

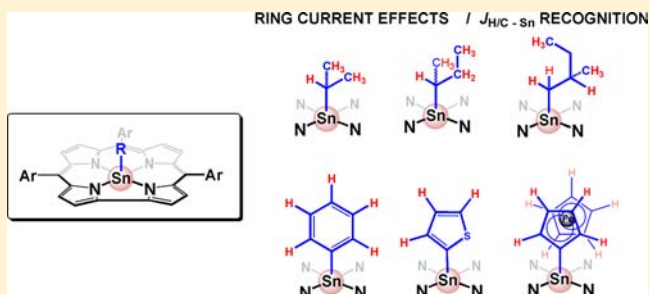
# Synthetic, $^{119}\text{Sn}$ NMR Spectroscopic, Electrochemical, and Reactivity Study of Organotin $\text{A}_3$ Corrolates Including Chiral and Ferrocenyl Derivatives

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## S Supporting Information

**ABSTRACT:** Various R/Ar-functionalized tin 5,10,15-tris-(pentafluorophenyl)corrolate derivatives are reported herein including the first ferrocenyltin corrolate species. The isopropyl, *sec*-butyl-, 2-methyl-*n*-butyl-, phenyl-, 2-thienyl-, and ferrocenyltin species have been prepared and characterized through  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  HMQC NMR spectroscopy, mass spectrometry, UV–vis and photoluminescent spectroscopy, and cyclic voltammetry studies.  $J_{\text{C}/\text{H}-\text{Sn}}$  NMR spectroscopic couplings and ring-current effects (upfield shifting) were determined for the R–Sn axial hydrogen and carbon atoms. This report adds to older conceptually similar reports, by, i.e., Janson et al. (*J. Am. Chem. Soc.* **1969**, *91*, 5210) and Walker et al. (*J. Am. Chem. Soc.* **1983**, *105*, 6923–6929), as discussed herein. Such NMR spectroscopic aspects are discussed for these model systems. Compound Sn–Ph bond cleavage was achieved by treatment with  $\text{I}_2$ .



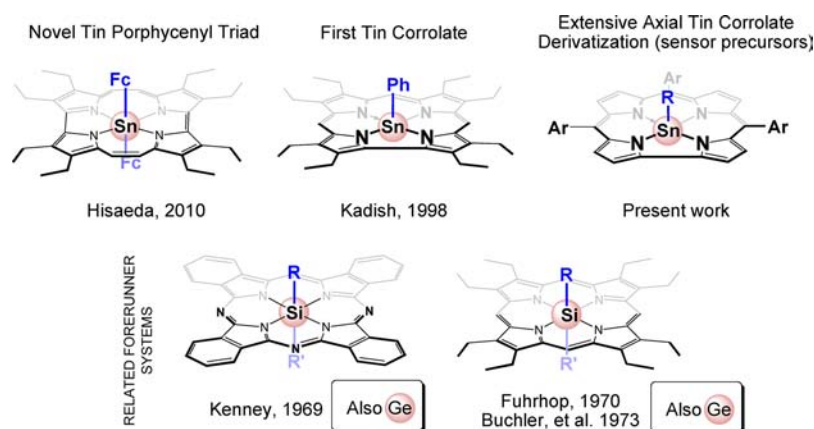
## I. INTRODUCTION

Natural cyclic polypyrroles and their metal complexes constitute a major compound class that serves as a vital basis for, e.g., essential iron and cobalt chemistry in biology. Synthetic systems also abound and have found important use in catalysis and model studies. The offerings in the literature on porphyrin and metalloporphyrin frameworks were described more than 35 years ago to have “mushroomed outwards and blossomed in a quite remarkable manner”.<sup>1a–d</sup> Therefore, lesser explored and newer cyclic polypyrrole skeleton types allow researchers to recapitulate important metalation and catalysis studies freely with an appreciation for the large changes that may occur in metal-centered reactivity, valence, and complex geometry upon seemingly relatively subtle formal changes in the macrocyclic ligand design. In recent years, one growing class of synthetic (contracted) porphyrin is the corroles and metal corrolates.<sup>1e–h</sup> Their interesting properties have been underscored by the research efforts of Gross et al.,<sup>2–4</sup> Kadish et al.,<sup>5–7</sup> Gryko et al.,<sup>7,8</sup> Paolesse et al.<sup>5,9,10</sup> and others and to a lesser extent by our research group.<sup>11</sup> There has been a relatively thorough treatment of transition-metal systems, with main-group derivatives being less thoroughly examined. Main-group corrolates are interesting because of the adaptation of the otherwise transition-metal-based  $[\text{N}_4]$  core system to various central elements that attenuate properties enabled by the contracted ligand. Group 14 corrolates of silicon, germanium, and lead have been reported.<sup>10b,12</sup> Furthermore, tin(4+) porphyrinoids have been previously reported by Hosseini et al. and Nemykin et al.<sup>13,14</sup> Tin(4+) corroles have been

previously reported by Kadish and others (Figure 1).<sup>12b,15,16</sup> Tin corroles are interesting to investigate because the static axial group involves atoms proximal to the metal that are under the influence of both (i) the macrocyclic ring current and (ii) inherent NMR-coupling characteristics imposed by NMR spectroscopically active tin nuclei. Thus, the axial position can impose a *dual* signature onto potentially *all* atoms of the axial group in a kind of “double stamping” that would be interesting to pursue in molecular recognition. Conceptually, however, reports of porphyrinoid systems with both metal axial–ligand and macrocyclic ring–ligand interactions originate from efforts decades ago.<sup>17</sup> A chapter by Scheer and Katz encompasses various kinds of transition-metal- and main-group-based systems (Figure 1).<sup>17b</sup> Additionally, certain subsequent reports stand out as well including interesting reports by Walker et al. on the NMR properties of iron porphyrins (Figure 2).<sup>17a</sup> This concept can now be extended to tin corroles here, in which the tin axial site can host a variety of aliphatic and aromatic groups; these strongly bound groups can serve as basic model systems for would-be analytes. Related porphyrinoid systems such as the octaethylporphyrin and phthalocyanine versions involving the *lighter* group 14 elements contain *dual* axial O–R groups ligands, as described in earlier reports (Figure 1).<sup>1b–d</sup> Additionally, aryl groups can extend to the cyclopentadienyl moiety; this ligand can be bound further to other metals. Here, the common, versatile, and robust ferrocenyl (Fc) system was

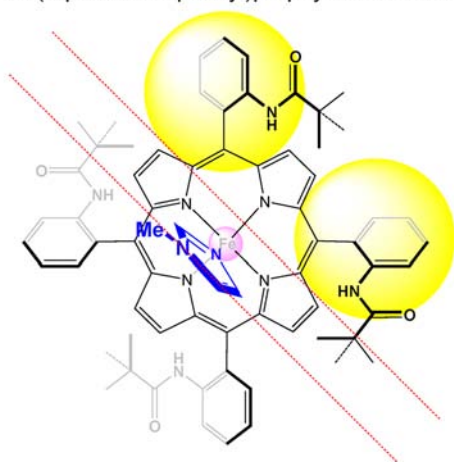
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**Figure 1.** Notable previous species: (top left) diferrocenyltin porphycene and (center and right) tin corrolates.<sup>25,15</sup> (right) Various R and Ar groups, including chiral and ferrocenyl groups, discussed herein. (bottom) Earlier porphyrinoid systems involving dual axial ligation at group 14 centers.<sup>1b–d</sup>

### Tetrakis(*o*-pivalamidophenyl)porphyrin FeCl derivatization



**Figure 2.** Forced axial ligand directionality (N-methyl-imidazole) in the abundant atropisomeric  $\alpha\alpha\beta\beta$  form (Walker, 1983).

**Figure 2.** Elegant earlier example of the “double-stamping” concept reported by Walker et al. involving the bulk of the meso groups able to “dial” the axial group to different metal-based orbital interactions. In this way, the nuclei of the axial ligands are under the influence of both (i) the macrocyclic ring current and (ii) electronic interactions from the metal center, and the nuclei of the atoms in the axial group can therefore be said to be “double-stamped”. Red dotted lines indicate the alignment of the *top* N-methylimidazole group (bottom one omitted for clarity) and that for the imposition of the proximal top pivalamidophenyl groups (spheres).<sup>17a</sup>

incorporated. There are only a few reports to date regarding Cor–Fc conjugates, but these examples do not contain Fc groups that are bound to the metal.<sup>18,19</sup> Previous reports relate mainly to catalysis, not to sensing. Ferrocenyl conjugation may be desired for chemosensing in its own right. It has been established for related systems for control of the redox activity,<sup>20</sup> robustness, optics,<sup>21</sup> and photoluminescence,<sup>14,22</sup> electron-transfer properties,<sup>23</sup> and charge-transfer capabilities.<sup>24,25</sup> Chirality has also been addressed with corrole complexes but sparingly; previous reports involve ligand N substitution and metal centers.<sup>26,27,3,11d</sup>

## II. EXPERIMENTAL SECTION

**Materials and Physical Measurements.** All chemicals used herein (e.g., pentafluorobenzaldehyde, SnCl<sub>2</sub>, phenylmagnesium

bromide, isopropylmagnesium bromide, *sec*-butylmagnesium bromide, 2-thienyllithium, CH<sub>2</sub>Cl<sub>2</sub>, hexane, and toluene) were of analytical grade and were used as received from commercial suppliers (Aldrich, TCI, and Junsei companies) except for pyrrole. Pyrrole was distilled over CaH<sub>2</sub> under vacuum prior to use. Analytical and preparative thin-layer chromatography (PTLC) was performed on the original plates (20 × 20 cm, 60 F silica gel, Merck). A Vilber Lourmat 4LC UV lamp (4 W, 365 nm, 50/60 Hz) was used to assay the colored and fluorescent TLC components of the reaction mixture. The silica gel used in column chromatography was of diameter 0.04–0.063 mm. The silica gel used for dry-column vacuum chromatography was of diameter 0.015–0.040 mm (Merck). All solvents used in NMR spectral analyses were purchased commercially and were of spectroscopic grade. One-dimensional <sup>1</sup>H and <sup>13</sup>C NMR spectra and two-dimensional heteronuclear multiple-quantum coherence (HMQC) spectra were measured on a Bruker Avance 400 MHz spectrometer; tetramethylsilane was used as an internal standard. <sup>119</sup>Sn NMR spectra were acquired on a Bruker Avance spectrometer (149.21 MHz) and quoted in ppm relative to *tetramethyltin* (SnMe<sub>4</sub>; <sup>119</sup>Sn = 0 ppm) as an external standard and are reported as fully decoupled spectra. UV–vis spectra were recorded with a JASCO V-503 UV–vis spectrophotometer (1000 nm/min). Emission spectra were obtained using a Shimadzu RF-5310pc spectrofluorophotometer. High-resolution matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Autoflex III [ionization method, laser source Nd YAG (355 nm); analyzer, 2.0 m linear mode; 3.0 reflector mode], and  $\alpha$ -cyano-4-hydroxycinnamic acid was used as the matrix. High-resolution mass spectrometry (HRMS) spectra were recorded on Bruker micrOTOF-Q II mass spectrometer [electrospray ionization (ESI-TOF), positive mode]. Time-correlated single-photon-counting spectra were collected using a FL920 spectrofluorimeter (Edinburgh Instruments) utilizing the pulses from an EPL 470-ps-pulsed diode laser and a H5773-04 detector (Hamamatsu). Cyclic voltammetry (CV) was carried out with a CHI 900B electrochemical analyzer (CH instruments) using a solution of 0.1 M TBAP in acetonitrile. A three-electrode system was used and consisted of a platinum disk working electrode, a platinum wire counter electrode, and an Ag/Ag<sup>+</sup> reference electrode containing 0.01 M AgNO<sub>3</sub>. All solutions for electrochemical measurements were deoxygenated by sparging with argon prior to experimentation. All potentials are referenced against the Ag/Ag<sup>+</sup> redox couple. Values of *E*<sub>1/2</sub> of the ferrocene/ferrocenium ion couple were –0.01 V under our experimental conditions.

**General Procedure for the Preparation of Tin(IV) Corrolate Complexes with Alkyl and Aryl Axial Ligands.** Details for the synthesis of 5,10,15-tris(pentafluorophenyl)corrole<sup>4,28</sup> and [5,10,15-tris(pentafluorophenyl)corrolato]tin(IV) chloride [Sn(tpfc)Cl; **1**] have been previously reported.<sup>12b</sup> To a stirred solution of **1** in dry tetrahydrofuran (THF; 5 mL) was added 4.0 equiv of alkyl- or arylmagnesium bromide or aryllithium under an inert atmosphere; the

reaction mixture was stirred for 5 min at room temperature. Aqueous ammonium chloride was added, after which dichloromethane was added. The organic layer was separated and washed with water two times and then evaporated to dryness. Residue was subjected to dry-column vacuum chromatography; the title compound was purified again by PTLC. Detailed purification systems for individual compounds are given below.

**Isopropyl [5,10,15-Tris(pentafluorophenyl)corrolato]tin(IV) [Sn(tpfc)Pr; 2].** This reaction was performed by the following literature procedure,<sup>15</sup> starting from 242 mg (0.26 mmol) of **1** and 520  $\mu\text{L}$  (1.04 mmol) of isopropylmagnesium chloride (2.0 M in THF). Dry-column vacuum chromatography (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.2:1) and PTLC (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.5:2) afforded the pure compound (67 mg, 0.07 mmol, 27%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 7.24 ppm):  $\delta$  9.21 (d,  $^3J(\text{H,H}) = 4.2$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.96 (d,  $^3J(\text{H,H}) = 3.4$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.75 (m,  $4\text{H}_{\beta\text{-pyrrole}}$ ), -1.85 (d,  $^3J(\text{H,H}) = 7.24$  Hz, satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 66.8$  and 74.3 Hz, 6H,  $\text{H}_b$  and  $\text{H}_c$ ), -2.06 (m, 1H,  $\text{H}_a$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 77 ppm):  $\delta$  148.3 (br), 146.9 (br), 145.8 (br), 144.5 (br), 143.9 ( $\text{C}_{6,14}$  or  $9,11$ ), 140.9 ( $\text{C}_{9,11}$  or  $6,14$ ), 139.5 ( $\text{C}_{1,19}$  or  $4,16$ ), 137.6 ( $\text{C}_{4,16}$  or  $1,19$ ), 127.9 ( $\text{C}_{7,13}$ ), 125.4 ( $\text{C}_{3,17}$  or  $8,12$ ), 124.3 ( $\text{C}_{3,17}$  or  $8,12$ ), 118.6 ( $\text{C}_{2,18}$ ), 115.8, 114.8, 99.9 ( $\text{C}_{5,15}$ ), 93.1 ( $\text{C}_{10}$ ), 19.5 ( $\text{C}_a$ ), 15.6 ( $\text{C}_b$  and  $\text{C}_c$ ).  $^{119}\text{Sn}$  NMR (149.21 MHz,  $\text{CDCl}_3$ ):  $\delta$  -371. HRMS: 956.0034 ( $\text{M}^+$ , obsd), 956.0079 (calcd for  $\text{C}_{40}\text{H}_{15}\text{F}_{15}\text{N}_4\text{Sn}$ ). MALDI-TOF  $[(\text{M} + \text{H})^+]$ : 956.583 (44%), 913.509 (100%) (obsd).  $\lambda_{\text{max}}$  (toluene),  $\text{nm}$  ( $\epsilon \times 10^{-4}$ ,  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 428 (36.1), 536 (1.3), 577 (2.2), 608 (3.0).

**2-Butyl [5,10,15-Tris(pentafluorophenyl)corrolato]tin(IV) [Sn(tpfc)<sup>sec</sup>Bu; 3].** This reaction was performed following a general procedure<sup>15</sup> starting from 100 mg (0.10 mmol) of **1** and 440  $\mu\text{L}$  of *sec*-butylmagnesium bromide (1.0 M in THF). Dry-column vacuum chromatography (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.2:1.0) and PTLC (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.5:2.0) afforded the pure product compound (14 mg, 0.014 mmol, 14%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 7.24 ppm):  $\delta$  9.20 (d,  $^3J(\text{H,H}) = 4.32$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.89 (d,  $^3J(\text{H,H}) = 4.45$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.71 (m,  $4\text{H}_{\beta\text{-pyrrole}}$ ), -1.13 (m,  $\text{H}_c$ ), -1.45 (t,  $^3J(\text{H,H}) = 7.2$  Hz,  $\text{H}_d$ ), -1.71 (m,  $\text{H}_a$ ), -1.94 (d,  $J(\text{H,H}) = 7.56$  Hz,  $\text{H}_b$ ), -2.17 (m,  $\text{H}_e$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 77 ppm):  $\delta$  148.3 (br), 147.0 (br), 145.8 (br), 144.5 (br), 143.9 ( $\text{C}_{6,14}$  or  $9,11$ ), 140.9 ( $\text{C}_{6,14}$  or  $9,11$ ), 139.4 ( $\text{C}_{1,19}$  or  $4,16$ ), 137.6 ( $\text{C}_{1,19}$  or  $4,16$ ), 127.8 ( $\text{C}_{7,13}$ ), 125.3 ( $\text{C}_{3,17}$  or  $8,12$ ), 124.3 ( $\text{C}_{3,17}$  or  $8,12$ ), 118.1 ( $\text{C}_{2,18}$ ), 115.6, 114.8, 99.9 ( $\text{C}_{5,15}$ ), 93.1 ( $\text{C}_{10}$ ), 29.4 ( $\text{C}_a$ ), 24.2 ( $\text{C}_c$ ), 13.0 ( $\text{C}_b$ ), 10.6 ( $\text{C}_d$ ).  $^{119}\text{Sn}$  NMR (149.21 MHz,  $\text{CDCl}_3$ ):  $\delta$  -376.64. HRMS: 970.0185 ( $\text{M}^+$ , obsd), 970.0236 (calcd for  $\text{C}_{41}\text{H}_{17}\text{F}_{15}\text{N}_4\text{Sn}$ ). MALDI-TOF  $[(\text{M} + \text{H})^+]$ : 970.674 (19%), 913.562 (100%) (obsd).  $\lambda_{\text{max}}$  (toluene),  $\text{nm}$  ( $\epsilon \times 10^{-4}$ ,  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 428 (30.68), 536 (0.92), 577 (1.78), 606 (2.46).

**2-Methyl-*n*-butyl [5,10,15-Tris(pentafluorophenyl)corrolato]tin(IV) [Sn(tpfc)(2-Me-*n*-Bu); 4].** The reaction was performed following a general procedure<sup>15</sup> starting from 190 mg (0.2 mmol) of **1** and 1.0 mL of 2-methyl-*n*-butylmagnesium bromide (1.2 M in diethyl ether) prepared in situ from 0.408 mL of (*S*)-(+)-1-bromo-2-methylbutane. Dry-column vacuum chromatography (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.2:1) and PTLC (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.5:2) afforded a pure compound (27 mg, 0.027 mmol, 14%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 7.24 ppm):  $\delta$  9.21 (d,  $^3J(\text{H,H}) = 4.14$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.94 (d,  $^3J(\text{H,H}) = 4.6$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.74 (m,  $4\text{H}_{\beta\text{-pyrrole}}$ ), -0.54 (t,  $^3J(\text{H,H}) = 9.69$  Hz, 3H, satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 49.5$  Hz,  $\text{H}_c$ ), -1.04 (m, 2H,  $\text{H}_d$ ), -1.53 (d,  $^3J(\text{H,H}) = 6.21$  Hz, 3H, satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 49.4$  Hz,  $\text{H}_c$ ), -1.78 (m, 1H,  $\text{H}_b$ ), -2.66 (dd,  $J(\text{H,H}) = 7.56$  Hz, 2H,  $\text{H}_a$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 77 ppm):  $\delta$  148.3 (br), 147.0 (br), 145.8 (br), 144.5 (br), 143.6 ( $\text{C}_{6,14}$  or  $9,11$ ), 140.6 ( $\text{C}_{6,14}$  or  $9,11$ ), 139.3 ( $\text{C}_{1,19}$  or  $4,16$ ), 137.4 ( $\text{C}_{1,19}$  or  $4,16$ ), 128.0 ( $\text{C}_{7,13}$ ), 125.4 ( $\text{C}_{3,17}$  or  $8,12$ ), 124.4 ( $\text{C}_{3,17}$  or  $8,12$ ), 118.2 ( $\text{C}_{2,18}$ ), 115.8, 114.8, 100.0 ( $\text{C}_{5,15}$ ), 93.2 ( $\text{C}_{10}$ ), 29.9 ( $\text{C}_b$ ), 28.3 ( $\text{C}_d$ ), 22.5 ( $\text{C}_a$ ), 19.6 ( $\text{C}_c$ ), 9.9 ( $\text{C}_e$ ).  $^{119}\text{Sn}$  NMR (149.21 MHz,  $\text{CDCl}_3$ ):  $\delta$  -362.52. HRMS: 984.0339 ( $\text{M}^+$ , obsd), 984.0392 (calcd for  $\text{C}_{42}\text{H}_{19}\text{F}_{15}\text{N}_4\text{Sn}$ ). MALDI-TOF  $[(\text{M} + \text{H})^+]$ : 984.664 (65%), 913.562 (100%) (obsd).  $\lambda_{\text{max}}$  (toluene),  $\text{nm}$  ( $\epsilon \times 10^{-4}$ ,  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 428 (36.6), 535 (1.1), 576 (2.17), 606 (2.98).

**Phenyl [5,10,15-Tris(pentafluorophenyl)corrolato]tin(IV) [Sn(tpfc)Ph; 5].** The reaction was performed following a general

procedure<sup>15</sup> starting from 219 mg (0.22 mmol) of **1** and phenylmagnesium bromide (308  $\mu\text{L}$  of a 3.0 M solution in diethyl ether). Dry-column vacuum chromatography (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.2:1) and preparative TLC (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.5:2) afforded the pure expected compound (120 mg, 0.12 mmol, 55% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 7.24 ppm):  $\delta$  9.25 (d,  $^3J(\text{H,H}) = 4.18$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 9.06 (d,  $^3J(\text{H,H}) = 4.75$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.86 (m,  $4\text{H}_{\beta\text{-pyrrole}}$ ), 6.20 (t,  $^3J(\text{H,H}) = 7.49$  Hz, 1H,  $\text{H}_d$ ), 5.96 (t,  $^3J(\text{H,H}) = 7.6$  Hz; satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 31.6$  and 46.7 Hz,  $\text{H}_c$  and  $\text{H}_e$ ), 3.63 (d,  $^3J(\text{H,H}) = 7.0$  Hz, satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 88.5$  Hz, 2H,  $\text{H}_b$  and  $\text{H}_f$ ),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 77 ppm):  $\delta$  148.3 (br), 147.1 (br), 145.9 (br), 144.5 (br), 143.7 (s), 140.7 (s), 139.5, 137.5, 133.6, 131.2 (satellites  $J(^{13}\text{C}, ^{119}\text{Sn}) = 59.1$  Hz,  $\text{C}_b$  and  $\text{C}_f$ ), 129.5 ( $\text{C}_d$ ), 128.1, 127.4 (satellites  $J(^{13}\text{C}, ^{119}\text{Sn}) = 48.7$  Hz,  $\text{C}_c$  and  $\text{C}_e$ ), 125.8, 124.6, 118.4, 115.5, 114.8, 100, 93.45.  $^{119}\text{Sn}$  NMR (149.21 MHz,  $\text{CDCl}_3$ ):  $\delta$  -404.60. HRMS: 989.9878 ( $\text{M}^+$ , obsd), 989.9923 (calcd for  $\text{C}_{43}\text{H}_{13}\text{F}_{15}\text{N}_4\text{Sn}$ ). MALDI-TOF  $[(\text{M} + \text{H})^+]$ : 990.463 (100%), 913.404 (8%) (obsd).  $\lambda_{\text{max}}$  (toluene),  $\text{nm}$  ( $\epsilon \times 10^{-4}$ ,  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 426 (39.3), 536 (1.06), 575 (2.29), 604 (3.07).

**2-Thienyl [5,10,15-Tris(pentafluorophenyl)corrolato]tin(IV) [Sn(tpfc)-2-thienyl; 6].** The reaction was performed following a general procedure<sup>15</sup> starting from 184 mg (0.19 mmol) of **1** and 760  $\mu\text{L}$  of 2-thienyllithium (1.0 M in THF). Dry-column vacuum chromatography (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.2:1) and PTLC (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.4:1.5) afforded compound **6** in pure form (63 mg, 0.063 mmol, 33% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 7.24 ppm):  $\delta$  9.27 (d,  $^3J(\text{H,H}) = 4.22$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.99 (d,  $^3J(\text{H,H}) = 4.65$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.81 (m,  $4\text{H}_{\beta\text{-pyrrole}}$ ), 6.48 (d,  $^3J(\text{H,H}) = 4.76$  Hz, satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 34$  Hz,  $\text{H}_d$ ), 5.94 (t,  $^3J(\text{H,H}) = 4.5$  Hz, satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 18.3$  Hz,  $\text{H}_c$ ), 3.92 (d,  $^3J(\text{H,H}) = 3.47$  Hz, satellites  $J(^1\text{H}, ^{119}\text{Sn}) = 45$  Hz,  $\text{H}_b$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 77 ppm):  $\delta$  148.3 (br s), 146.9 (br s), 145.7 (br s), 144.5 (br), 143.5 ( $\text{C}_{6,14}$  or  $9,12$ ), 140.6 ( $\text{C}_{6,14}$  or  $9,11$ ), 139.3 ( $\text{C}_{1,19}$  or  $4,16$ ), 137.3 ( $\text{C}_{4,16}$  or  $1,19$ ), 133.6 (satellites  $J(^{13}\text{C}, ^{119}\text{Sn}) = 69$  Hz,  $\text{C}_b$ ), 131.3 (satellites  $J(^{13}\text{C}, ^{119}\text{Sn}) = 49.4$  Hz,  $\text{C}_d$ ), 128.2 ( $\text{C}_{7,13}$ ), 126 ( $\text{C}_c$ ), 125.9 ( $\text{C}_{3,17}$  or  $8,12$ ), 124.7 ( $\text{C}_{3,17}$  or  $8,12$ ), 122.0 ( $\text{C}_a$ ), 118.6 ( $\text{C}_{2,18}$ ), 115.1, 114.5, 100 ( $\text{C}_{5,15}$ ), 93.5 ( $\text{C}_{10}$ ).  $^{119}\text{Sn}$  NMR (149.21 MHz,  $\text{CDCl}_3$ ):  $\delta$  -394.11. HRMS: 995.9448 ( $\text{M}^+$ , obsd), 995.9487 (calcd for  $\text{C}_{41}\text{H}_{11}\text{F}_{15}\text{N}_4\text{SSn}$ ). MALDI-TOF  $[(\text{M} + \text{H})^+]$ : 996.554 (100%) (obsd).  $\lambda_{\text{max}}$  (toluene),  $\text{nm}$  ( $\epsilon \times 10^{-4}$ ,  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 425 (39.2), 535 (1.07), 574 (2.37), 601 (2.93).

**Ferrocenyl [5,10,15-Tris(pentafluorophenyl)corrolato]tin(IV) [Sn(tpfc)Fc; 7].** Diethyl ether (1.5 mL) was added to magnesium (turnings, 103 mg, 4.24 mmol) under an inert atmosphere. A solution of bromoferrocene (280 mg, 1.06 mmol) and 1,2-dibromoethane (182  $\mu\text{L}$ , 2.12 mmol) in diethyl ether (3 mL) was added dropwise. When heating and boiling are stopped, the freshly prepared Grignard reagent solution was added to the solution of **1** (100 mg, 0.106 mmol) in dry THF (2.5 mL). After 10 min, the reaction was quenched with water. Methylene chloride was added, and the organic layer was separated and washed with water two times and then evaporated to dryness. Dry-column vacuum chromatography (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.2:1) and PTLC (silica,  $\text{CH}_2\text{Cl}_2/\text{hexane}$ , 0.5:1 and then 2:0.5) afforded compound **7** in pure form (33 mg, 0.30 mmol, 28.5%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 7.24 ppm):  $\delta$  9.26 (d,  $^3J(\text{H,H}) = 4.26$  Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.93 (dd,  $^3J(\text{H,H}) = 4.7$  and 1.17 Hz,  $2\text{H}_{\beta\text{-pyrrole}}$ ), 8.75 (m,  $4\text{H}_{\beta\text{-pyrrole}}$ ), 3.1 (t,  $^3J(\text{H,H}) = 1.79$  Hz,  $^{119}\text{Sn}$  satellites  $J(\text{H,Sn}) = 16.8$  Hz, 2H,  $\text{H}_c$ ), 2.65 (s, 10H,  $\text{H}_d$ ), 0.94 (t,  $^3J(\text{H,H}) = 1.73$  Hz,  $^{119}\text{Sn}$  satellites  $J(\text{H,Sn}) = 15.9$  Hz, 2H,  $\text{H}_b$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 53.8 ppm):  $\delta$  148.7, 147.5, 145.2, 145, 144.1 ( $\text{C}_{6,14}$  or  $9,11$ ), 143.7 ( $\text{C}_{6,14}$  or  $9,11$ ), 141.1 ( $\text{C}_{1,19}$  or  $4,16$ ), 139.8 ( $\text{C}_{1,19}$  or  $4,16$ ), 137.7, 137.0, 128.5 ( $\text{C}_{7,13}$ ), 126.1 ( $\text{C}_{3,17}$  or  $8,12$ ), 124.9 ( $\text{C}_{3,17}$  or  $8,12$ ), 118.9 ( $\text{C}_{2,18}$ ), 115.9, 115.1, 100.3 ( $\text{C}_{5,15}$ ), 93.6 ( $\text{C}_{10}$ ), 69.8 (satellites  $J(^{13}\text{C}, ^{119}\text{Sn}) = 90.8$  Hz,  $\text{C}_c$ ), 69.5 (satellites  $J(^{13}\text{C}, ^{119}\text{Sn}) = 106.9$  Hz,  $\text{C}_b$ ), 67.7 ( $\text{C}_d$ ), 60.2 ( $\text{C}_a$ ).  $^{119}\text{Sn}$  NMR (149.21 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -352.7. HRMS: 1097.9552 ( $\text{M}^+$ , obsd), 1097.9585 (calcd for  $\text{C}_{47}\text{H}_{17}\text{F}_{15}\text{FeN}_4\text{Sn}$ ). MALDI-TOF  $[(\text{M} + \text{H})^+]$ : 1098.647 (100%) (obsd).  $\lambda_{\text{max}}$  (toluene),  $\text{nm}$  ( $\epsilon \times 10^{-4}$ ,  $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 425 (31.4), 535 (1.09), 576 (2.19), 606 (2.87).

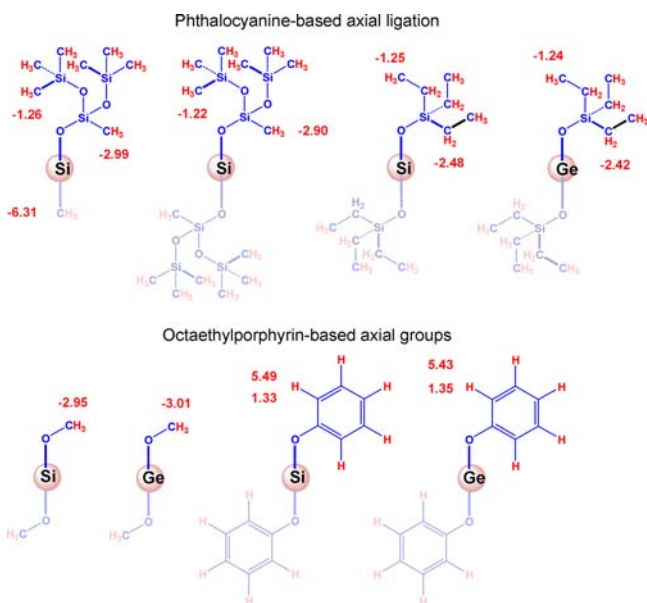
**Reactivity of Sn-C Bond Cleavage with  $\text{I}_2$ .** A small amount of compound **5** was taken into a sealable NMR tube for reaction with 10 equiv of  $\text{I}_2$  (0.018 mmol). The reaction was monitored conveniently

by  $^1\text{H}$  NMR spectroscopy, whereupon after 2 days quantitative conversion of the starting materials to a new product was observed, devoid of the original phenyl group and with  $^1\text{H}$  NMR spectroscopic signals consistent with tin–iodine corrole and PhI (see Figure S2 in the Supporting Information).

**Testing for Halide Sensing.** A solution of compound **6** ( $1.0\ \mu\text{M}$  in MeCN) was taken and treated with a small excess (10 equiv) of iodide (KI) to effect the exposure of the corrolate–tin alkyl with  $\text{I}^-$  ions. This was performed in a cuvette, where a control sample allowed for gauging possible optical fluorescent changes. There was no spectral change upon treatment with  $\text{I}^-$ , signifying no chemical change, in contrast with that found for  $\text{I}_2$ . Also, analogous trials were done for  $\text{Br}^-$  and  $\text{Cl}^-$  and shown to give no optical responses.

### III. RESULTS AND DISCUSSION

Three main steps were taken to prepare model systems **2–7**: (i) corrole free-base synthesis, (ii) stannylation, and (iii) arylation/alkylation. First, the well-known tris-(pentafluorophenyl)corrole species  $\text{tpfc}(\text{H})_3$  was prepared.<sup>28</sup> Next, the derivative **1** was then synthesized by treatment of  $\text{tpfc}(\text{H})_3$  with  $\text{SnCl}_2$  in *N,N*-dimethylformamide.<sup>9,12b,15</sup> Finally, target compounds **2–7** (Figure 4) were synthesized according



**Figure 3.**  $^1\text{H}$  NMR spectral shifts for related phthalocyanine and octaethyl porphyrin group 14 systems. Here, there are two axial ligands; the nuclei here do not afford secondary coupling such as that found for tin.

to the procedure provided by the Kadish report.<sup>15</sup> Hydrocarbon axial groups (R/Ar) were incorporated onto **1** in the form of Grignard reagents, except for 2-thienyl and ferrocenyl groups, which were prepared as lithium salts (see the Experimental Section). These reagents afforded the respective isopropyl (**2**), *sec*-butyl (**3**), 2-methyl-*n*-butyl (**4**), phenyl (**5**), 2-thienyl (**6**), and ferrocenyl (**7**) derivatives (Figure 4). For the synthesis of **4**, (*S*)-(+)-1-bromo-2-methylbutane was first converted to 2-methyl-*n*-butylmagnesium bromide, which was then able to be used directly in the preparation of **4** (observation of a very weak Cotton effect; see the Supporting Information). The compounds were characterized in solution by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{119}\text{Sn}$  NMR spectroscopy. The various axial ligands in **2–7** were further assigned through the use of  $^1\text{H}$ – $^{13}\text{C}$  HMQC NMR spectroscopy. In  $^1\text{H}$  NMR spectra, the eight expected

macrocylic  $\beta$ -proton signals are present ( $\delta \sim 8\text{--}9.5$ )<sup>29</sup> (Supporting Information). Upfield shifting was clearly observed: 0.12 ppm differences for aryl groups and 0.20 ppm for alkyl groups, relative to **1**.<sup>12b</sup>  $^{119}\text{Sn}$  NMR spectral signals of  $\delta -350$  to  $-400$  were obtained, supporting pentacoordination of the tin atom and comparable to values previously published for closely related compounds.<sup>30</sup> These tin values are the first values obtained for corroles. HRMS spectra revealed  $\text{M}^+$  signals within acceptable limits of error ( $\leq 5$  ppm); MALDI-TOF mass spectral data featured prominent signals in accordance with the calculated values (see reproductions of these spectra in the Supporting Information). The ferrocenyl derivative is the first such ferrocenyl–metal corrolate conjugate. Unfortunately, attempts to obtain solid-state structural data led to a tentative crystal structure of compound **7** only (Supporting Information).

NMR spectroscopic details were further analyzed, especially with respect to the axial moieties. These values are both connected covalently to tin, which is NMR-active<sup>30</sup> and which reveals  $^nJ(^1\text{H}, ^{119}\text{Sn})$  coupling values that allow for a handle for determining the  $\text{Sn}\cdots\text{H}$  through-bond distance. Additionally, these hydrocarbon atoms also fall under the influence of the macrocyclic ring current, seeing as they are proximal enough to the mean macrocyclic plane. As shown before for related systems, the ring-current axial group ligand proton signals are found far upfield:<sup>1</sup> aromatic signals, 6 to 3 ppm; aliphatic signals,  $-1$  to  $-4$  ppm (Figure 4 and figures in the Supporting Information). This is typified by compound **7**: Fc-based protons are *also* shifted to higher field because of the effects of the ring current (ferrocene:  $\delta$  4.1,  $\text{CDCl}_3$ , Supporting Information).<sup>31</sup> In Figure 4,  $\Delta\delta$  ( $\delta_{\text{complex}} - \delta_{\text{ferrocene}}$ ) values are more pronounced for the ferrocenyl atoms proximal to the tin atom in **7** (Table S2 in the Supporting Information). The other substituents (isopropyl, *sec*-butyl, 2-methyl-*n*-butyl, phenyl, and 2-thienyl) have also been spectroscopically characterized. These values in the  $^1\text{H}$  NMR spectrum are also all found upfield; reproductions of these spectra and those for  $^{13}\text{C}$  NMR spectroscopic data are provided in the Supporting Information. Larger  $\Delta\delta$  values are found in related porphyrin complexes (i.e., *trans*- $\text{SnFc}_2\text{TPP}$ ; Figure S39 and Table S2 in the Supporting Information).<sup>14</sup> In addition to the ring current,  $^{119}\text{Sn}$  nuclei ( $I = 1/2$ ) impose a secondary identifier on these axially positioned nuclei in the form of  $^nJ(^1\text{H}, ^{119}\text{Sn})$  and  $^nJ(^{13}\text{C}, ^{119}\text{Sn})$  coupling constant values (Figure 4 and the Supporting Information).<sup>32,33</sup>

These through-bond coupling constants show a clear trend of decreasing intensity as a function of the internuclear distance, as expected; they are gauged for the first time with a variety of  $\text{sp}^2$ - and  $\text{sp}^3$ -hybridized carbon groups. The interest in C/H-based ligands that bear these hallmarks could be in future molecular detection modalities, whereby analyte binding occurs at the single axial position in tin corrolates and the atoms are both upfield-shifted and tin-coupled.

In the context of this present scrutiny with these tin corrolate systems, related details of previously reported systems of group 14 porphyrinoid systems are depicted here (Figure 3).  $^1\text{H}$  NMR spectral chemical shifts of axial ligand atoms are provided for comparison. With these early examples, we can plainly see the ring-current effects for related group 14 systems, albeit for porphyrin species. In one report, the silicon(IV) thiocyanine species were characterized (Figure 1); specifically, three silicon versions and one germanium version bearing alkyl and siloxyl groups were obtained.<sup>1b</sup> For the reported silicon ( and germanium) octaethylporphyrins, the methoxide and phen-

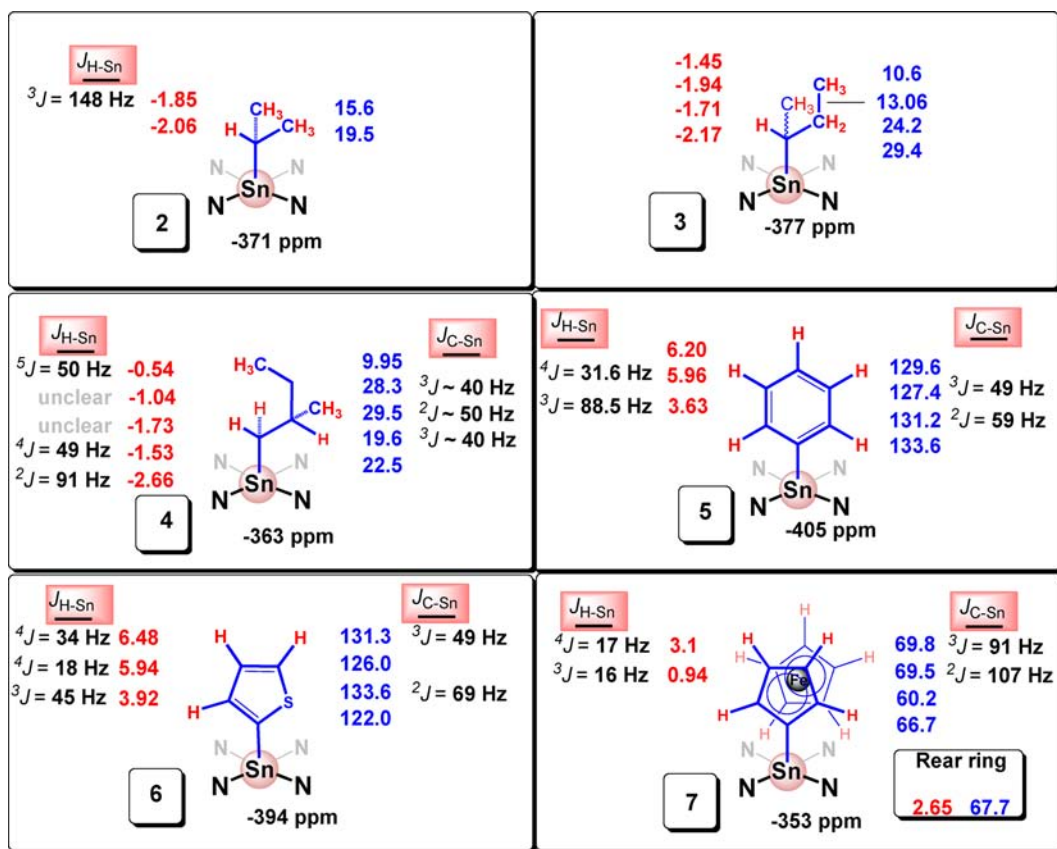


Figure 4. Alkyl and aryl moieties for compounds 2–7 and their ring-current-shifted  $\delta$  and their  $J(\text{H/C,Sn})$  values obtained herein.

oxide derivatives were also obtained (Figure 3).<sup>1c,d</sup> The differences in the proton chemical shift in the axial ligand are very small upon comparison of the silicon and germanium analogues.

Optically, the absorption spectra of corroles 2–7 in toluene at room temperature revealed characteristic Q and Soret bands. The Q bands are found at 535–536, 574–577, and 601–608 nm, and the Soret bands are found at values of 425–428 nm; additional bands that appear as shoulders to the principal Soret signal at 404–407 nm are also found but are less pronounced for compound 7 (Figure 5). In general, the bathochromic shifting of bands was observed for compounds 2–4 with alkyl axial groups in comparison with that for compounds 5–7. Emission spectra ( $\lambda_{\text{ex}} = \sim 530 \text{ nm}$ ) of 2–6 in toluene are also shown in Figure 5. No emission was detected for the ferrocenyl derivative (7) under our experimental conditions. For comparison, in porphyrin species, the incorporation ferrocenyl moiety leads to a 2.7-fold drop in the fluorescence quantum yield.<sup>14</sup> The emission peaks, Stokes shifts, and calculated fluorescence quantum yields of all compounds are provided in Table 1. Time-correlated single photon counting was also undertaken, and these spectra are displayed in the Supporting Information. The data reveal short fluorescence lifetimes of  $\sim 0.307\text{--}0.353 \text{ ns}$ . The longest lifetime was that obtained for 6, which showed a higher fluorescence quantum yield ( $6.71 \pm 0.12$ )  $\times 10^{-3}$  than the other samples. Both  $\Phi_{\text{F}}$  and  $\tau$  values obtained (Table 1) are of the same order of magnitude as that for the tin–chlorine corrolate [ $\Phi_{\text{F}} = (9.4 \pm 0.9) \times 10^{-3}$ ,  $\tau = 140 \pm 50 \text{ ps}$ , toluene, 77 K], reported by the research groups of Guillard and Harvey.<sup>16d</sup>

Cyclic voltammograms were obtained for compounds 2–7 and allow for a solution analysis of the electronic capacity of the different derivatives (Figure 6 and the Supporting Information). Single, reversible one-electron reductions were observed at  $E_{1/2} = -1.50 \pm 0.03 \text{ V}$ . The values for the alkyl derivative (compounds 2–4) were found clustered at a value of ca.  $-1.5 \text{ V}$  with subtle differences between them. Values for the aryl derivative compounds 5–7 varied and were found shifted slightly positive. By comparison, tin porphyrins bear *two* one-electron reductions.<sup>14,15</sup> Compounds 2–7 undergo three quasi-reversible oxidations. In general, the second oxidation peak is 2- or 3-fold larger than the first, pointing to an unstable doubly oxidized species that partially reverts to being singly oxidized before being *reoxidized* (Figure 6). Compound 7 has an additional oxidation peak at  $E_{\text{p}} = 0.23 \text{ V}$ , ascribed to the presence of the ferrocenyl group, oxidized at higher potential than that for the free ferrocene ( $E_{\text{p}} = -0.01 \text{ V}$ ). Taken together and in the context of all corrole compounds, these measurements underscore the *electron-withdrawing* nature of the supporting tpfc ligand. This macrocyclic ligand is also electrochemically different from the porphyrin analogue found at lower potential.<sup>14</sup> Also, the first corrole ring oxidation in compound 7 is shifted positively ( $E_{\text{p}} = 0.70 \text{ V}$ ) relative to the other compounds. The absolute potential difference  $\Delta E_{1/2}$  between the first reversible oxidation/reduction in 2–6 is  $\sim 2.04 \pm 0.02 \text{ V}$ , indicative of exclusive corrole-based redox activity (see the Supporting Information).  $\text{Sn}^{4+}$  is effectively inactive toward reduction. For compound 7, the ferrocenyl moiety is oxidized at 0.20 V before oxidation of the macrocycle occurs. The value of the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap

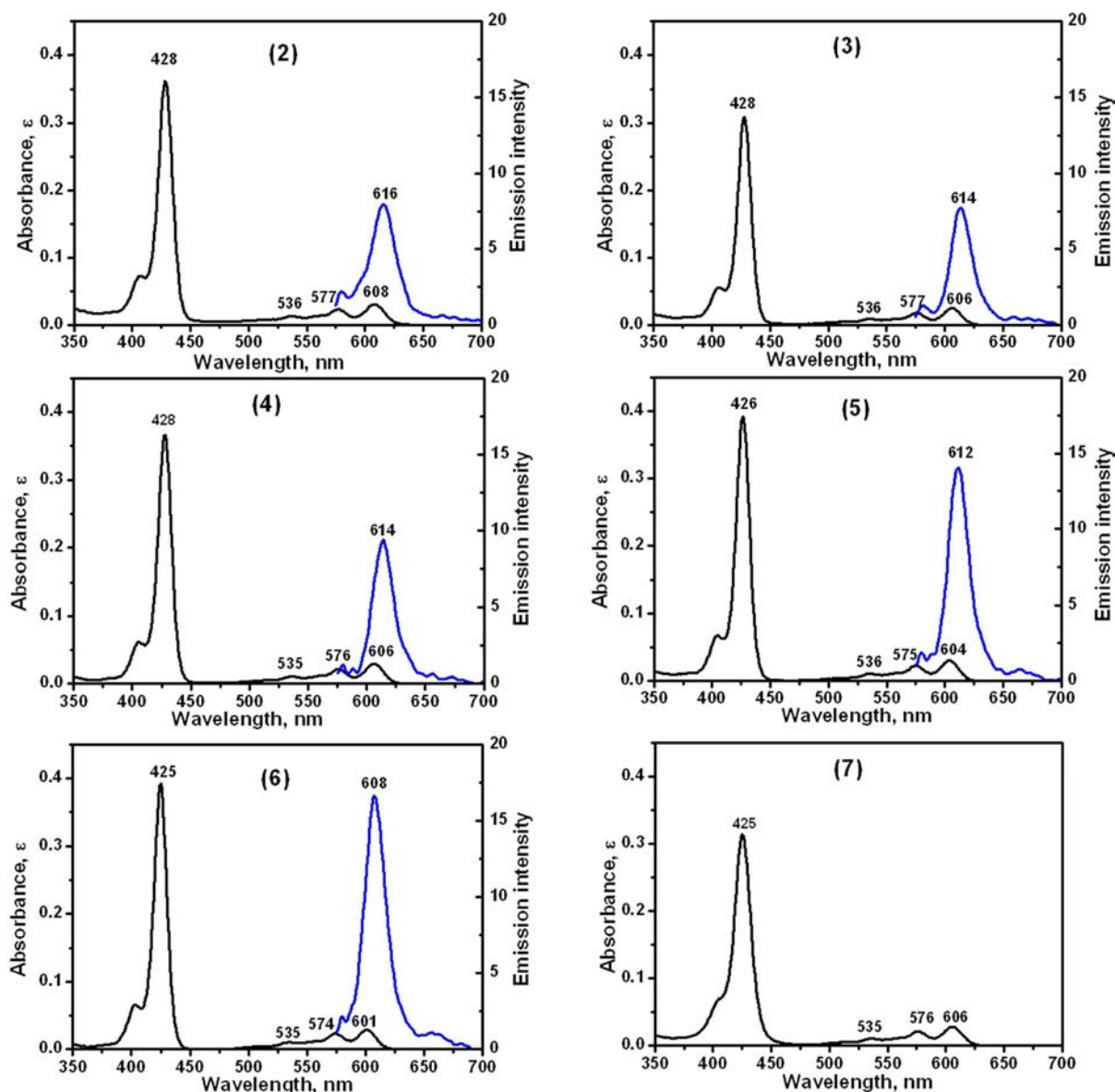


Figure 5. Absorption (black lines) and emission spectra (blue lines) of compounds 2–7 (toluene,  $1.0 \times 10^{-6}$  M). Excitation at Q bands.

Table 1. Photophysical Properties for Compounds 2–7 (Toluene, 290 K)

compound	Soret bands (nm)	Q bands (nm)	$\lambda_{\text{emis}}$ (nm) <sup>a</sup>	Stokes shift, (cm <sup>-1</sup> )	$\Phi_{\text{F}}^b \times 10^3$	$\tau_1$ (ns)	$\tau_2$ (ns)
2	428	536, 577, 608	616	217	$5.0 \pm 0.31$	0.310	1.784
3	428	536, 577, 606	614	213	$4.57 \pm 0.08$	0.310	2.371
4	428	535, 576, 606	614	213	$4.23 \pm 0.22$	0.307	2.005
5	426	536, 575, 604	612	216	$5.04 \pm 0.14$	0.312	1.25
6	425	535, 574, 601	608	192	$6.71 \pm 0.12$	0.353	
7	425	535, 576, 606	c	c	c	c	c

<sup>a</sup>Excited at Q band. <sup>b</sup>Relative to the fluorescence of ZnTPP ( $\Phi = 0.033$ ).<sup>38</sup> <sup>c</sup>Too weak to be measured.

of  $2.04 \pm 0.02$  V, obtained experimentally by electrochemical methods, is in good agreement with previously reported values for metallocorroles<sup>15,12b</sup> and metalloporphyrins.<sup>34</sup> However, this value is smaller than that for compound 1 ( $\Delta E_{1/2} = 2.14$  V).<sup>12b</sup> This electronic gap is consistent with other acquired data; the observed red-shifted Soret and Q bands also define a shift toward lower energy for the  $S_0$ – $S_2$  and  $S_0$ – $S_1$  transitions. This bathochromic shift is a desirable feature for potential near-IR emission sensing purposes based on this design (Figure 5).

Organotin transformations were also studied, as monitored by <sup>1</sup>H NMR spectroscopic and UV–vis/photoluminescent cuvette studies. In these reactions, the axial ligand generally undergoes a facile reaction to cleanly afford a new axial group. Treatment of compound 5 with I<sub>2</sub> gives clean Sn–C<sub>6</sub>H<sub>5</sub> bond cleavage and corrole–Sn–I bond formation (Figure 7).<sup>30,35</sup> The proton signals assigned to the phenyl group in 5 completely disappear after 2 days at 25 °C. New signals that appear in the aromatic region can be confidently assigned to the

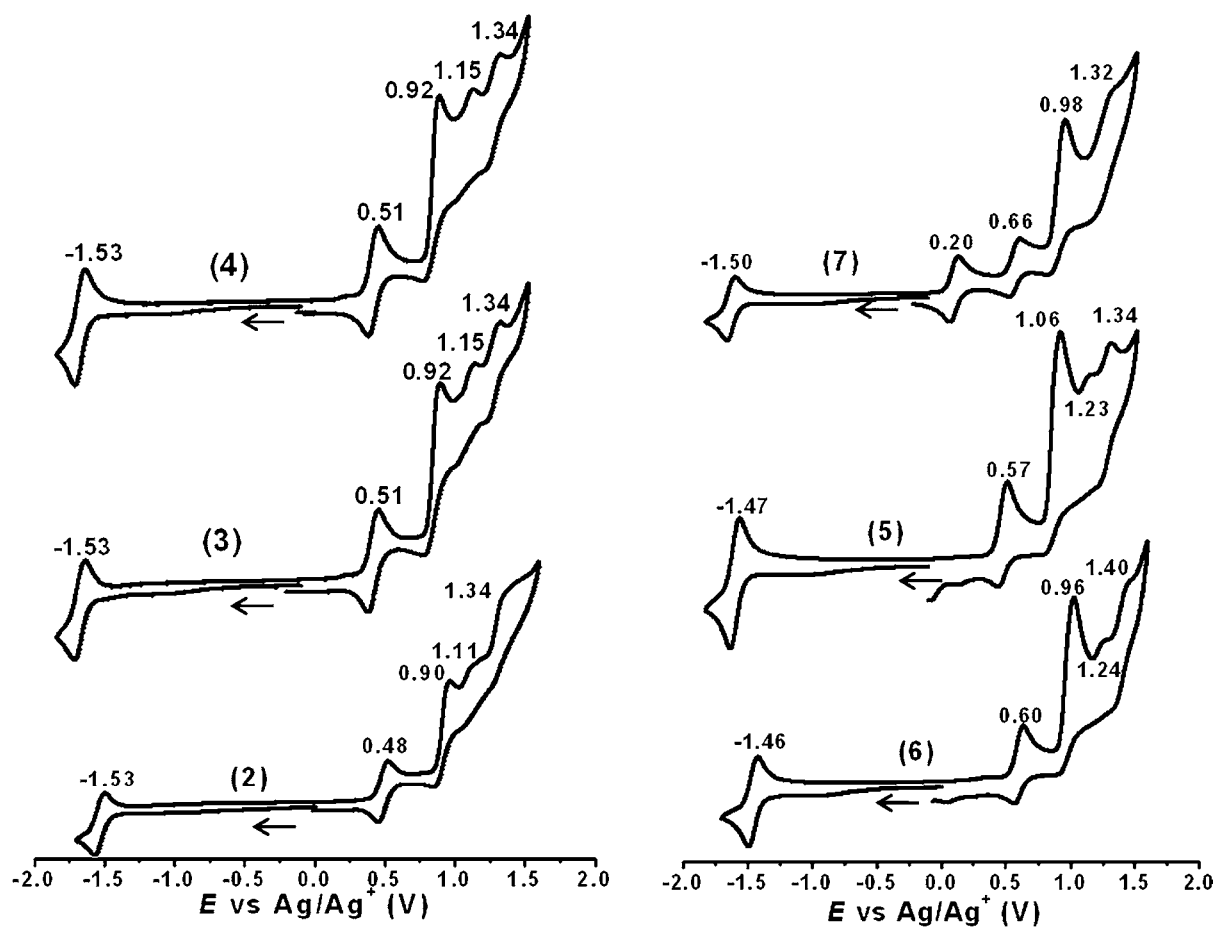


Figure 6. Compilation of cyclic voltammogram data for compounds 2–7. The  $\text{CH}_3\text{CN}$  solvent was used with 0.1 M TBAP at a scan rate of  $0.1 \text{ V}\cdot\text{s}^{-1}$ , with  $E_{1/2}$  in volts.

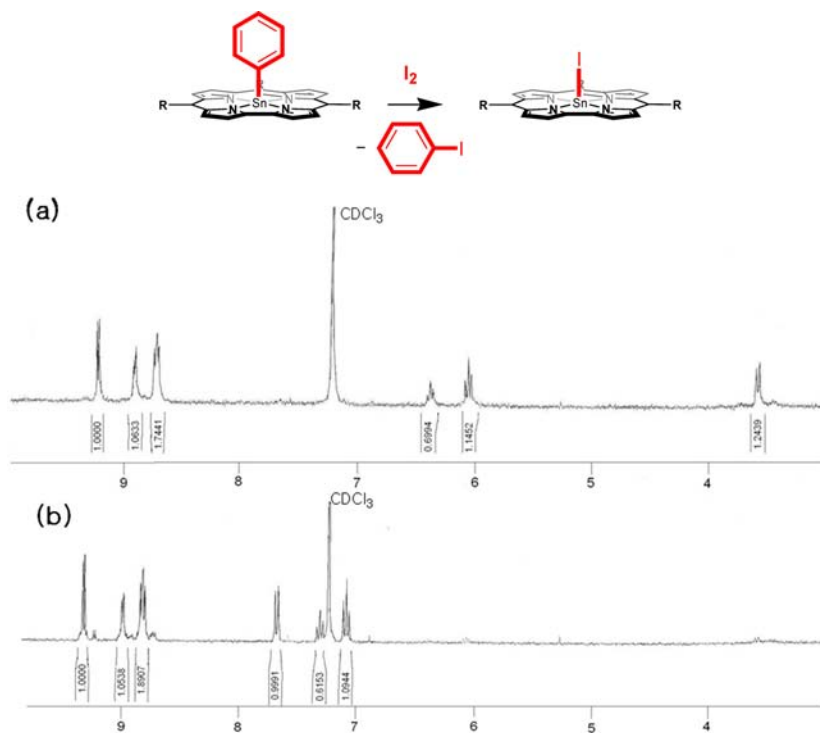


Figure 7. Scheme of, and spectroscopic data supporting, the cleavage of the Sn–C bond in compound 5 upon treatment with  $\text{I}_2$ .  $^1\text{H}$  NMR spectra are of compound 5 before (a) and after (b) the addition of  $\text{I}_2$ .

protons of phenyl iodide.<sup>36</sup> Also, signals of  $\beta$ -pyrrolic protons are shifted downfield by 0.1 ppm; chemical shift values are close to those of the chloride derivative **1** but not to the metal-free corrole.<sup>12b</sup> This NMR spectroscopic observation helps for the easy assignment of tin–iodide derivative formation. Further, it was noticed that, under the same conditions, the aryl–Sn bond is more reactive to halogens than the alkyl–Sn bond.<sup>30,37</sup> When the same reaction was carried out for compound **2**, no product formation was detected by <sup>1</sup>H NMR spectroscopy, even after 1 week (25 °C). Anions such as iodide were also tested for completeness to determine whether oxidation is possible with closely related species. Unlike I<sub>2</sub>, I<sup>−</sup> gave no optical/photoluminescent change; Br<sup>−</sup> and Cl<sup>−</sup> (as K<sup>+</sup> salts) also gave no responses (see the Supporting Information).

#### IV. CONCLUSIONS

In conclusion, alkyl and aryl derivatives of tin 5,10,15-tris(pentafluorophenyl)corrolate have been prepared and studied by different characterization techniques. The derivatives include the isopropyl-, *sec*-butyl-, 2-methyl-*n*-butyl-, phenyl-, 2-thienyl-, and ferrocenyltin species characterized through <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and HMQC NMR spectroscopy, mass spectrometry, UV–vis and photoluminescent spectroscopy, and CV studies. Among other data, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic signals of the axial group were assigned and closely inspected to help quantify various positional effects imposed on one these atoms by the ring-current and tin-proton (<sup>119</sup>Sn–<sup>1</sup>H and <sup>119</sup>Sn–<sup>13</sup>C) through-bond coupling. The influence of the ring current and the presence of *J*(H/C,Sn) coupling constants in fully characterized Sn(tpfc)R/Ar derivatives help round out a fuller understanding of the organometallic chemistry of tin corrolates. This so-called “double stamping” has now been expanded here with these systems and is a detailed recapitulation of a concept borne out of data from earlier systems.<sup>1,17</sup> Furthermore, compound **7** is the first ferrocenyl–metal corrolate species. The reactivity was observed for I<sub>2</sub>. Aryl–tin derivatives are more reactive than alkyl–tin corrole derivatives. Combined ring-current and NMR-coupling effects, CV, optical studies, and Fc–Sn conjugation were determined and discussed. Future studies may address particular issues in the realm of chemosensing in which the analyte directionality in the metalloporphyrin pocket and its proximity to the central metal (or element) may be pursued in the context of data from various older porphyrinoid reports from the literature.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Multinuclear NMR, full reproductions of NMR spectra, compiled UV–vis spectra, mass spectra, tables, textual passages of discussion and experimental protocol, X-ray diffraction structures, and packing diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

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##### Notes

The authors declare no competing financial interest.

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