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Synthesis and Characterization of Fluorescent Pyrrolyldipyrrinato Sn(IV) Complexes

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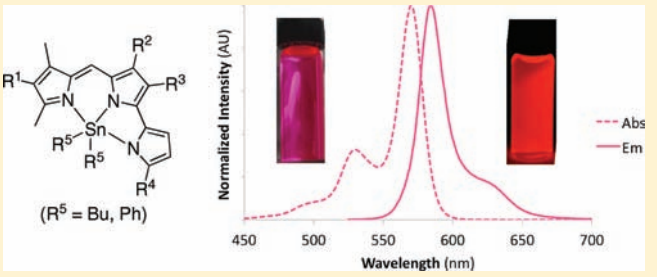
Supporting Information

ABSTRACT: A series of neutral, 5-coordinate pyrrolyldipyrrinato Sn(IV) complexes have been synthesized via reaction of a pyrrolyldipyrrin, or its corresponding hydrochloride salt, with dibutyltin or diphenyltin oxide. The complexes are structurally unique in that all three nitrogen atoms of the pyrrolyldipyrrinato ligand bind to the tin center, making these complexes the first examples of pyrrolyldipyrrins behaving as LX_2 ligands. The complexes are highly fluorescent, exhibiting fluorescence quantum yields between 0.28 and 0.61, and display interesting preliminary biological activity.



INTRODUCTION

Dipyrrinato boron complexes (BODIPYs) are the largest and most well-studied class of dipyrrinato complexes due to their high thermal, photochemical, and physiological stability, chemical robustness, and high fluorescence efficiency.[1] There has been an increasing number of reports of dipyrrinato complexes of other metals, which also exhibit fluorescence. Indeed, homoleptic dipyrrinato complexes (ML_2 and ML_3) of Zn(II),[2,3] In(III), and Ga(III)[4] where the *meso*-aryl groups of the corresponding dipyrrinato ligand are rotationally restricted exhibit small to moderate fluorescence quantum yields. Furthermore, a homoleptic Rh(III) complex (ML_3) with rotationally unrestricted *meso*-aryl groups has also been reported to be weakly fluorescent.[5] Heteroleptic dipyrrinato complexes (MLX_n) of Zn(II),[6] Sn(II),[7] and Pt(II)[8] where the *meso*-aryl groups of the corresponding dipyrrinato ligand are rotationally restricted also exhibit small to large fluorescence quantum yields. Recently, several strongly fluorescent π-extended dipyrrinato zinc(II) and calcium(II)[9] complexes (MLX) have been reported along with some highly fluorescent aluminum(III)[10] dipyrrinato complexes (MLX_2). With these examples, the development of fluorescent dipyrrinato metal complexes is underexplored.

Pyrrolyldipyrrins are a subclass of dipyrrins extended through the presence of a pyrrole in the 9-position. Many pyrrolyldipyrrins, including the natural product prodigiosin, have been isolated and synthesized, in part due to interest in the biological activity of members of the prodigiosene family.[11] In contrast, pyrrolyldipyrrinato complexes are rare (Figure 1). Homoleptic zinc(II) complexes, where two dipyrrinato units of two identical pyrrolyldipyrrins bind to the zinc metal center, are known for prodigiosin[12] and several synthetic pyrrolyldipyrrins.[13−15] Fluorescent boron difluoride complexes (*F*-BODIPYs) of synthetic pyrrolyldipyrrins are also known.[16,17] There is also an example of a tripyrrolic analogue, with an oxidized C-ring, cf. prodigiosin, coordinating to copper(II) through all three atoms of the tripyrrolic core;[12] however, in this case, the prodigiosin C-ring is oxidized, and so the tripyrrolic core is no longer a pyrrolyldipyrrin.

Despite these few examples, pyrrolyldipyrrins are potentially interesting ligands as they can coordinate in the same fashion as a dipyrrinato ligand and have a pyrrolic substituent in the 9-position. The pyrrole, or pyrrolide, could also coordinate to a metal center, either in an η^1 interaction through the nitrogen atom or in an η^5 interaction to give a π complex. Herein, we report the synthesis and properties of fluorescent pyrrolyldipyrrinato Sn(IV) complexes that exhibit moderate to high fluorescence quantum yields.

A small amount of a highly fluorescent material (**2a**) was isolated from an attempted transesterification reaction of **1a**,[18] which employed catalytic amounts of dibutyltin oxide.[19] We postulated that **2a** was a 5-coordinate, pyrrolyldipyrrinato Sn(IV) complex in which the tin center was coordinated to all three nitrogen atoms of the pyrrolyldipyrrinato core. To our knowledge, there are no examples of dipyrrinato Sn(IV) complexes; however, there are a number of Sn(IV) dipyrromethane complexes. Such complexes are formed by adding dibutyltin dichloride to a solution of the dipyrromethane and were developed as part of a purification strategy for dipyrromethanes.[20] There are a number of restrictions on the scope of the Sn(IV) complexation: only tin complexes of dipyrromethanes with diketo,[20] diformyl,[20] and diester[21] substituents in the 1- and 9-positions are known, and these flanking carbonyl moieties play a coordinative role. There is only one example of a diester dipyrromethane tin complex, and it was synthesized using hexabutylditin as the tin reagent.[21]

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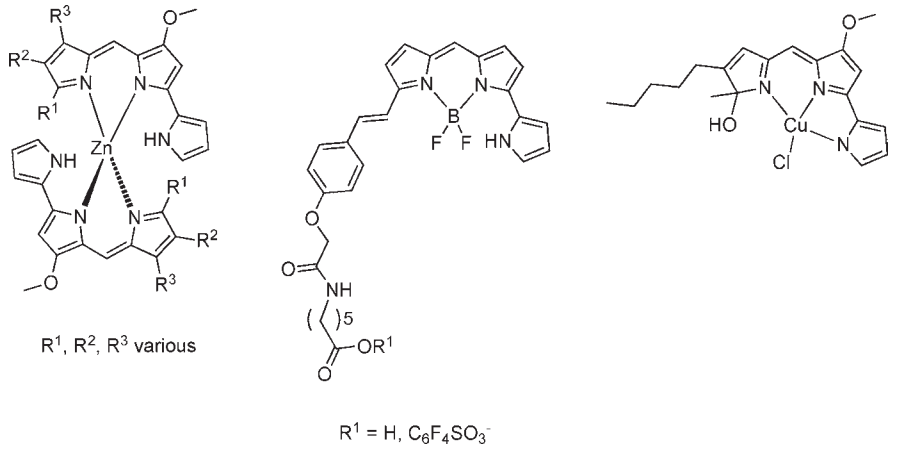


Figure 1. Complexes of pyrrolyldipyrrins.

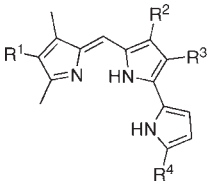
To further investigate the scope, structure, and optical properties of pyrrolydipyrrinato Sn(IV) complexes, a series of pyrrolyldipyrrinato tin complexes were synthesized by varying the substituents about the pyrrolyldipyrrin skeleton and the substituents on the tin center. Pyrrolyldipyrrins **1a**−**1f** (or their corresponding hydrochloride salts) (Figure 2) were selected as pyrrolyldipyrrins for further investigation.

The selected pyrrolyldipyrrins contain a variety of substituents about the pyrrolyldipyrrin skeleton. Compounds **1a**−**1c** contain a methoxy group at the R^2 position, making them members of the prodigiosene family, which is characterized by the 7-methoxypyrrolyldipyrrin unit. Compounds **1d** and **1e** maintain the ester functionality at R^1 but contain alkyl substituents at the R^2 and R^3 positions. Compound **1f** also contains an alkyl group at the R^1 position. To our knowledge, there are no dipyrrinato complexes, other than the pyrrolyldipyrrinato complexes previously discussed, that contain a methoxy group in the 7-position. For that reason, we chose compounds **1d**−**1f**, containing the alkyl- and carbonyl-based substituents, to mirror typical dipyrrinato complexes.[22] Utilizing a ligand (**1f**) that was free of carbonyl functionality was also of interest because the carbonyl functionality could potentially play a role in stabilizing the tin center in an intermolecular interaction, as such an interaction had been observed to be key to the stability of the Sn(IV) dipyrromethane complexes.[20]

Pyrrolyldipyrrins **1a**[18] and **1c**[23] are known compounds and were synthesized according to literature procedures. Pyrrolyldipyrrin **1b** was synthesized via the acylation of pyrrolyldipyrrin **1a** using a known procedure.[24] Compounds **1d** and **1e** were synthesized in four steps using a modification of D'Alessio's methodology,[24,25] and **1f** was synthesized via a Suzuki coupling between an unsymmetrical bromodipyrrin[26] and *N*-Boc-pyrrole-2-boronic acid. Details of the syntheses of **1b**, **1d**, **1e**, and **1f** including synthetic schemes and characterization of intermediates can be found in the Supporting Information.

EXPERIMENTAL SECTION

General Experimental. All ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), ^{11}B NMR (160 MHz), ^{19}F NMR (285.2 MHz), and ^{119}Sn NMR (186 MHz) spectra were recorded on a Bruker Avance AV-500 spectrometer. Chemical shifts are expressed in parts per million (ppm) using the solvent signal [$CDCl_3$ (^{1}H 7.26 ppm; ^{13}C 71.16 ppm)] as an internal reference for ^{1}H and ^{13}C, $BF_3\cdot OEt_2$ as an external reference for ^{11}B, $C_6H_5CF_3$ as an external reference for ^{19}F, and $Sn(CH_3)_4$ as an external reference for ^{119}Sn. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants (J) are reported in Hertz (Hz). Mass spectra were obtained using ion trap (ESI) instruments operating in positive mode. Melting points are reported uncorrected. Column chromatography was performed using 230−400 mesh ultra pure silica or 150 mesh Brockmann III activated, basic alumina oxide, as indicated.



1a: R^1 = CO_2Et, R^2 = OMe, R^3 = H, R^4 = H
1b: R^1 = CO_2Et, R^2 = OMe, R^3 = H, R^4 = C(O)Me
1c: R^1 = CO_2Bn, R^2 = OMe, R^3 = H, R^4 = H
1d: R^1 = CO_2Bn, R^2 = Et, R^3 = Me, R^4 = H
1e: R^1 = CO_2Me, R^2 = Et, R^3 = Me, R^4 = H
1f: R^1 = Et, R^2 = Et, R^3 = Me, R^4 = H

Figure 2. Pyrrolyldipyrrins (**1**).

General Procedure for the Synthesis of Dibutyl Tin Complexes (GP1). To a solution of prodigiosene **1** (free base or HCl salt) (0.05 mmol) in methanol (3 mL) was added dibutyltin oxide (0.07 mmol). The resulting solution was stirred at 65 °C for 18 h and then dried in vacuo. The residue was dissolved in ethyl acetate and poured onto a saturated aqueous solution of sodium bicarbonate (20 mL) and extracted with ethyl acetate (3 × 20 mL). The organic fractions were combined, dried with sodium sulfate, and the solvent was removed in vacuo to give the crude product.

General Procedure for the Synthesis of Diphenyl Tin Complexes (GP2). To a solution of prodigiosene **1** (free base or HCl salt) (0.05 mmol) in methanol (3 mL) was added diphenyltin oxide (0.10 mmol). The resulting solution was stirred at 65 °C for 18 h and then dried in vacuo. The residue was dissolved in ethyl acetate and poured onto a saturated aqueous solution of sodium bicarbonate (20 mL) and extracted with ethyl acetate (3 × 20 mL). The organic fractions were combined, dried with sodium sulfate, and the solvent was removed in vacuo to give the crude product.

General Procedure for Absorbance and Emission Measurements. The absorbance measurements were performed using a CARY 100 Bio UV/visible spectrophotometer. The fluorescence measurements were performed using a Shimadzu RF-5301PC spectrofluorimeter. A 10 mm quartz cuvette was used in all measurements. For the fluorescence experiments, the slit width was 3 nm for both excitation and emission. Relative quantum efficiencies of derivatives were obtained by comparing the areas under the emission spectra of the

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test with that of a solution of rhodamine 101 in ethanol ($\Phi_F = 0.96$) or rhodamine 6G in ethanol ($\Phi_F = 0.94$).[27] The excitation wavelength was 520 nm for rhodamine 6G, **2a**, **2b**, **2c**, **3c**, and **4a**. The excitation wavelength was 546 nm for rhodamine 101, **2d**, **3d**, **2e**, and **3d**. Quantum yields were determined using eq 1.[28]

$$\phi_X = \phi_{st}\left(\frac{I_X}{I_{st}}\right)\left(\frac{A_{st}}{A_X}\right)\left(\frac{\eta_X^2}{\eta_{st}^2}\right) \quad (1)$$

where ϕ_{st} is the reported quantum yield of the standard, I is the area from the integrated emission spectra, A is the absorbance at the excitation wavelength, and η is the refractive index of the solvent used. The X subscript denotes the unknown, and "st" denotes the standard.

Synthesis. *[(Bu)$_2$(**1a**)Sn(IV)] **2a** Was Synthesized Using GP1.* Purification over basic alumina using dichloromethane as an eluent and removal of the solvent in vacuo gave **2a** as a purple film (26 mg, 0.046 mmol, 93%). mp = 115−117 °C; δ_H (500 MHz, $CDCl_3$) 6.97−6.95 (2H, m), 6.82 (1H, d, J = 3), 6.43 (1H, dd, J = 2,3), 6.06 (1H, s), 4.29 (2H, q, J = 7), 4.00 (3H, s), 2.64 (3H, s), 2.45 (3H, s), 1.65−1.18 (15H, m), 0.75 (6H, t, J = 7); δ_C (125 MHz, $CDCl_3$) 168.5, 166.1, 157.2, 152.1, 137.3, 133.4, 132.1, 132.0, 129.5, 115.7, 114.1, 113.8, 112.3, 92.7, 59.4, 58.6, 27.0, 26.4, 24.0, 17.3, 14.7, 13.6, 12.2; δ_{Sn} (186 MHz, $CDCl_3$) −245.9; δ_N (50.7 MHz, $CDCl_3$) −229.9, −165.5; UV/vis (EtOH) λ_{max} (nm): 568, ε 85 000 mol L^{-1} cm^{-1}. Fluorescence (EtOH) λ_{exci} (nm), 520; λ_{max} (nm), 579. Φ_F: 0.57. m/z ESI$^+$ found 594.1749 $[M + Na]^+$, calculated for $C_{27}H_{37}N_3NaO_3Sn$ 594.1755.

*[(Bu)$_2$(**1b**)Sn(IV)] **2b** Was Synthesized Using GP1.* Purification over neutral alumina using 5% ethyl acetate in hexanes as an eluent and removal of the solvent in vacuo gave **2b** as a purple film (29 mg, 0.047 mmol, 95%). mp = 162−164 °C; δ_H (500 MHz, $CDCl_3$) 7.18 (1H, s), 6.99 (1H, d, J = 3.5), 6.64 (1H, d, J = 3.5), 6.13 (1H, s), 4.30 (2H, q, J = 7.5), 4.00 (3H, s), 2.66 (3H, s), 2.50 (3H, s), 2.56 (3H, s), 1.66−1.49 (4H, m), 1.38 (3H, t, J = 7.5), 1.12−0.97 (8H, m), 0.59 (6H, t, J = 7); δ_C (125 MHz, $CDCl_3$) 189.6, 167.6, 165.8, 156.0, 153.9, 142.5, 139.6, 137.6, 135.3, 128.3, 120.0, 118.3, 117.5, 110.5, 93.0, 59.6, 58.6, 27.1, 25.8, 25.6, 23.9, 17.3, 14.7, 13.5, 12.3; δ_{Sn} (186 MHz, $CDCl_3$) −221.9; UV/vis (DCM) λ_{max} (nm): 568, ε 85 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{exci} (nm), 520; λ_{max} (nm), 579. Φ_F: 0.57. m/z ESI$^+$ found 614.1993 $[M + H]^+$, calculated for $C_{29}H_{39}N_3O_4Sn$ 614.2035. A crystal suitable for X-ray crystallography was obtained from a slow evaporation of a solution of compound **2b** in dichloromethane in the presence of few drops of methanol. Data for **2b**: $C_{29}H_{38}N_3O_4Sn$, M = 611.34 g, dark-red needle, 0.42 × 0.23 × 0.12 mm^3, primitive triclinic, space group P-1 (No. 2), a = 12.1339 Å, b = 13.04640(10) Å, c = 19.65300(10) Å, V = 2903.79(3) Å^3, Z = 4, T = 200(1) K, ρ = 1.398 g cm^{-3}, μ(Mo Kα) = 9.167 cm^{-1}, 106 009 reflections (22 429 unique, R_{int} = 0.065), R = 0.0358, Rw = 0.0439, GOF = 1.082.

*[(Bu)$_2$(**1c**)Sn(IV)] **2c** Was Synthesized Using GP1.* Purification over basic alumina using dichloromethane as an eluent and removal of the solvent in vacuo gave **2c** as a purple film (57 mg, 0.09 mmol, 90%). mp = 120−122 °C; δ_H (500 MHz, $CDCl_3$) 7.46−7.44 (2H, m), 7.40−7.37 (2H, m), 7.34−7.31 (1H, m), 6.95−6.94 (1H, m), 6.94 (1H, s), 6.83 (1H, dd, J = 1,3), 6.43 (1H, dd, J = 2,3), 6.13 (1H, s) 5.30 (2H, s), 4.00 (3H, s), 2.63 (3H, s), 2.45 (3H, s), 1.52−1.39 (8H, m), 1.22−1.18 (4H, m), 0.75 (6H, t, J = 8); δ_C (125 MHz, $CDCl_3$) 168.6, 165.8, 157.4, 152.2, 137.3, 137.1, 133.4, 132.2, 132.2, 132.0, 129.6, 128.6, 128.2, 128.0, 115.3, 114.2, 113.7, 112.5, 65.4, 58.6, 27.0, 26.4, 24.0, 17.4, 13.6, 12.3; δ_{Sn} (186 MHz, $CDCl_3$) −209.5; UV/vis (DCM) λ_{max} (nm): 561, ε 88 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{exci} (nm), 520; λ_{max} (nm), 584, Φ_F: 0.53. m/z ESI$^+$ found 634.2082 $[M + H]^+$, calculated for $C_{32}H_{40}N_3O_3Sn$ 634.2086.

*[(Bu)$_2$(**1d**)Sn(IV)] **2d** Was Synthesized Using GP1.* The crude material was dissolved in dichloromethane and filtered through basic alumina eluting with dichloromethane, and the solvent was removed in vacuo. Purification over basic alumina using 1:1 dichloromethane:hexanes as an eluent and removal of the solvent in vacuo gave **2d** as a dark purple solid (36 mg, 0.056 mmol, 86%). mp = 91−93 °C; δ_H (500 MHz, $CDCl_3$) 7.47−7.45 (2H, m), 7.40−7.38 (2H, m), 7.35−7.32 (1H, m), 6.99 (1H, m), 6.93 (1H, dd, J = 2,3), 6.83 (1H, s), 6.47 (1H, dd, J = 2,3), 5.32 (2H, s), 2.74 (2H, q, J = 7), 2.65 (3H, s), 2.48 (3H, s), 2.27 (3H, s), 1.49−1.41 (8H, m), 1.26−1.18 (7H, m), 0.75 (6H, t, J = 8); δ_C (125 MHz, $CDCl_3$) 165.8, 157.2, 152.7, 144.6, 138.2, 137.8, 137.1, 134.2, 132.0, 131.8, 131.3, 128.6, 128.2, 128.0, 115.6, 115.5, 114.2, 113.0, 65.4, 27.0, 26.5, 23.9, 18.5, 17.4, 14.2, 13.6, 12.4, 9.9; δ_{Sn} (186 MHz, $CDCl_3$) −214.2; UV/vis (DCM) λ_{max} (nm): 585, ε 87 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{exci} (nm), 546; λ_{max} (nm), 607. Φ_F: 0.52. m/z ESI$^+$ found 645.2473 $[M + H]^+$, calculated for $C_{34}H_{44}N_3O_2Sn$ 645.2450.

*[(Bu)$_2$(**1f**)Sn(IV)] **2f** Was Synthesized Using GP1.* Purification over basic alumina using an eluent gradient of hexanes to 1:10 ethyl acetate: hexanes and removal of the solvent in vacuo gave **2f** as a blue film (17 mg, 0.049 mmol, 22%). mp = 99−101 °C; δ_H (500 MHz, $CDCl_3$) 6.91−6.90 (1H, m), 6.79 (1H, dd, J = 1,3) 6.75 (1H, s), 6.43 (1H, dd, J = 2,3), 2.65 (2H, q, J = 7), 2.41 (2H, q, J = 7), 2.37 (3H, s), 2.26 (3H, s), 2.02 (3H, s), 1.49−1.38 (9H, m), 1.26−1.18 (9H, m), 1.07 (3H, t, J = 7), 0.78 (3H, t, J = 7); δ_C (125 MHz, $CDCl_3$) 153.9, 150.3, 149.0, 135.1, 134.52, 134.50, 132.4, 129.7, 129.3, 121.2, 115.8, 112.7, 109.8, 27.1, 26.7, 23.3, 18.2, 17.9, 16.4, 15.2, 14.7, 13.6, 10.4, 10.0; δ_{Sn} (186 MHz, $CDCl_3$) −253.3; UV/vis (DCM) λ_{max} (nm): 599, ε 120 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{max} (nm): 617. Φ_F: 0.28. m/z ESI$^+$ found 540.2354 $[M + H]^+$, calculated for $C_{28}H_{42}N_3Sn$ 540.2395.

*[(Ph)$_2$(**1c**)Sn(IV)] **3c** Was Synthesized Using GP2.* Purification over basic alumina using dichloromethane as an eluent and removal of the solvent in vacuo gave **3c** as a purple film (40 mg, 0.059 mmol, 82%). mp = 262 −264 °C; δ_H (500 MHz, $CDCl_3$) 7.61−7.59 (4H, m, tin satellites at tin satellites at 7.69−7.67 and 7.52−7.51, ^3J (^{119}Sn−^{1}H) = 40), 7.44−7.31 (12H, m), 7.12 (1H, s), 6.82 (1H, dd, J = 1,3), 6.49 (1H, dd, J = 2,3), 6.04 (1H, s), 5.29 (2H, s), 3.98 (3H, s), 2.58 (3H, s), 2.14 (3H, s); δ_C (125 MHz, $CDCl_3$) 168.9, 165.8, 157.1, 154.3, 141.0, 138.1, 137.4, 136.9, 135.4, 134.2, 133.5, 131.6, 130.1, 129.9, 129.2, 128.9, 128.8, 128.6, 128.3, 128.0, 127.4, 127.3, 115.9, 114.8, 113.7, 93.0, 65.5, 58.7, 18.1, 12.6. δ_{Sn} (186 MHz, $CDCl_3$) 367.1; UV/vis (DCM) λ_{max} (nm): 561, ε 74 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{max} (nm), 520; λ_{max} (nm), 583. Φ_F: 0.55. m/z ESI$^+$ found 674.1465 $[M + H]^+$, calculated for $C_{36}H_{32}N_3O_3Sn$ 674.1460.

*[(Ph)$_2$(**1e**)Sn(IV)] **3e** Was Synthesized Using GP2.* The crude material was dissolved in dichloromethane, the resulting solution was filtered through basic alumina eluting with dichloromethane, and the solvent was removed in vacuo. Purification over basic alumina using 1:1 dichloromethane:hexanes as an eluent and removal of the solvent in vacuo gave the methyl ester **3e** as a dark purple film (41 mg, 0.06 mmol, 75%). mp = 254−256 °C; δ_H (500 MHz, $CDCl_3$) 7.60−7.59 (4H, m, tin satellites at 7.69−7.67 and 7.52−7.51, ^3J (^{119}Sn−^{1}H) = 40), 7.52−7.51 (1H, m), 7.36−7.31 (6H, m), 6.99 (1H, s), 6.92−6.91 (1H, m), 6.52 (1H, dd, J = 2,3), 3.81 (3H, s), 2.68 (2H, q, J = 8), 2.60 (3H, s), 2.27 (3H, s), 2.12 (3H, s), 1.19 (3H, t, J = 8); δ_C (125 MHz, $CDCl_3$) 166.5, 156.9, 154.7, 145.0, 141.1, 138.7, 138.3, 135.4, 135.0, 133.3, 132.1, 131.0, 130.0, 129.2, 116.5, 115.6, 114.9, 113.9, 50.8, 18.5, 18.0, 14.1, 12.4, 9.9; ^{15}N HMBC δ_N ($CDCl_3$) −178.2, −217.9; δ_{Sn} (186 MHz, $CDCl_3$) 363.5; UV/vis (DCM) λ_{max} (nm): 587, ε 86 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{exci} (nm), 546; λ_{max} (nm), 609. Φ_F: 0.51. m/z ESI$^+$ found 610.1524 $[M + H]^+$, calculated for $C_{32}H_{32}N_3O_2Sn$ 610.1511.

*[(Ph)$_2$(**1f**)Sn(IV)] **3f** Was Synthesized Using GP2.* The crude material was dissolved in dichloromethane, the resulting solution was filtered through basic alumina eluting with dichloromethane, and the solvent was removed in vacuo. Purification over basic alumina using 1:5 dichloromethane:hexanes as an eluent and removal of the solvent in vacuo gave **3f** as a blue film (13 mg, 0.022 mmol, 33%). mp = 225−227 °C; δ_H (500 MHz, $CDCl_3$) 7.64−7.62 (4H, m, with tin

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Scheme 1. General Synthetic Scheme for the Synthesis of Pyrrolyldipyrrinato Sn(IV) Complexes

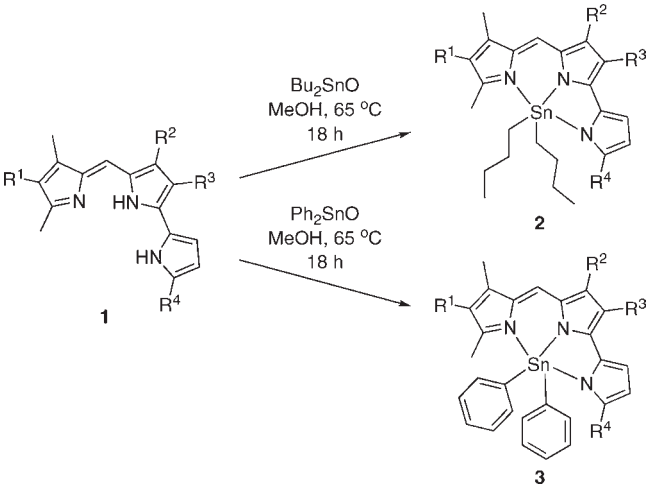


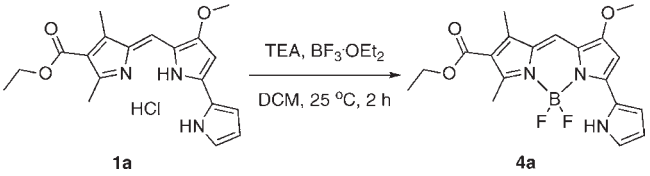
Table 1. Yields of Pyrrolyldipyrrinato Sn(IV) Complexes

	R^1	R^2	R^3	R^4	isolated yield/%
2a	CO_2Et	OMe	H	H	93
2b	CO_2Et	OMe	H	C(O)Me	95
2c	CO_2Bn	OMe	H	H	90
3c	CO_2Bn	OMe	H	H	82
2d	CO_2Bn	Et	Me	H	86
3e	CO_2Me	Et	Me	H	84
2f	Et	Et	Me	H	22
3f	Et	Et	Me	H	33

satellites at 7.72−7.70 and 7.56−7.54, ^3J (^{119}Sn−^{1}H) = 40), 7.40−7.31 (7H, m), 6.90 (1H, s), 6.77 (1H, dd, J = 1,3), 6.47 (1H, dd, J = 2,3), 2.66 (2H, q, J = 7), 2.39 (2H, q, J = 7), 2.32 (3H, s), 2.20 (3H, s), 1.79 (3H, s), 1.21 (3H, t, J = 7), 1.05 (3H, t, J = 7); δ_C (125 MHz, $CDCl_3$) 153.5, 152.7, 149.4, 141.8, 136.1, 135.8, 135.6, 134.8, 132.0, 131.0, 130.0, 129.7, 128.9, 121.7, 115.8, 113.4, 110.8, 18.3, 17.9, 16.3, 15.3, 15.2, 10.3 (1 C missing, alkyl region); δ_{Sn} (186 MHz, $CDCl_3$) 363.0; UV/vis (DCM) λ_{max} (nm): 603, ε 87 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{exci} (nm), 546; λ_{max} (nm), 622. Φ_F: 0.32. m/z ESI$^+$ found 579.1694 $[M]^+$, calculated for $C_{32}H_{33}N_3Sn$ 579.1691.

*[(**1a**)BF_2] (**4a**).* To a solution of **1aHCl** (25 mg, 0.07 mmol) in dry dichloromethane under a nitrogen atmosphere was added triethylamine (0.2 mL, 1.4 mmol, 21 equiv). The resulting reaction mixture was stirred for 10 min, then $BF_3 \cdot OEt_2$ (0.2 mL, 1.1 mmol, 17 equiv) was added slowly, and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was poured into a 5% aqueous solution of citric acid (20 mL) and extracted with ether (20 mL). The organic layer was washed with 5% aqueous citric acid (3 × 20 mL), dried over Na_2SO_4, and concentrated in vacuo. Filtration over a pad of silica eluting with dichloromethane followed by concentration in vacuo gave **4a** as a purple, crystalline solid (28 mg, 0.07 mmol, 100%). mp = 210−211 °C; δ_H (500 MHz, $CDCl_3$) 10.5 (1H, s), 7.15−7.13 (1H, m), 7.13 (1H, s), 6.94−6.92 (1H, m), 6.39−6.37 (1H, m), 6.14 (1H, s), 4.31 (2H, q, J = 7), 3.99 (3H, s), 2.80 (3H, s), 2.43 (3H, s), 1.37 (3H, t, J = 7); δ_C (125 MHz, $CDCl_3$) 165.4, 164.3, 152.9, 151.4, 136.5, 129.4, 129.3, 126.4, 123.5, 118.6, 117.8, 115.0, 111.7, 97.2, 59.7, 58.7, 14.6, 14.4, 11.8; δ_B (80.25 MHz, $CDCl_3$) 1.06 (t, J_{BF} = 36); δ_F (235.2 MHz, $CDCl_3$) −139 (q, J_{FB} = 31); ^{15}N HMBC δ_N ($CDCl_3$) −198.3, −221.6. UV/vis

Scheme 2. Synthesis of Pyrrolyldipyrrinato *F*-BOIDPY Complex 4a



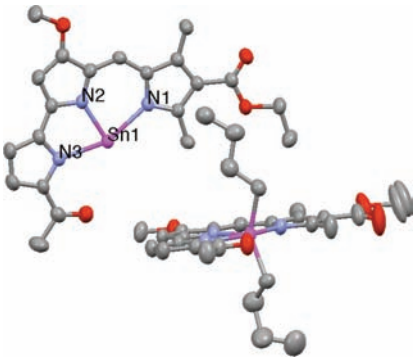


Figure 3. Thermal ellipsoid diagram (50%) of a twinned crystal of **2b**. Sn(1) butyl groups and all hydrogen atoms are removed for clarity. Selected bond distances (Å): Sn(1)−N(1), 2.309(2); Sn(1)−N(2), 2.128(2); Sn(1)−N(3), 2.239(2). Selected bond angles (deg): N(1)−Sn(1)−(N2), 81.46(9); N(1)−Sn(1)−N(3), 155.25(10); N(2)−Sn(1)−N(3), 73.85(10); C(43)−Sn(1)−C(47), 137.84(14) (C(43) and C(47) are the carbon atoms of each attached butyl group, respectively).

(DCM) λ_{max} (nm): 536, ε 184 000 mol L^{-1} cm^{-1}. Fluorescence (DCM) λ_{exci} (nm), 520; λ_{max} (nm), 551. Φ_F: 0.92. m/z ESI$^+$ found 410.1458 $[M + Na]^+$, calculated for $C_{19}H_{20}BF_2N_3O_3Na$ 410.1463. A crystal suitable for X-ray crystallography was obtained from a slow evaporation of a solution of compound **4a** in dichloromethane. Data for **4a**: $C_{19}H_{20}N_3O_3BF_2$, M = 387.19 g, dark-red, needle, 0.39 × 0.13 × 0.08 mm, primitive monoclinic, $P21/c$ (No. 14), a = 7.3029(4) Å, b = 25.1293(11) Å, c = 9.7763(5) Å, V = 1779.52(15) Å^3, Z = 4, T = 123(1) K, ρ = 1.445 g cm^{-3}, μ(Mo Kα) = 1.116 cm^{-1}, 52 752 reflections (19 174 unique, R_{int} = 0.074), R = 0.0441, Rw = 0.0557, GOF = 1.022.

RESULTS AND DISCUSSION

Pyrrolyldipyrrins **1a**, **1b**, **1c**, **1e**, and **1f** were converted to their corresponding dibutyltin complexes (**2a**, **2b**, **2c**, **2e**, and **2f**) by heating a methanolic solution of each pyrrolyldipyrrin with an excess of dibutyltinxide at reflux temperature for a period of 18 h. Similarly, pyrrolyldipyrrins **1c**, **1e**, and **1f** were converted into their corresponding diphenyltin complexes (**3c**, **3e**, and **3f**) by heating a methanolic solution of pyrrolyldipyrrin with an excess of diphenyltin oxide at reflux temperature (Scheme 1, Table 1).

The conversion of pyrrolyldipyrrin to the corresponding Sn(IV) complex was quantitative according to analysis using TLC, and the isolated yields of the pyrrolyldipyrrinato dibutyl and diphenyl Sn(IV) complexes were high with the exception of the fully alkyl substituted derivatives **2f** and **3f** (Table 1). The diphenyltin complexes (**3c**, **3d**, and **3f**) exhibited some decomposition to return the pyrrolyldipyrrin starting material upon purification over neutral or basic alumina, a procedure that was

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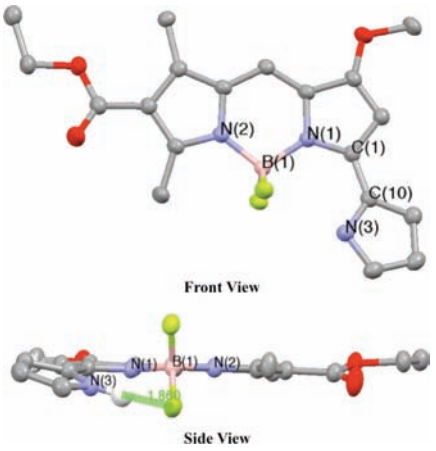

Figure 4. Thermal ellipsoid diagram (50%) of **4a**. Hydrogens removed for clarity. Selected bond distances (Å): B(1)−N(1), 2.309(2); B(1)−N(2), 2.128(2). Selected bond angles (deg): N(1)−B(1)−(N2), 81.46(9). Selected torsional angles (deg): N(1)−C(1)−C(10)−(N3), −16.09. Contact distance (Å): N(3)−H···F(1), 1.860.

Table 2. Optical Properties of Tin Pyrrolyldipyrrinato Complexes and BODIPY Complex 4a in DCM at 22 °C

complex	abs λ_{max} (nm)	ε ($\times 10^4$ mol L^{-1} cm^{-1})	em λ_{max} (nm)	Φ_F
2a	561	8.78	584	0.53[a]
2b	570	11.6	582	0.61[a]
2c	561	8.82	584	0.53[a]
2d	585	8.69	607	0.52[b]
2f	599	11.6	617	0.28[b]
3c	561	7.40	583	0.55[a]
3e	587	8.63	609	0.51[b]
3f	603	8.70	622	0.32[b]
4a	543	10.5	559	0.92[a]

[a] Relative to rhodamine 6G in EtOH (Φ_F = 0.94). [b] Relative to rhodamine 101 in EtOH (Φ_F = 0.96).

utilized to remove the excess diphenyltin oxide. Attempts to optimize the reaction and purification were conducted using pyrrolyldipyrrin **1c**. Unfortunately, if only 1 equiv of diphenyltin oxide was used in the reaction of **1c**, the reaction was sluggish, and small amounts of unreacted **1c** remained in the reaction mixture after 4 days at reflux temperature. Attempts to use crystallization as a purification strategy were similarly unsuccessful.

Notably, the diphenyltin complexes (**3**) are less stable in solution than their corresponding dibutyltin complexes (**2**) and decompose to free ligand (**1**) slowly over the period of a week. The diphenyltin and dibutyltin complexes are sensitive to acid, and the corresponding pyrrolyldipyrrin HCl salts are generated rapidly and quantitatively after adding aqueous hydrochloric acid to a solution of the corresponding tin complex in a 1:1 solution of dichloromethane and methanol.

For purposes of comparison in structure and fluorescence properties, the boron difluoride (*F*-BODIPY) complex (**4a**) of pyrrolydipyrrin **1a** was synthesized in quantitative yield (Scheme 2).

A crystal of the dibutyltin complex **2b** was obtained from a slow evaporation of a dichloromethane solution in the presence of a few drops of methanol. All crystals in the sample were found to be nonmerohedral twins, and solving the X-ray crystal

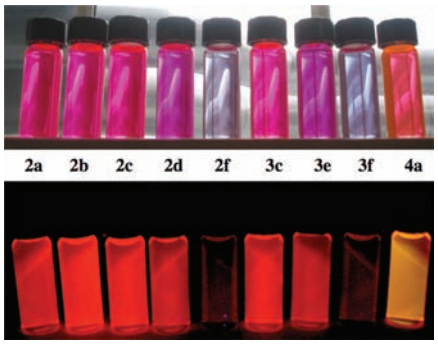

Figure 5. Complexes **2**, **3**, and **4** in dichloromethane solution (~7.0×10^{-5} M) visualized under ambient light (top) and long wave UV irradiation (bottom).

structure first with twinned data led to the possible location of the composite plane, which allowed for dissection of a fragment of untwinned crystal (Figure 3). The disorder still present in the crystal is likely dynamic as the crystal survives cooling to −73 °C, but shatters, after some time, when cooled to −93 °C. The structure shows a pentacoordinate tin atom with distorted trigonal bypyramidal geometry. All three nitrogen atoms of the pyrrolyldipyrrin are coordinated to the tin center, making this structure, to the best of our knowledge, the first of its kind.

The complex has distorted trigonal bipyramidal geometry. The N(3)−Sn(1)−N(1) bond angle of 155.25(10)° is the largest of the angles involving the tin center, suggesting that N(1) and N(3) are occupying the pseudoaxial positions in the complex. However, the C(43)−Sn(1)−C(47) bond angle is larger than the 120° normally separating equatorial substituents in a trigonal bipyramidal complex with a value of 137.84(14)°. The bond angles between N(1)−Sn(1) or N(3)−Sn(1) and the equatorial atoms (N(2), C(43), C(47)) range from 73° to 95°, while the bond angles between C(43)−Sn(1) or C(47)−Sn(1) and N(1), N(2), or N(3) range from 93° to 112°. The trigonal pyramidal geometry is significantly distorted in the complex, likely due to the restrictions imposed by the rigid pyrrolyldipyrrinato ligand framework. The tin−nitrogen bond lengths in complex **2b** range from 2.128 to 2.309 Å. These bond lengths are within the reported ranges of other nitrogen tin bonds in neutral, pentacoordinate Sn(IV) complexes.[29−31]

The coordinated pyrrolyldipyrrinato unit is essentially planar in complex **2b**. In the X-ray crystal structure of the hydrochloride salt of **1a**, which contains a pyrrolyldipyrrinato unit similar to **2b** (differing only in an acyl group on the pyrrole ring), the pyrrolydipyrrin is also planar (see Supporting Information, Figure S1). This planarity has also been observed in other crystal structures of pyrrolyldipyrrin hydrochloride salts and is enforced by hydrogen bonds between the chloride counteranion and the pyrrolyldipyrrin,[32] but not all hydrochloride salts exhibit this planarity.[33] Interestingly, in the *F*-BODIPY **4a**, the uncoordinated pyrrole unit is 16° out of the plane of the coordinated dipyrrinato unit (Figure 4). This twist may accommodate a hydrogen bond between the hydrogen attached to the pyrrolic nitrogen atom and the fluorine atom below the dipyrrinato plane with a contact distance of 1.860 nm.

Although the pyrrolyldipyrrin ligands do not display perceptible fluorescence, all of the synthesized tin complexes exhibit appreciable fluorescence quantum yields (Φ_F = 0.28−0.61) in dichloromethane with maximum wavelengths of emission in the

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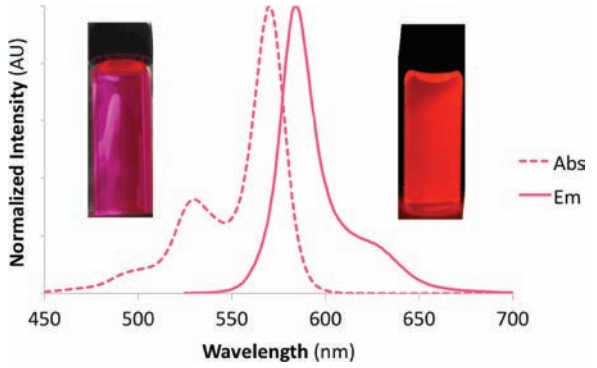

Figure 6. Normalized absorption (– – –) and emission (—) spectra of **2b** obtained using 520 nm excitation in DCM at 21 °C.

orange region (584 and 622 nm). The complexes also exhibit broad absorption bands between 550 and 625 nm (ε (7−11) × 10^4 M^{-1} cm^{-1}) (Table 2, Figure 5).

The *F*-BODIPY pyrrolyldipyrrinato complex (**4a**) has the highest fluorescence quantum yield of the compounds (Φ_F = 0.92), and this value is comparable to the fluorescence quantum yields of other strongly emitting *F*-BODIPYs.[1] The pyrrolyldipyrrinato tin complexes show an interesting pattern in their quantum yields based on the substitution pattern about the ligand. When the ligand contains a conjugated ester substituent (**2a**, **2b**, **2c**, **3c**, **2d**, and **3e**), the fluorescence quantum yield was high ($\Phi_F > 0.50$). However, when the ligand contained only alkyl substituents (**2f** and **3f**), the fluorescence quantum yields were much lower ($\Phi_F < 0.32$). The Stokes shifts of the complexes are small and range from 334 to 702 cm^{-1} (11−23 nm).

Dipyrrinato complexes with rotationally unrestricted *meso* substituents generally exhibit little or no detectable fluorescence. However, there are two examples of complexes that do exhibit fluorescence: π-extended dipyrrinato complexes of Ca(II) and Zn(II) (Φ_F = 0.58−0.70)[9] and a tetradentate N_2O_2-type dipyrrinato Al(III) complex (Φ_F = 0.23).[10] In the case of the aluminum complex, the ligand is held in a rigid position by the additional coordination of phenolic oxygens. In the case of the π-extended dipyrrinato complexes, the ligands contain esters in the 1- and 9-positions, and the proximate carbonyl oxygen atoms likely play a role in ligand−metal bond stabilization. Our series of pyrrolyldipyrrinato Sn(IV) complexes is a further example of dipyrrinato-type complexes without rotationally restricted *meso* groups that exhibit high fluorescence quantum yields. The added rigidity induced through coordination of the flanking pyrrolide binding unit reduces the number of pathways for nonradiative decay, thereby allowing for higher observed fluorescence quantum yields than those of traditional dipyrrinato complexes with only two coordination sites. *F*-BODIPY **4a** has the highest fluorescence quantum yield of the synthesized complexes. In this case, the pyrrolyldipyrrin rigidity is due to the presence of the hydrogen bond between the unbound pyrrole and the neighboring fluorine.

The effects of changing the substituents around the pyrrolydipyrrinato core of the complexes are evident after analysis of the wavelengths of maximum absorption. When the pyrrolyldipyrrinato ligand contained both ester and methoxy groups (**2a** and **2c**), the wavelength of maximum absorption was 561 nm (**2a** and **2c**). When the methoxy group was replaced with an alkyl group (**2d**), the wavelength of maximum absorption shifted 24 nm bathochromically, and when the ester group was also replaced with an alkyl group (**2f**), the wavelength of maximum absorption was bathochromically shifted 14 nm. The same trend is observable for the diphenyltin complexes (**3**). When the pyrrolyldipyrrinato ligand was not modified, but the groups on the tin center were changed from butyl to phenyl, there was little to no effect on the wavelength of maximum emission or the quantum yields of fluorescence for the related complexes (compare **2c** and **2f** with butyl substituents to **3c** and **3f** with aryl substituents).

All of the absorption spectra have a similar band structure in the visible region: a large peak with a shoulder. This band structure is commonly observed for dipyrrinato complexes.[2,34] For each complex, the emission spectra are approximately the mirror image of the absorption profile; however, the vibronic features are less prominent in the emission spectra. The normalized absorption and emission spectrum of tin complex **2b** is shown in Figure 6 as a representative example. The absorption and emission spectra of the tin complexes **2** and **3** and BODIPY **4a** can be found in the Supporting Information.

This high yielding route to dibutyltin complexation and decomplexation allows for a potential new pyrrolyldipyrrin purification strategy, similar to that for 1,9-carbonyl substituted dipyrromethanes.[20] Many pyrrolyldipyrrins of the prodigiosene family are generated via a Suzuki coupling reaction with a boronic acid containing pyrrole. If the reaction is not clean, the resulting mixture is often difficult to purify, and so tin complexation has promise as a useful purification strategy.

Many organotin(IV) complexes with nitrogen-containing ligands exhibit antimicrobial activity.[35] Compound **2a** was tested for antimicrobial activity against several *S. aureus*, *S. epidermidis*, *P. aeruginosa*, *E. faecalis*, and *B. subtilis* strains. However, the erythromycin control had activity comparable to or better than that against all of the strains with the exception of *S. aureus* 623 (a clinical methicillin resistant *Staphylococcus aureus* isolate);[36] compound **2a** was found to have a MIC of 2 μg mL^{-1} against *S. aureus* 623, while the erythromycin control had a MIC of >128 μg mL^{-1}.

Pyrrolyldipyrrins of the prodigiosin family are known to exhibit anticancer activity through several different mechanisms, some of which require complexation of the tripyrrolic core to a metal or anion.[11] In addition, there are also several examples of neutral, 5-coordinate tin complexes, which exhibit in vitro anticancer activity.[31,37] Preliminary tests against the NCI 60 cancer cell lines indicate that compound **2c** shows activity in all 60 cancer cell lines, and further evaluation of compounds **2c** and **3c** is ongoing.

These biological results are preliminary as further studies are necessary to address the stability of the tin−nitrogen bonds under the test conditions. Although the observed biological activities may be specific, they could alternatively be due to the nonspecific action of hydrolyzed R_2Sn^+ moieties that are known for their undesirable neurotoxicity and immune suppression.[37]

■ CONCLUSION

A methodology to access both dibutyl and pyrrolyldipyrrinato complexes has been developed. Pyrrolyldipyrrins or their corresponding HCl salts can be converted to there pyrrolyldipyrrinato Sn(IV) complexes in high yields, with the exception of two cases, by treatment with a diphenyl or dibutyl tin oxide. These complexes exhibit a previously unknown binding mode in which the pyrrolyldipyrrin is a tridentate dianionic ligand. These complexes are strongly fluorescent (Φ_F = 0.28−0.61), and substitution about the pyrrolyldipyrrin skeleton has been shown to

influence the fluorescence quantum yields. Further studies into their biological properties are ongoing.

■ ASSOCIATED CONTENT

Supporting Information. Synthetic schemes, experimental procedures, and characterization data for prodigiosene ligands (free bases or HCl salts) (**1b**, **1d**, **1e**, and **1f**); ^{13}C NMR spectra for all new compounds; and X-ray crystallographic data for compounds **1aHCl**, **2b**, and **4a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891–4932.
(2) Sazanovich, I. V.; Kirmaier, C.; Hindin, E.; Yu, L.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Am. Chem. Soc.* **2004**, *126*, 2664–2665.
(3) Maeda, H. *J. Inclusion Phenom. Macrocyclic Chem.* **2009**, *64*, 193–214.
(4) Thoi, V. S.; Stork, J. R.; Magde, D.; Cohen, S. M. *Inorg. Chem.* **2006**, *45*, 10688–10697.
(5) Hall, J. D.; McLean, T. M.; Smalley, S. J.; Waterland, M. R.; Telfer, S. G. *Dalton Trans.* **2010**, *39*, 437–445.
(6) Sutton, J. M.; Rogerson, E.; Wilson, C. J.; Sparke, A. E.; Archibald, S. J.; Boyle, R. W. *Chem. Commun.* **2004**, 1328–1329.
(7) Kobayashi, J.; Kushida, T.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, *131*, 10836–10837.
(8) Bronner, C.; Baudron, S. A.; Hosseini, M. W.; Strassert, C. A.; Guenet, A.; Cola, L. D. *Dalton Trans.* **2010**, *39*, 180–184.
(9) Filatov, M. A.; Lebedev, A. Y.; Mukhin, S. N.; Vinogradov, S. A.; Cheprakov, A. V. *J. Am. Chem. Soc.* **2010**, *132*, 9552–9554.
(10) Ikeda, C.; Ueda, S.; Nabeshima, T. *Chem. Commun.* **2009**, 2544–2546.
(11) Furstner, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3582–3603.
(12) Park, G.; Tomlinson, J. T.; Melvin, M. S.; Wright, M. W.; Day, C. S.; Manderville, R. A. *Org. Lett.* **2003**, *5*, 113–116.
(13) Gerber, N. N. *J. Heterocycl. Chem.* **1973**, *10*, 925–929.
(14) Sáez Díaz, R. I.; Bennett, S. M.; Thompson, A. *ChemMedChem* **2009**, *4*, 742–745.
(15) Wasserman, H. H.; Rodgers, G. C.; Keith, D. D. *Tetrahedron* **1976**, *32*, 1851–1854.
(16) Invitrogen. BODIPY 650/665-X, SE, http://products.invitrogen.com/ivgn/product/D10001.
(17) Gee, K. R.; Archer, E. A.; Kang, H. C. *Tetrahedron Lett.* **1999**, *40*, 1471–1474.
(18) Regourd, J.; Al-SheikhAli, A.; Thompson, A. *J. Med. Chem.* **2007**, *50*, 1528–1536.
(19) Baumhof, P.; Mazitschek, R.; Giannis, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3672–3674.
(20) Tamaru, S.; Yu, L. H.; Youngblood, W. J.; Muthukumaran, K.; Taniguchi, M.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 765–777.
(21) Kitamura, C.; Yamashita, Y. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1443–1448.
(22) Wood, T. E.; Thompson, A. *Chem. Rev.* **2007**, *107*, 1831–1861.
(23) Uddin, M. I.; Thirumalairajan, S.; Crawford, S. M.; Cameron, T. S.; Thompson, A. *Synlett* **2010**, *2010*, 2561–2564.
(24) D'Alessio, R.; Bargiotti, A.; Carlini, O.; Colotta, F.; Ferrari, M.; Gnocchi, P.; Isetta, A.; Mongelli, N.; Motta, P.; Rossi, A.; Rossi, M.; Tibolla, M.; Vanotti, E. *J. Med. Chem.* **2000**, *43*, 2557–2565.
(25) D'Alessio, R.; Rossi, A. *Synlett* **1996**, 513–514.
(26) Paine, J. B.; Hiom, J.; Dolphin, D. *J. Org. Chem.* **1988**, *53*, 2796–2802.
(27) Rurack, K. Fluorescence Quantum Yields: Methods of Determination and Standards. In *Standardization and Quality Assurance in Fluorescence Measurements I*; Resch-Genger, U., Ed.; Springer: Berlin, Heidelberg, 2008; Vol. 5, pp 101−145.
(28) Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067–1071.
(29) Basu, S.; Gupta, G.; Das, B.; Rao, K. M. *J. Organomet. Chem.* **2010**, *695*, 2098–2104.
(30) Ramírez, A.; Gómez, E.; Hernández, S. N. *J. Organomet. Chem.* **2009**, *694*, 2965–2975.
(31) Wiecek, J.; Dokorou, V.; Ciunik, Z.; Kovala-Demertzi, D. *Polyhedron* **2009**, *28*, 3298–3304.
(32) Jenkins, S.; Incarvito, C. D.; Parr, J.; Wasserman, H. H. *CrystEngComm* **2009**, *11*, 242–245.
(33) Sessler, J. L.; Eller, L. R.; Cho, W.-S.; Nicolaou, S.; Aguilar, A.; Lee, J. T.; Lynch, V. M.; Magda, D. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 5989–5992.
(34) Kee, H. L.; Kirmaier, C.; Yu, L.; Thamyongkit, P.; Youngblood, W. J.; Calder, M. E.; Ramos, L.; Noll, B. C.; Bocian, D. F.; Scheidt, W. R.; Birge, R. R.; Lindsey, J. S.; Holten, D. *J. Phys. Chem. B* **2005**, *109*, 20433–20443.
(35) Basu Baul, T. S. *Appl. Organomet. Chem.* **2008**, *22*, 195–204.
(36) Jakeman, D. L.; Bandi, S.; Graham, C. L.; Reid, T. R.; Wentzell, J. R.; Douglas, S. E. *Antimicrob. Agents Chemother.* **2009**, *53*, 1245–1247.
(37) Nath, M.; Eng, G.; Song, X.; Beraldo, H.; de Lima, G. M.; Pettinari, C.; Marchetti, F.; Whalen, M. M.; Beltrán, H. I.; Santillan, R.; Farfán, N. *Medicinal/Biocidal Applications of Tin Compounds and Environmental Aspects*; John Wiley & Sons, Ltd.: New York, 2008; pp 413−496.