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Synthesis, Structure, and Optical Properties of the Platinum(II)
Complexes of Indaphyrin and Thiaindaphyrin

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The novel free base meso-di(5′-methylthien-2′-yl)thiaindaphyrin, 10, was prepared from the corresponding meso-tetra(thien-2-yl)porphyrin using a methodology analogous to that for the preparation of known meso-diphenylindaphyrin, 5: β,β′-Dihydroxylation of the porphyrin is followed by oxidative diol cleavage. The resulting aldehyde moieties undergo an acid-catalyzed intramolecular Friedel–Crafts alkylation of the adjacent meso-thienyl groups with concomitant oxidation. Insertion of Pt(II) into either of the chromophores is facile, producing 5Pt and 10Pt. The crystal structure of 5Pt, the first for any indaphyrin, shows that the conformation of the indaphyrinato ligand is strongly ruffled, while the N4 donor set that coordinates the central Pt(II) maintains a near-perfect square-planar coordination geometry around the central metal ion (crystal data for C22H26N2O2Pt: triclinic space group P1 with a = 8.8735(4) Å, b = 12.9285(6) Å, c = 14.3297(6) Å, α = 88.785(1)°, β = 82.248(1)°, γ = 72.422(1)°; Z = 2). The UV–vis and emission spectra, triplet yields, and lifetimes of the Pt(II) complexes 5Pt and 10Pt were determined. Both complexes luminesce (in EtOH at 77 K) in the NIR (5Pt: λmax-emission = 864, 974 nm, lifetime 2 µs; 10Pt: λmax-emission = 990, 1112, 1276 nm) with modest to low quantum yields (Φp ∼ 1% and ∼ 6 × 10−3 %, respectively).

Introduction

The triplet oxygen-mediated quenching of the triplet excited-state of many chromophores (Stern–Volmer quenching) allows a correlation between the degree of quenching and a particular oxygen partial pressure.1 This gives rise to the development of optical oxygen sensors that find applications in medicine, engineering, and chemical and environmental analyses.1–3

One particularly well-studied class of compounds for oxygen sensing applications is that of the Pt(II) porphyrins, such as [meso-tetraphenylporphyrinato]Pt(II) (1Pt) and related compounds.1,4–7 In Pt(II) and Pd(II) porphyrins, ligand-based emissions are observed (λmax-emission for 1Pt = 650, 712 nm, 990, 1112, 1276 nm).

nm). This allows a modulation of the excitation and emission wavelengths through alterations of the porphyrinic chromophore. Examples include the use of the Pd(II) and Pt(II) complexes of porpholactones, 2Pt,β-oxo-porphyrins,\textsuperscript{12} or benzoporphyrs, such as complex 3Pt.\textsuperscript{13}

A red shift of the excitation or luminescence spectra into the red or NIR range ($\lambda_{\text{max-emission}} > 750$ nm) is desirable for a number of applications, particularly in the life sciences.\textsuperscript{14} By utilizing red to near-infrared (NIR) wavelengths, an increase in the sensitivity of luminescence-based assays in biological systems measurements can be achieved because no natural chromophore emits in this region. The NIR is also the region of the “spectroscopic window” in tissue, and chromophores emitting in this range may allow the detection of events deep in the tissue. Last, longer wavelengths are scattered less in opaque media than shorter ones, increasing the resolution of the emission images obtained.

This emission red shift was the driving force behind the development of π-extended porphyrins such as 3Pt ($\lambda_{\text{max-emission}} = 745$ nm)\textsuperscript{15} or the bimetallic complex of an N-confused calyx[6]phyrin 4Pt$_2$ ($\lambda_{\text{max-emission}} = 1010$ nm).\textsuperscript{16} An ideal sensor molecule should fulfill other key requirements such as high extinction coefficients and high emission quantum yields (i.e., possessing high brightness), and excellent photostability. Ancillary properties such as nonaggregation in a polymer matrix, good processability, and excellent photostability. Ancillary properties such as nonaggregation in a polymer matrix, good processability, and excellent photostability.

We reported recently the synthesis of a novel class of porphyrin derivatives, the indaphyrins, 5. This class of compounds, synthesized from meso-tetraphenylporphyrin, contains a ββ'-ring-cleaved pyrrole moiety. The former β-carbons have become ketone moieties that are fused to the β-position of the neighboring meso-phenyl rings, thus giving rise to the formation of indane moieties.\textsuperscript{17,18} It was computed that the short linkage forces the indane groups into near coplanarity with the mean plane of the greatly ruffled porphyrinoid chromophore, thus allowing for extensive conjugation between the two π systems.\textsuperscript{18} This, and the two conjugated ketone functionalities, rationalize the unusual UV-vis spectra of indaphyrins ($\lambda_{\text{max-absorption}} = 810$ nm) when compared to those of porphyrins ($\lambda_{\text{max-absorption}} \sim 650$ nm).\textsuperscript{18}

Now, the question arises whether the Pt(II) complexes of indaphyrin, 5, can be prepared, whether they are emissive in the NIR, and whether they can be used as oxygen sensors.

In unrelated studies, we, and others, reported that meso-thienyl-porphyrins and corroles possess red-shifted electronic spectra.\textsuperscript{19,20} This observation was attributed to the smaller ring size of thiophenes compared to that of phenyl groups, which allows for their greater degree of coplanarity with the porphyrin chromophore. This prompts the question of whether meso-thienyl substitution and an indaphyrin-type linkage can be combined to achieve a bathochromic shift in the as-yet unknown \textit{meso}-thienylporphyrin-derived thiaindaphyrins, and their Pt(II) complexes, as compared to their phenyl analogues.

This contribution will demonstrate that these questions can largely be answered in the affirmative. We report here on the preparation, photophysical characteristics, and oxygen-sensing abilities of the Pt(II) complexes of indaphyrin and thiaindaphyrin, 5Pt and 10Pt, respectively. We will also report the X-ray single-crystal structure of [\textit{meso}-phenylindaphyrinato]Pt(II) (5Pt), the first structural characterization of any indaphyrin, proving their predicted highly ruffled chromophore structure.

\begin{thebibliography}{99}
\item (14) König, K. \textit{J. Microscopy} 2000, 200, 83–104.
\end{thebibliography}
Pt(II) Complexes of Indaphyrin and Thiaindaphyrin

Experimental Section

**Instruments and Materials—Synthesis.** All solvents and reagents were used as received. *meso*-Tetraphenylporphyrin (I),21 diiodochlorin (7),22 free-base indaphyrin (5),18 and *meso*-tetra(5'-methylthien-2'-yl)porphyrin (6)19 were prepared as described before. The analytical thin-layer chromatography (TLC) plates (aluminium-backed, silica gel 60, 250 μm thickness), preparative TLC plates (20 × 20 cm, glass-backed, silica gel 60, 500 or 1000 μm thickness), and flash column silica gel (standard grade, 60 Å, 32–63 μm) used were provided by Sorbent Technologies, Atlanta, Georgia.1 H and 13C NMR spectra were recorded on a Bruker DRX400 spectrometer. The NMR spectra are expressed on the δ scale and were referenced to residual solvent peaks or internal MeSi (for copies of the NMR spectra, see the Supporting Information). IR spectra were recorded on a Perkin-Elmer Spectra-Tech 460 spectrophotometer. Mass spectra were provided by the Mass Spectrometry Facilities of the Chemistry, University of Connecticut or the Department of Chemistry and Biochemistry, University of Notre Dame.

**Instruments and Materials—Photophysical Characterizations.** UV–vis spectra were recorded on a Cary 50 spectrophotometer and the fluorescence spectra on a Cary Eclipse spectrophotofluorometer (both Varian Inc.). NIR emission spectra were recorded, at 77 K, of samples dissolved in the solvents specified and contained in a quartz of the approximate dimensions 0.43 × 0.12 × 0.09 cm. A Cary 50 spectrophotofluorometer (both Varian Inc.) was used to determine the fluorescence spectra on a Cary Eclipse spectrofluorometer (Varian Inc.). NIR emission spectra were recorded, at 77 K, of samples dissolved in the solvents specified and contained in a quartz of the approximate dimensions 0.43 × 0.12 × 0.09 cm. A Cary 50 spectrophotofluorometer (both Varian Inc.) was used to determine the fluorescence spectra on a Cary Eclipse spectrofluorometer (Varian Inc.).

**Oxygen-Sensing Experiments.** Complex 5Pt (5 mg) was dissolved in a solution of silirancarboxylic acid LR 3320 (500 mg, General Electric, Fairfield, CT) in CH2Cl2 (20 mL). The sensor film was cast and tested following a standard procedure.23,24 In an alternative approach, the PtDPI was dispersed directly onto 1 × 2 cm TLC plates (500 μm silica on glass).

**X-Ray Diffractometry of 5Pt.** A dark green needle-shaped crystal of 5Pt of the approximate dimensions 0.43 × 0.12 × 0.09 mm was obtained by the slow evaporation of a CH2Cl2/CH3CN solution. Diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using monochromatic Mo Ka radiation with the Ω scan technique in the range from θ = 1.43 to 28.28°; the limiting indices were −11 ≤ h ≤ 11, −17 ≤ k ≤ 16, and −19 ≤ l ≤ 19. A total of 16 206 reflections were collected, with 7670 independent reflections (Rint = 0.0188), completeness to θ = 28.28°, 99.6%. The SADABs multiscan absorption correction was applied.25a The data were collected using SMART,25b and the data integration and unit cell determination were made using SAINT+.25a The structure was solved by direct methods and refined by full-matrix least-squares against F2 using SHELXTL.25c The goodness-of-fit on F2 was 1.074; the largest differential peak and hole were 1.879 and −0.940 e·Å−3. Full-matrix refinement method on the least-squares on F2 was applied. Data, restraints, and parameters were 7670, 0, and 460. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and were isotropically refined with a displacement parameter of 1.2 times that of the adjacent carbon atom. The refinement converged satisfactorily. The crystal structure and refinement data for 5Pt are summarized in Table 1. Selected bond lengths and angles are tabulated in Table 2.

| Table 1. Selected Crystallographic Data and Structure Refinement Details for 5Pt† |
|---------------------------------|-----------------|---------------|-----------------|-----------------|
| empirical formula              | Cu2H3N4O2Pt     |
| fw, g/mol                      | 835.76          |
| space group                    | P1 (No. 2)      |
| λ, Å                           | 0.71073         |
| a, Å                           | 8.8735(4)       |
| b, Å                           | 12.9285(6)      |
| c, Å                           | 14.3297(6)      |
| α, deg                         | 88.7850(10)     |
| β, deg                         | 82.2480(10)     |
| γ, deg                         | 72.4220(10)     |
| volume, Å³                     | 1552.50(12)     |
| dmax, g/cm³                    | 1.78            |
| Z                              | 2               |
| μ, mm−1                        | 4.569           |
| transmission coeff             | 0.663, 0.377    |
| final R indices [I > 2σ(I)]    | R1 = 0.0247, wR2 = 0.0628 |
| R indices (all data)           | R1 = 0.0260, wR2 = 0.0635 |

† The weighted R factor wR and goodness of fit are based on F2; conventional R factor R is based on F2. The threshold expression of F2 > 2σ(F2) is used only for calculating R factors.

Ka radiation with the Ω scan technique in the range from θ = 1.43 to 28.28°; the limiting indices were −11 ≤ h ≤ 11, −17 ≤ k ≤ 16, and −19 ≤ l ≤ 19. A total of 16 206 reflections were collected, with 7670 independent reflections (Rint = 0.0188), completeness to θ = 28.28°, 99.6%. The SADABs multiscan absorption correction was applied. The data were collected using SMART, and the data integration and unit cell determination were made using SAINT+. The structure was solved by direct methods and refined by full-matrix least-squares against F2 using SHELXTL. The goodness-of-fit on F2 was 1.074; the largest differential peak and hole were 1.879 and −0.940 e·Å−3. Full-matrix refinement method on the least-squares on F2 was applied. Data, restraints, and parameters were 7670, 0, and 460. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and were isotropically refined with a displacement parameter of 1.2 times that of the adjacent carbon atom. The refinement converged satisfactorily. The crystal structure and refinement data for 5Pt are summarized in Table 1. Selected bond lengths and angles are tabulated in Table 2.

[meso-Diphenylindaphyrinato]Pt(II) (5Pt). To a solution of free-base indaphyrin, 5 (59 mg, 0.09 mmol), in PhCN (15 mL) was added bis-2,4-pentanedionate [Pt(acac)2] (108 mg, 0.28 mmol, 3 equiv). The reaction mixture was refluxed and monitored by TLC and UV–vis until the starting material was exhausted (5 h). The solvent was removed in vacuo. The mixture was passed through a plug of silica with CH2Cl2. The residue was further purified by preparative TLC (silica-CH2Cl2/hexane 4:1) and recrystallized from CHCl3/EtOH to give 5Pt as a purple solid (50 mg, 0.06 mmol, 65%). Rf (silica-CH2Cl2): 0.42. UV–vis (CH2Cl2) λmax (log ε): 391 (3.86), 462 (sh), 495 (sh), 525 (4.16), 632 (3.54), 677 (3.48) nm, IR (neat) νmax: 1706 (C=O) cm−1. 1H NMR (400 MHz, CDCl3): 7.37 (t, J = 7.6 Hz, 1H), 7.50–7.60 (br s, 1H), 7.67 (t, J = 7.6 Hz, 2H), 7.75 (br t, 3H), 7.90 (d, J = 7.6 Hz, 1H), 8.26 (d, J = 7.6 Hz, 1H), 8.43 (s, 1H), 8.66 (d, J = 5.2 Hz, 1H), 9.25 (d, J = 5.2 Hz, 2H) ppm. 13C NMR (100 MHz, CDCl3): 117.2, 125.0, 126.2, 126.7, 127.0, 128.3, 129.0, 129.1, 131.4, 132.3, 136.3, 136.4, 137.1, 137.9, 138.6, 140.1, 146.2, 187.2 ppm. MS (EI⁺, 100% CH2CN): m/z: 835 (M⁺). HRMS (EI, 30 eV): m/z2 calculated for Cu2H3N4O2Pt: (M⁺) 835.1547. Found: 835.1546. Anal. calc. for Cu2H3N4O2Pt: C, 63.23; H, 2.89; N, 6.70. Found: C, 63.19; H, 2.88; N, 6.68.

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13C NMR (100 MHz, CDCl3) δ 40.7 (1H), 41.9, 141.9, 142.1, 142.6, 154.2, 163.2 ppm. HRMS (ESI+) m/z calc'd for C40H33N4O2S4·H2O: 725.1169. Found: 725.1163.

meso-Tetra(5′-methylthien-2′-yl)-2,3-cis-dihydroxy-2,3-chlorin (8). Caution! The synthesis requires a rotary evaporator in a well-ventilated fume hood as the particularly volatile and toxic reagents O3SO and H2S are used! A solution of meso-tetra(5′-methylthien-2′-yl)porphin, 6 (500 mg, 0.72 mmol), and O3SO (250 mg, 0.98 mmol) in EtOH-stabilized chloroform/50% pyridine (120 mL) was stirred at room temperature for 4 days. The reaction was quenched at ambient conditions, by purging with gaseous H2S for 5 min, followed by stirring for an additional 30 min. The solution was filtered through a plug of Celite. The filtrate was evaporated to dryness by rotary evaporation, and the residue was separated by column chromatography (silica gel gradient of CHCl3/MeOH). Two fractions were isolated: the first was recovered purple porphin 6 (224 mg, 45%; Rf = 0.90 (silica-CHCl3)), and the second fraction was the purple-brown chlorin 8 (193 mg, 26% yield). Rf = 0.22 (silica-CHCl3). UV–vis (CHCl3) λmax (log ε): 428 (5.21), 547 (4.31), 660 (4.39) nm. 1H NMR (400 MHz, CDCl3) δ 2.58 (s, 3H), 7.19 (d, J = 1.9 Hz, 1H), 1.99 (d, J = 3 Hz, 1H), 1.96 (d, J = 3 Hz, 1H), 1.87 (s, 1H), 1.77 (s, 1H), 1.70 (d, J = 3 Hz, 1H), 1.67 (d, J = 4 Hz, 1H). 13C NMR (100 MHz, CDCl3): δ 15.5, 15.6, 15.9, 16.0, 110.7, 119.6, 120.5, 125.1, 125.2, 126.3, 131.4, 131.6, 132.2, 133.4, 134.1, 134.8, 135.4, 137.5, 137.8, 138.2, 139.0, 140.4, 142.4, 143.7, 144.9, 154.0, 154.4, 161.3, 165.3, 181.5, 183.5 ppm. HRMS (ESI+) m/z calc'd for C40H33N4O2S4·H2O: 725.1169. Found: 725.1163.

meso-Di(5′-methylthien-2′-yl)thiaindophyrin (10). Monoaldehyd e 9 (100 mg, 0.14 mmol) was dissolved in 2% TFA/CH2Cl2 (25 mL). The solution was stirred at ambient temperature overnight and then was washed twice with aqueous NaHCO3 and once with H2O. The solution was dried over anhydrous Na2SO4 and evaporated to dryness. The residue was separated by column chromatography (silica gel-CHCl3). The purple compound 10 (33 mg, 33% yield) was isolated. Rf = 0.65 (silica-CHCl3). UV–vis (CHCl3) λmax (log ε): 432 (4.54), 570 (4.31) nm. IR (neat) νmax: 1678, 1694 (C=O) cm−1. 1H NMR (400 MHz, CDCl3) δ 1.16 (s, 1H), 2.55 (s, 3H), 2.72 (s, 3H), 6.88 (s, 1H), 7.01 (d, J = 3.0 Hz, 1H), 7.39 (d, J = 3.0 Hz, 1H), 8.35 (s, 1H), 8.61 (d, J = 4.7 Hz, 1H), 8.64 (d, J = 4.7 Hz, 1H). 13C NMR (100 MHz, CDCl3): δ 15.5, 15.9, 114.6, 116.3, 119.7, 122.6, 124.8, 129.2, 131.4, 132.9, 133.9, 134.8, 138.7, 138.8, 141.2, 144.9, 148.2, 157.2, 161.8, 183.3 ppm. HRMS (ESI+) m/z calc'd for C40H33N4O2S4·H2O: 725.1169. Found: 725.1163.

meso-Di(5′-methylthien-2′-yl)thiaindophyrinatoPt(II) (10Pt). A solution of 10 (40 mg, 6 mmol) and [Pt(acac)]2 (65 mg, 3 equiv) in PhCN (10 mL) was heated until, using TLC and UV–vis reaction control, the starting material was exhausted (either for 8 h at ~160 °C or 5 h at reflux temperature). The solvent was evaporated under high vacuum conditions, and the residue was separated by column chromatography (silica gel–CHCl3). The red compound 10Pt (31 mg, 61% yield) was isolated. Rf = 0.42 (silica-CHCl3). UV–vis (CHCl3) λmax (log ε): 414 (4.02), 529 (4.23), 648 (3.62) nm. IR (neat) νmax: 1680, 1696 (C=O) cm−1. 1H NMR (400 MHz, CDCl3) δ 2.59 (s, 3H), 2.75 (s, 3H), 6.90 (br s, 1H), 7.04 (d, J = 3.6 Hz, 1H), 7.41 (d, J = 4.0 Hz, 1H), 8.39 (s, 1H), 8.64 (d, J = 4.0 Hz, 1H), 8.67 (d, J = 4.0 Hz, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ 15.5, 16.0, 114.5, 116.6, 119.8, 122.6, 124.9, 129.2, 131.6, 133.0, 133.7, 134.8, 138.8, 139.5, 142.9, 144.9, 148.3, 161.8, 183.2 ppm. MS (ESI+), 100% (CH3CN): m/z calcd for C40H33N4O2P2S4·H2O·CH3CN: 915 (M+H)+. HRMS (EI, 30 eV) m/z calcd for C40H33N4O2P2S4·H2O·CH3CN: 915 (M+H)+. Found: 915.0418.

Results and Discussion

Synthesis of 5Pt, the Pt(II) complex of indaphyrin 5. The synthesis of diphenylindaphyrin 5 proceeded along the pathway described previously (Scheme 1).18 Thus, dihydroxylation of meso-tetraphenylporphin 12 was followed by the oxidative diol cleavage of diol 7. The resulting bisaldehyde underwent, in situ, an acid-catalyzed intramolecular Friedel–Crafts alkylation with concomitant air oxidation. Insertion of Pt(II) into porphins generally requires the heating of a Pt(II) salt, such as the acetate, chloride, or acetyl acetone, in benzonitrile at reflux temperatures (191
Appreciable Pt(II) insertion into indaphyrin already takes place in benzonitrile at 140–160 °C. At reflux temperatures, the reaction is completed within 3–5 h. We attribute this to the much greater conformational flexibility of the indaphyrin chromophore as compared to that of a porphyrin. Chromatography, followed by recrystallization, produced Pt(II) indaphyrin in good yields. The spectroscopic and analytical data were all consistent with the structure of 5Pt. In particular, its 1H and 13C NMR spectra were very similar to those of free-base 5, an indication that the insertion of Pt(II) did not lead to dramatic structural changes. As detailed below, a single-crystal structure analysis of 5Pt confirms its connectivity and highlights its conformation. The optical properties of all chromophores synthesized are discussed below.

Metal complexes of indaphyrins were described before. However, the Ni(II) complexes of indaphyrins are unstable and form ring-opened products within days in solution, though the larger ions Cu(II) and Zn(II) form stable indaphyrinato complexes. Complex 5Pt is stable in solution for days and as a solid for at least 2 years.

X-Ray Structure of 5Pt. Figures 1 and 2 and Table 2 show the results of a single-crystal diffractometry analysis of crystals of 5Pt. The structure, the first X-ray structure of any indaphyrin, confirms the spectroscopically derived connectivity of 5Pt. It shows the significant degree of ruffling of the chromophore, with a root-mean-square (rms) deviation from the average plane of the C20N4Pt core of 0.448 Å.28 In comparison, an example of a severely nonplanar [morpholinonoclorinato]Ni(II) complex shows an rms deviation from planarity of its C20N4Ni core of 0.468 Å.22,29 As a result of the ruffling, a 46° dihedral angle between the mean planes of the two indanone moieties is observed.

The ruffling observed in Ni(II) porphyrins is caused by the presence of the small metal ion.29–31 The ruffling distortion mode allows for a shortening of the N–Ni bonds without any deviation of the nitrogens from a square-planar coordination sphere around the central metal. Indeed, in 5Pt, the N4Pt bond lengths and angles are also nearly perfectly square-planar (deviations from the C20N4Pt mean plane lie between 0.006(2) Å for N1 and 0.148(2) Å for N2). In
contrast to the Ni(II) porphyrins, however, the distortion is intrinsic to the indapyrin ligand. This is because the conformation of the ligand in 5Pt is, albeit slightly more pronounced, very similar to that computed for free-base 5 (rms deviation of the C20N4 core from planarity was 0.39 Å). Interestingly, the observed N—Pt bond lengths (average of 2.003(2) Å) are identical to those observed in the slightly ruffled [porphyrinato]Pt(II) complexes (2.005 Å in 1Pt at 295 K).25

The cleavage of the pyrrole and fusion of two indanone units into the macrocycle results in a significant dissymmetry of the bond lengths and angles within the porphyrinoid macrocycle (Table 2). For instance, the N(1) imine bond lengths (average of 1.376 Å and an average Rδ+ in 1Pt lie, respectively) compared to the corresponding and unusually long N(2 or 3)pyrrole bond lengths (1.402(4) Å), respectively.

The crystal is composed of offset columns of π-stacked pairs of 5Pt that are held together by π–π interactions between meso-phenyl groups. No major channels or cavities are discernible. Complex 5Pt is chiral and crystallizes as a racemate in the nonchiral space group P1.

Synthesis of the Dithienylthiaindaphyrin 10 and Its Pt(II) Complex 10Pt. The synthetic methodology toward indaphyrin 5 is perceiveably transferable to any meso-arylporphyrin with an ortho position on the meso-aryl group that is susceptible to electrophilic aromatic substitution, including also meso-thien-2-ylporphyrin, 6 (Scheme 1). Thus, osmylation/reduction of the meso-tetra(4-methyl-thien-2-yl)porphyrin,34 6, resulted in the formation of the corresponding diol chlorin 8. Its HRMS (ESI+, m/z = 729.1488 for [M + H]+) spectrum confirms its composition (C30H29N4O2S4), and diagnostic peaks in the 1H and 13C NMR spectrum confirm its structure. Moreover, the UV–vis spectrum of 8 is a typical chlorin spectrum, with λmax at 658 nm the most intense of all side bands. It is, as expected, based on the comparison of thienylporphyrins with phenylporphyrins,19 ~12 nm bathochromically shifted compared to that of meso-phenyl-based chlorin 7 (Figure 3).22,34

Oxidative diol cleavage of diol 8 using NaIO4 heterogenized on silica gel results in the formation of a putative bisaldehyde intermediate that, analogous to the reactivity of its meso-phenyl analogue,17,18 spontaneously undergoes a Friedel–Crafts alkylation with concomitant oxidation to form monothiaindanone monoaldehyde 9. It is identified by the characteristic loss of symmetry in the 1H and 13C NMR spectra; an ESI+ HRMS indicative of the expected composition for MH+ (C40H29N4O2S4); and the appearance of one aldehyde signal in the 1H NMR (9.28 ppm, s, 1H) and two carbonyl signals in the 13C NMR (181.1, 185.0 ppm) and IR (ν = 1691, 1648 cm⁻¹) spectra. Product 9 possesses, however, only limited stability in solution. Using 2% TFA in CH2Cl2, this orange product is converted to a brown-purple and slightly less polar product that could be identified as the meso-di(S’-methylthien-2-yl)-substituted thiaindaphyrin 10. Its HR-MS spectrum indicates the loss of two hydrogens compared to the composition of its precursor 9. Its 1H and 13C NMR spectra suggest a molecule of 2-fold symmetry with diagnostic signals for the presence of an ortho-linked π-stacking π–π interactions between meso-phenyl groups. No major channels or cavities are discernible. Complex 5Pt is chiral and crystallizes as a racemate in the nonchiral space group P1.

(33) This particular thiophen-2-yl porphyrin derivative was chosen, as it was characterized by a significantly red-shifted UV–vis spectrum compared to the corresponding non-methylated compound, see ref 19.
(34) Interestingly, the unique acid–base dependency of the optical properties of chlorin 8 vs chlorin 7 is similar to the shifts observed for the porphyrins, see ref 19. The spectra are shown in the Supporting Information.
aryl group, only three types of thienyl β-protons, and one type of ketone functionality (183.3 ppm in the 13C NMR). Further, a comparatively high-field-shifted signal assigned to the NH protons can be discerned (1.16 ppm, br s, 1H), another characteristic of indaphyrins that is likely a reflection of the great distortion from planarity in these porphyrinoids. Taken together, the spectroscopic data confirm the structure of 10. It is interesting to note that the formation of a thiaindanone moiety in the target compound 10 appears to be similarly facile as in the phenyl derivative 5, despite the fact that the steric requirements of forming the indanone moiety (one five- and six-membered fused ring) are different from those for the formation of a thiaindanone unit (two fused five-membered rings).

The insertion of Pt(II) into 10 also proceeded smoothly, and 10Pt could be isolated as a microcrystalline powder in 65% yield. It possesses all of the expected spectroscopic and analytical properties. Aside from the disappearance of the signals for the NH protons, only minor shifts in the 1H NMR spectrum are observed upon the insertion of Pt(II) into free-base 10. This is likely a testimony to the preservation of the conformation of the free ligand in its complex. A Pt(II) insertion into thiaindaphyrin monoaldehyde 9 failed due to the instability of the ligand.

**Photophysical Properties of 5 and 10, and Their Pt(II) Complexes.** The UV–vis spectra of free-base meso-tri(thien-2-yl)formylthiaindaphyrin, 9, and meso-di(thien-2-yl)thiaindaphyrin, 10, in comparison to that of known meso-diphenylindaphyrin, 5, are shown in Figure 4. The spectrum of thienyl derivative 10 is, as hoped for, red-shifted compared to that of the phenyl analogue 5, though the number and relative intensities of the bands also vary slightly. This is a reflection of the differing π systems of the two chromophores and the differing conformation and conformational flexibility. The relatively broad and far-into-the-red-reaching bands of 5 and 10 allow a prediction for ligand-based emissions in the NIR for their Pt(II) complexes. The spectrum of the formylated “half-thiaindaphyrin” 9 possesses larger extinction coefficients and appears to be more “porphyrin-like”, an observation also made for its phenyl analogue. 

The UV–vis absorption spectra (CH2Cl2, r.t.) of 1Pt (solid black trace), 5Pt (solid green trace), and 10Pt (solid red trace) in CH2Cl2; phosphorescence emission spectra (EtOH glass, 77 K) of 5Pt (dotted green trace; λ<sub>excitation</sub> = 524 nm) and 10Pt (dotted red trace; λ<sub>excitation</sub> = 529 nm). The emission spectra were confirmed using excitation emission scans.

Figure 5 shows the absorption spectra of the Pt(II) complexes 5Pt and 10Pt in comparison to that of 1Pt. The main absorption bands of 5Pt and 10Pt are a Soret-like band (for 5Pt at ~525 nm; ε = 14 500 M<sup>−1</sup> cm<sup>−1</sup>) and two side bands (at 632 and 677 nm, ε = 3500 and 3000 M<sup>−1</sup> cm<sup>−1</sup>, respectively) with a vibrational spacing of 1070 cm<sup>−1</sup>, assuming that the origin of the bands is similar to that of 1Pt. The absorption spectrum of 5Pt has little resemblance to that of a platinum porphyrin complex (1Pt). It is much broader, spanning almost the entire visible spectral region up to ~680 nm, albeit the extinction coefficients of the bands are only ~10% of those of 1Pt. A broad absorption spectrum has the advantage that it allows for the use of many readily available excitation light sources. As predicted, the absorption spectrum of 10Pt is slightly bathochromically shifted compared to that of 5Pt. Also reflecting the trend seen in the free base thiaindaphyrin, the spectrum of 10Pt is relatively broad.

Spin–orbit interactions with the coordinated 5d<sup>8</sup> ion Pt(II) increase the intersystem crossing rate of photoexcited Pt(II) porphyrin, resulting in very high triplet yields. Subsequent phosphorescence emissions are on the nanosecond to microsecond scale. Ideally, the observed lifetimes of the 3T<sub>1</sub> state are above ~10 μs, allowing ample opportunity for the quenching of the triplet state by O<sub>2</sub>. In this triplet lifetime regime, high sensitivity with respect to the oxygen-pressure measurement can also be achieved through a time-resolved recording of the luminescence.

The phosphorescence emission spectra of 5Pt and 10Pt in EtOH at 77 K are shown in Figure 5. The emission spectra are two-band spectra that are strongly solvatochromic (5Pt: λ<sub>max-emission</sub> = 850 and 965 nm in EtOH and λ<sub>max-emission</sub> = 880 and 995 nm in methylcyclohexane, see Supporting Information) with a minimum Stokes shift of 2880 cm<sup>−1</sup>. No detectable spectral sharpening was detected for the 10<sup>−6</sup> M solution of 5Pt in n-octane, a Shopl’skii-type matrix. The emissions around 1000 nm are several hundreds of nanometers red-shifted compared to those observed in Pt porphyrins and related derivatives and are comparable to that of the

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(35) The formal name for the resulting moiety is cyclopenta[b]thiophen-4-one, also referred to as thiaindanone: Aparajithan, K.; Thompson, A. C.; Sam, J. J. Heterocycl. Chem. 1966, 3, 466–469.

structurally more complex calyx[6]phyrin Pt₂ complex 4Pt₂.¹⁶

While the phosphorescence quantum yield for the phenyl
derivative 5Pt, at 77 K in an deoxygenated EtOH glass, is
≈1%, it is about 3 orders of magnitude less in the thio
analogue 10Pt (~6 × 10⁻³ %). In comparison, the quantum
yield for 1Pt is near unity, and that of the 2Pt is 70%.²³

This low quantum yield (and short triplet lifetime, see below)
are likely caused by a larger conformational flexibility of
the indaphyrin and the conjugated ketone oxygens.

The triplet lifetime of 5Pt was determined to be a relatively
short 2 µs. In comparison, the triplet lifetime for 1Pt is 120
µs, and that for 2Pt is 70 µs,⁹ while the Pt₂ complexes of
calix[6]phyrin are characterized by two-digit nanosecond
lifetimes (at r.t.).¹⁶

Testing of 5Pt as Oxygen Sensor. One notable application
of oxygen sensors is in air flow visualization. In this
application, also referred to as phosphorescence barometry,
a sensor is incorporated into an oxygen-permeable polymer
matrix that is applied to a surface. The resulting thin layer
serves as a two-dimensional air pressure profile sensor for
objects exposed to wind flow.²,¹⁰,¹¹

The oxygen sensitivity of 5Pt was first tested by incor-
porating it into a gas-permeable silicon–polycarbonate
copolymer matrix. Disappointingly, no oxygen sensitivity
was detected. Subsequently, 5Pt was dispensed directly onto
a silica TLC plate. TLC plates provide a chemically neutral
flat surface that is highly reflective, and serves as an open
configuration with a highly oxygen-permeable surface.

Upon irradiation with light of 520 nm, the oxygen partial pressure
dependency of the phosphorescence emission of 5Pt in the
range from 700 to 1400 nm was recorded. In the range from
0 to 100% O₂, the intensity of the emission was quenched
by only 15% (see Supporting Information), indicating that
this dye is not a practical dye for O₂ sensing. The low
sensitivity of 5Pt towards a variation of [O₂] can likely be
attributed to the short phosphorescence lifetime of the Pt(II)
indaphyrin.

Summary and Conclusions

The Pt(II) complex of indaphyrin 5, 5Pt, forms readily
and is stable. Its nonplanar conformation was proven to be
most similar to the computed conformation of the free-base
ligand 5. Their meso-thienyl analogues, free-base thiainda-
phyrin 10 and its Pt(II) complex 10Pt, can also be formed
in acceptable yields. They are the first examples of non-
meso-phenylporphyrin-derived indaphyrins. Significantly, 5Pt
and 10Pt possess the expected NIR emission spectra, but
their short triplet lifetimes, relatively low emission yields,
and impractically low sensitivity of the emission intensity
variation with respect to changing oxygen partial pressure
render these complexes unsuitable as practical oxygen
sensors.

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Supporting Information Available: The X-ray crystallographic
file in CIF format for the reported structure 5Pt. ¹H, ¹³C NMR,
and IR spectra of 5Pt, 8, 9, 10, and 10Pt and more details on the
photophysical investigations. This material is available free of
charge via the Internet at http://pubs.acs.org.

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