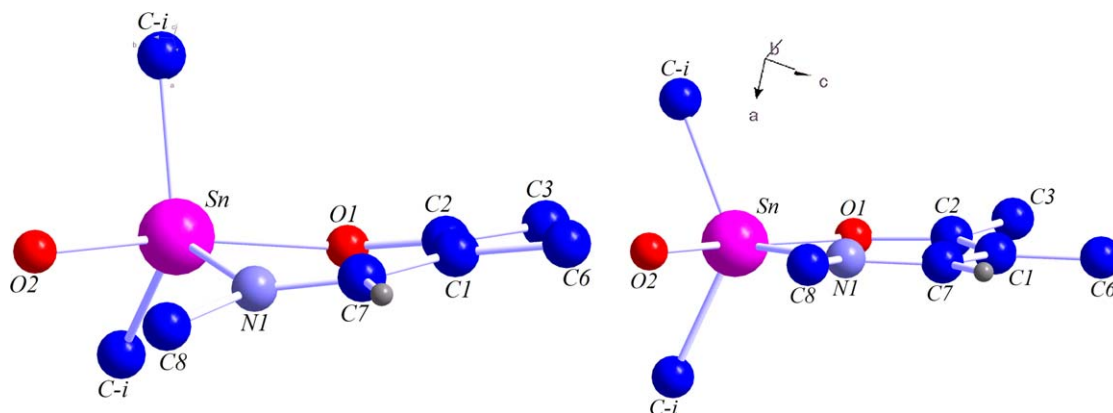Fig. 3. Envelope conformation in the five membered rings of compounds $SnL^1(Ph)_2$ (left) and $SnL^4(Ph)_2$ (right).

Fig. 4. Planar conformation in the six membered rings of compounds $SnL^2(Ph)_2$ (left) and $SnL^3(Ph)_2$ (right).

through organic conjugated pathway [41], like in the present case (Scheme 2). Therefore, the analysis of the optical spectra should provide the ultimate understanding of the origin of the NLO response.

Unfortunately, ZINDO being not parametrized for tin, the electronic spectrum can be evaluated for the ligands, only. In the representative H_2L^1 example, the experimental spectrum (Fig. 5) reveals a single low lying band located at 396 nm, with a shoulder at higher energy. The origin of this band as calculated by ZINDO is shown in Table 3. The table reveals that the band arises from two $1 \rightarrow 2$ and $1 \rightarrow 3$ electronic transitions, very close in energy. Although there is a shift in energy between calculated and experimental data, the presence of these two single transitions at nearly the same energy makes the agreement satisfactory. Interestingly, both transitions are dominated by the HOMO → LUMO excitation, leading to the conclusion that the knowledge of these frontier orbitals, and furthermore the knowledge of the associated charge transfer provides the understanding of the properties, in full agreement with the description of NLO response in π-conjugated systems (Eq. (3)).

In a second step, it is interesting to observe that the HOMO and LUMO of H_2L^1 and $SnL^1(Ph)_2$ calculated by DFT are similar to the ZINDO data (Fig. 6). This result suggests that the diphenyltin fragment is not involved in the description of the frontier orbitals, and finally that the origin of the NLO response, in term of charge transfer, remains located on the π-conjugated ligand, as anticipated in the case of molecular chromophores.

The quadratic ($\propto E^2$) NLO properties of the four organotin derivatives are summarized in Table 4, and compared with the computational DFT values available. The
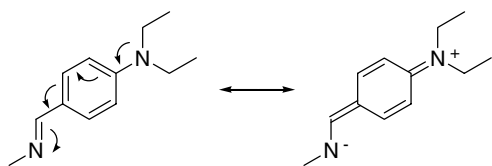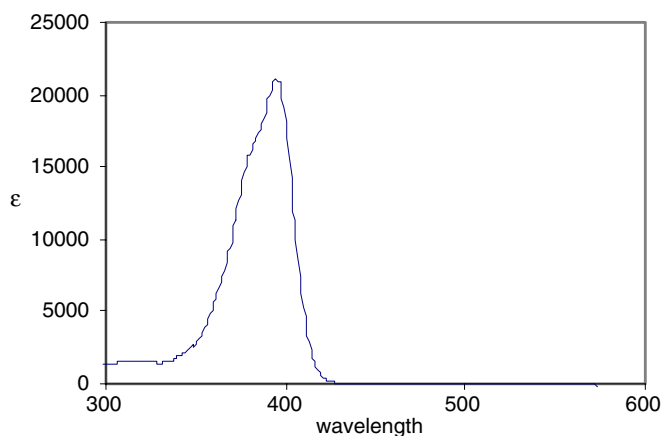

Fig. 5. UV–Vis (ε in $dm^3 mol^{-1} cm^{-1}$, wavelength in nm) spectra for H_2L^1.

computed β values lie grossly in the same ($20 \times 10^{-30} cm^5 esu^{-1}$) magnitude, which qualitatively agrees with the previous assumption that the same charge transfer behavior is present in the different compounds. Before discussing the experimental data, it must be emphasize that in the EFISH technique, the NLO response is induced by dipolar orientation. The signal is therefore proportional to $\beta_{vec} \times \mu$, μ being the dipole moment of the chromophores, and β_{vec} the projection of β along the dipole moment direction. In strictly 1-dimensional ("push–pull") molecules, β_{vec} and μ are parallel, then $\beta_{vec} = \beta$ and the DFT

Scheme 2.

Table 3
Comparison of the experimental (λ_{max} in nm, and ε in $dm^3 mol^{-1} cm^{-1}$) and ZINDO calculated (oscillator strength f, and main composition of the configuration interaction) low lying intense bands in ligand H_2L^1

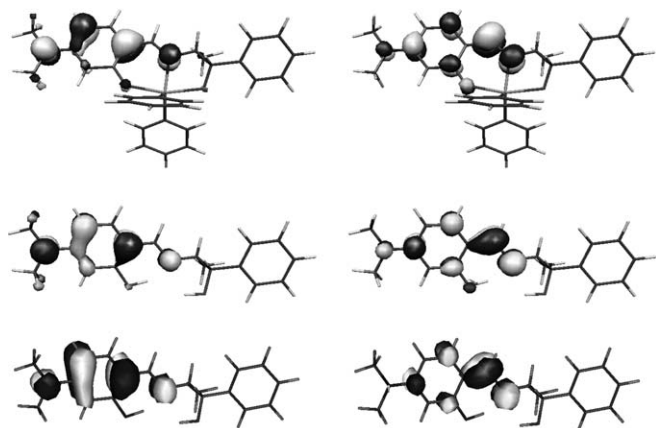| Transition	Experimental data		Computational (ZINDO) data		
	λ_{max}	ε	λ_{max}	f	Dominant CI composition
$1 \rightarrow 2$	395	21 100	311	0.28	HOMO → LUMO
$1 \rightarrow 3$	∼380	sh	296	0.53	HOMO → LUMO

Fig. 6. Comparison of the HOMO (left) and LUMO (right) orbitals of H_2L^1 calculated by ZINDO (bottom), and by DFT (middle), with the HOMO and LUMO of $SnL^1(Ph)_2$ calculated by DFT (top).

Table 4
Experimental NLO (SHG efficiencies in solid state, and EFISH data) properties

	Experimental data		DFT data	
	SHG efficiencies[a]	EFISH[b]		
		$\mu \times \beta_{vec}$	β	μ
$SnL^1(Ph)_2$	0	21	19	6.6
$SnL^2(Ph)_2$	11	27	19	6.5
$SnL^3(Ph)_2$	6	105	16	6.3
$SnL^4(Ph)_2$	0	91	22	6.8

[a] Efficiencies in second harmonic generation are given versus that of urea at 1.907 μm.
[b] β_{vec} (projection of β along the μ direction) in 10^{-30} cm^5 esu^{-1}, and μ in D.

prediction leads to an optimized $\beta_{vec} \times \mu$ value of $20 \times 6 = 120$. The data gathered in Table 4 indicate that, except for $SnL^3(Ph)_2$, β and μ are probably far from being parallel in these derivatives.

Additionally, the NLO properties have been investigated in solid states for the four derivatives (Table 4). As is well known, chirality provides a mean of guaranteeing that pure enantiomers necessarily crystallize in noncentrosymmetric space groups, and consequently must exhibit some efficiency in second harmonic generation (SHG). However, the use of a pure enantiomer does not guarantee that the crystal packing is optimized for NLO purpose, and the different charge transfer pathway may oppose each other, thus cancelling the major part of β. This deleterious situation is encountered in $SnL^1(Ph)_2$, and $SnL^4(Ph)_2$. By contrast, an efficiency up to 11 times that of urea is observed in $SnL^2(Ph)_2$, which is comparable to values obtained in Mn^{III} ($8 \times$ urea) [42] and Ni^{II} ($13 \times$ urea) [43] derivatives, built up with the same kind of Schiff base ligands.

4. Conclusion

A set of molecular (EFISH) and solid state (powder efficiencies) measurements have been reported for the first time on diorganotin(IV) derivatives. Although the semi empirical (ZINDO) approach is not possible for tin based derivatives, the computational DFT method suggests that the hyperpolarizabilities (β) are around 20×10^{-30} cm^5 esu^{-1} in these complexes. This prediction is partially supported by the experimental EFISH investigation, with the assumption that hyperpolarizabilities and dipole moments may not be strictly parallel. These molecular NLO responses in concert with noncentrosymmetric crystal structures lead to potential macroscopic effects, and eventually to a solid state SHG efficiencies equal to 11 times that of urea in the $SnL^2(Ph)_2$ derivative. This study illustrates that chromophores with rather modest β values can exhibit sizeable SHG efficiencies, once an optimized molecular orientation is achieved in solid state.

5. Supplementary data

Calculated structures for the four tin derivatives, and for H_2L^1. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with deposition number CCDC 287837 ($SnL^1(Ph)_2$), CCDC 287839 ($SnL^2(Ph)_2$), CCDC 287838 ($SnL^3(Ph)_2$), and CCDC 287836 ($SnL^4(Ph)_2$). Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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