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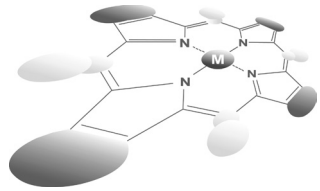

Quinoline-annulated porphyrin platinum complexes as NIR emitters

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Dedicated to Professor Atsuhiro Osuka on the occasion of his 65th birthday.

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ABSTRACT: The platinum(II) complexes of known quinoline-annulated porphyrins were prepared and spectroscopically characterized. Their optical properties (UV-vis absorption and phosphorescence spectra and phosphorescence lifetimes) were recorded and contrasted against their 2,3-dioxoporphyrin precursor platinum(II) complex. The absorbance and emission spectra (in EtOH glass at 77 K) of the quinoline-annulated porphyrins fall within the NIR optical window of tissue, ranging, depending on the derivative, between ~950 and 1200 nm. The much red-shifted optical spectra, when compared to their non-quinoline-annulated precursors, are attributed to the π-extension and conformational non-planarity that the annulation causes. The emission yields of the mono-quinoline-annulated derivatives are too low and their lifetimes too short to be practical emitters, but the bis-annulated derivative possesses a practical lifetime and emission yield, suggesting its further exploration, particularly since the methodology toward the solubilization of the quinoline-annulated porphyrins in biological media through derivatization is known.

KEYWORDS: platinum porphyrins, π-extended porphyrins, NIR emission, phosphorescence.

INTRODUCTION

The high extinction coefficients, triplet emission, and singlet oxygen photosensitization quantum yields of platinum(II) porphyrinoids make them attractive for use in biomedical applications as luminescent markers [1, 2] or photochemotherapeutics [2–5]. Platinum porphyrins have also aroused interest as emitters in NIR-emitting organic LEDs [6–8]. Furthermore, the correlation between the degree of the triplet oxygen-mediated quenching of the triplet excited state of platinum porphyrins (among a number of chromophores) with a particular oxygen partial pressure, p_{o_2} (Stern–Volmer quenching) is the physical basis for the development of optical oxygen sensors and bioassays that find applications in medicine, engineering, chemical, and environmental analyses [9–16]. The advantage of this technology is that direct quantitative p_{O_2} measurements at high spatial resolution can be obtained. Aside from the emission intensity modulation measurements, lifetime-based approaches can be used. The advantages of this include that readings are independent of excitation intensity, detector sensitivity, and probe concentration [17]. Time- and frequency-domain methods have also been realized; using long-lifetime (>1 μs) probes in combination with gated acquisition modalities much suppresses background emission signals [17]. Platinum porphyrinoids, either used in molecular forms or in polymeric formulations, have been a particularly well-studied class of oxygen sensors [12, 16–23].

Biological applications require that a chromophore absorb or emit light within the ~650–1100 nm wavelength

◊ SPP full member in good standing.

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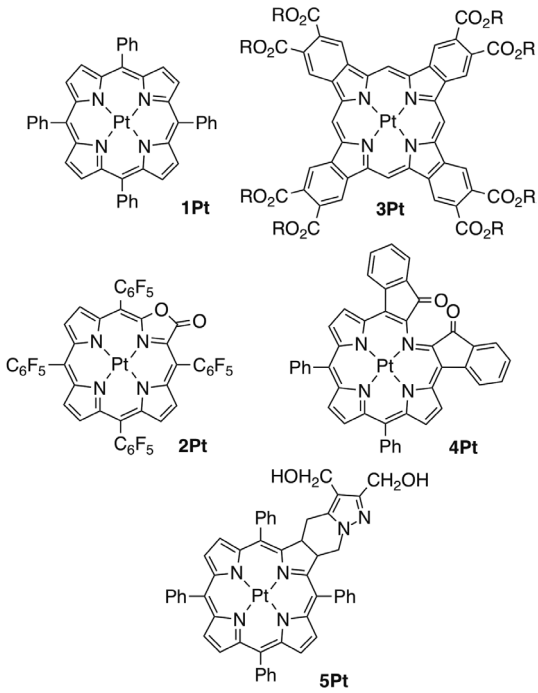


Chart 1. Literature-known examples of platinum porphyrins, porphyrinoids, and chlorins

regime referred to as the "optical window" of tissue [24], but regular porphyrins and chlorins generally do not fulfill this optical criterium. However, the ligand-based emissions of the platinum porphyrins ($\lambda_{max\text{-}emission}$ for **1Pt** = 650, 712 nm) [9] allow a modulation of the excitation and emission wavelengths through alterations of the porphyrinic chromophore. Examples for platinum(II) porphyrinoids with altered chromophores include the complexes of porpholactones, **2Pt** ($\lambda_{max\text{-}emission}$ = 740 nm) [25–28], β-oxo-porphyrins [29] and benzoporphyrins, such as complex **3Pt** ($\lambda_{max\text{-}emission}$ = 745 nm) [30–32], indaphyrin **4Pt** ($\lambda_{max\text{-}emission}$ = 850, 965 nm) [33, 34] or platinum(II) chlorin **5Pt** ($\lambda_{max\text{-}emission}$ = 756 nm) [5].

Strategies employed to red-shift the optical spectra of platinum (and the closely related palladium(II)) porphyrins include the utilization of hydroporphyrins [5], the incorporation of pyrrole β-substitutions or non-pyrrolic heterocycles [26–29], the expansion of the conjugated π-system by increasing the number of conjugated pyrroles [35], or the establishment of expanded π-systems by annulation [18, 20, 31, 33, 36]. Among the latter class of porphyrins are *meso*-arylporphyrin derivatives that bear a covalent linkage between one or more β-positions and the flanking *meso*-phenyl/aryl groups [37–44]. The short single atom linkage removes one of the $H_{\beta\text{-pyrrole}}$–$H_{o\text{-phenyl}}$ steric interaction that prevents the *meso*-aryl groups from adopting low-energy coplanar conformations [45]. It thus forces the phenyl group(s) into idealized co-planarity with the porphyrinic chromophore, thereby extending the π-conjugation pathway. However, this energetic benefit is somewhat offset by the enforced $H_{\beta\text{-pyrrole}}$–$H_{o\text{-phenyl}}$ steric interaction on the backside of the linked phenyl group.

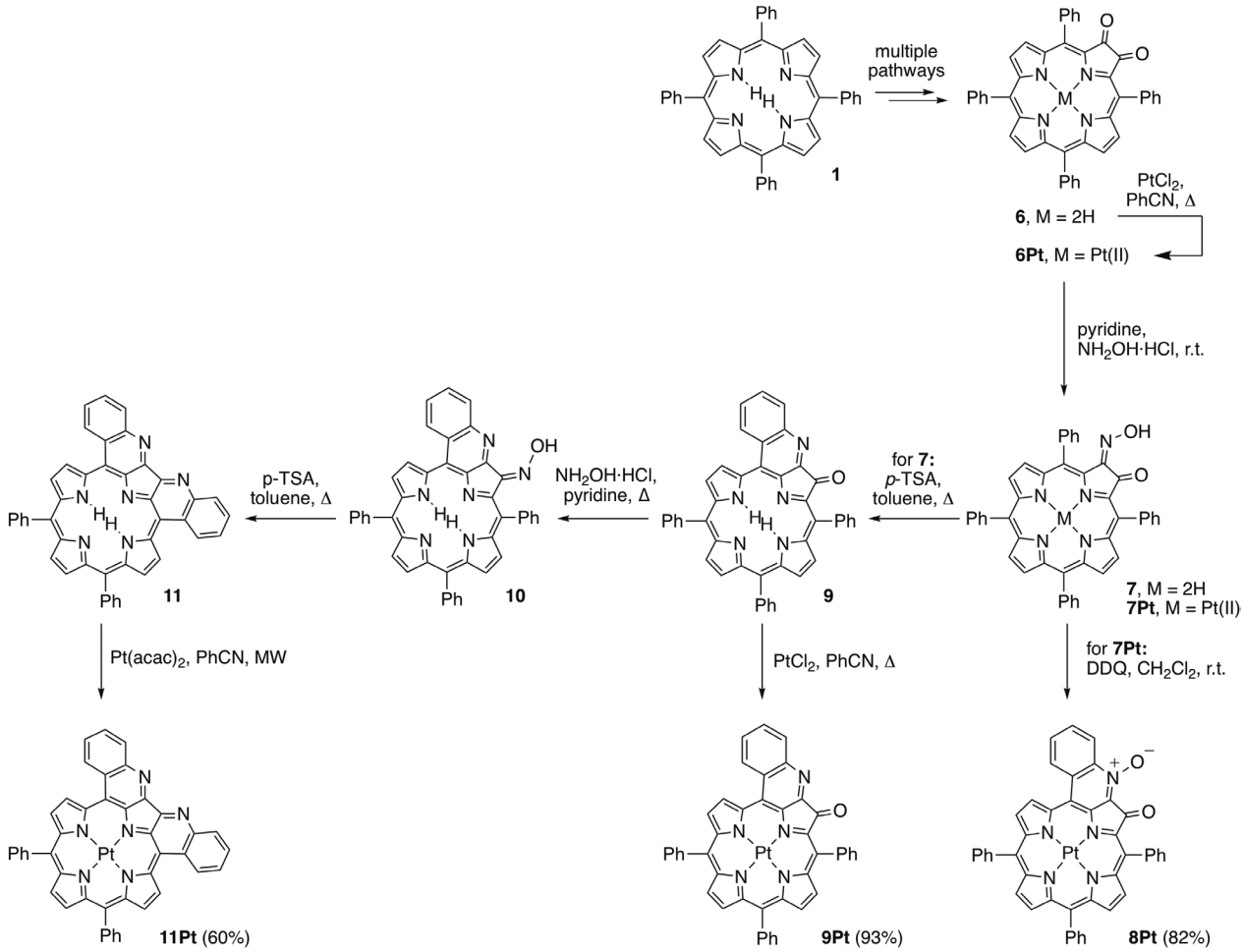
Jeandon and Ruppert, building on the extensive work by the group of Callot and co-workers [46–52], published the formation of bisquinoline-annulated porphyrin **11** [42]. Concurrently with Jeandon and Ruppert, we described an independent pathway toward mono- and bis-quinoline-annulated porphyrins [53, 54] and the conversion to their chlorin analogues [55]. We found these derivatives, as their free bases, to be characterized by remarkably bathochromically shifted optical spectra when compared to regular porphyrins, to possess negligible fluorescence, but to be excellent photoacoustic contrast agents [56, 57]. Osuka and co-workers reported an alternative way of annulating quinolines to porphyrins to generate red-shifted chromophores [36].

We report here on the platinum(II) complexes of some representative examples of the class of quinoline-annulated porphyrins, their absorption and NIR emission properties, and excited state lifetimes. We compare the strongly structure-dependent optical properties of the mono- (**8Pt** and **9Pt**) and bis-quinoline-substituted porphyrins (**11Pt**) to those of the parent porphyrin that also contains two adjacent β-positions that are substituted with sp^2-hybridized heteroatoms, 2,3-dioxoporphyrin platinum complex **6Pt** [58]. This work establishes these compounds firmly as another promising class of readily accessible NIR emitters.

RESULTS AND DISCUSSION

Synthesis of the quinoline-annulated porphyrin platinum(II) complexes

Insertion of platinum(II) into the known free bases tetraphenyl-2,3-dioxoporphyrin **6** [59] and mono- and bisquinoline-annulated porphyrins **9** and **11**, synthesized along established pathways [53, 54, 57], generated the corresponding platinum complexes **6Pt**, **9Pt**, and **11Pt**, respectively (Scheme 1). Metal insertion reactions using standard conditions [60–62] were generally facile, likely assisted by the pronounced non-planarity of the chromophores [54]. The ability of the quinoline-annulated porphyrins **7** or **9** (and closely related derivatives) to coordinate to metal ions with their quinoline-*N*-atom(s) has been previously demonstrated [49, 50, 52]. Particularly, the potential chelate **11** was expected to form a stable external chelate with the much kinetically deactivated platinum(II), since its first report noted its potential ability to act as a bidendate *N,N*-ligand [42]. However, none of the external (likely kinetic) chelation products could be observed under the metal coordination conditions used (PhCN, $PtCl_2$, 191 °C, 2 h, for **7** and **9**; PhCN, $Pt(acac)_2$, microwave heating to 250 °C for 20 min for **11**) and



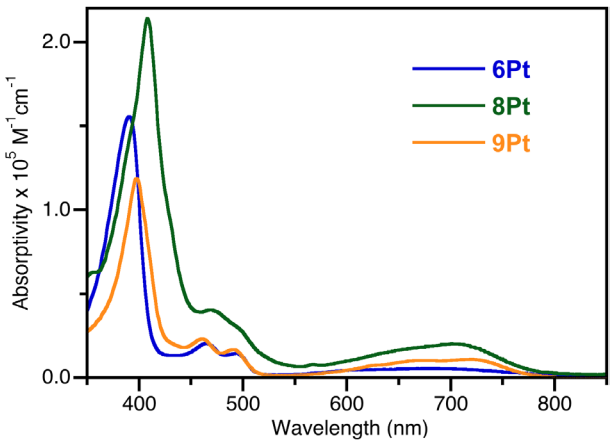
Scheme 1. Synthesis of the quinoline-annulated porphyrin platinum(II) complexes studied

only the thermodynamic products, the internal platinum chelates, were isolated.

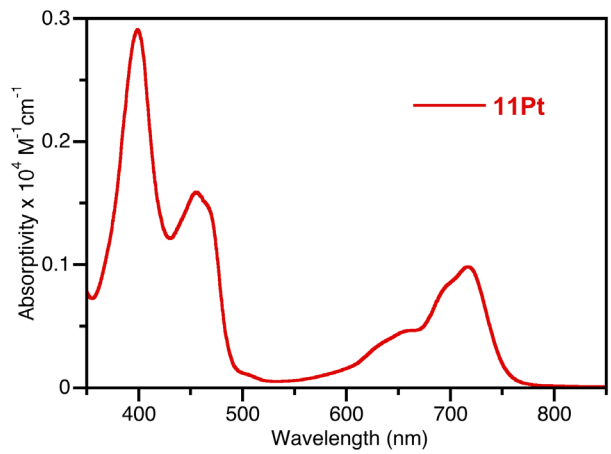
The *N*-oxide oxygen atom of quinoline-annulated *N*-oxide **8** was lost when subjected to platinum insertion conditions (or the insertion of nickel or even zinc) [54], thus forming **9Pt**. Hence, the synthesis of its platinum complex **8Pt** required a synthetic path that involved an early platinum insertion. Thus, known [tetraphenyl-2,3-dioxoporphyrinato]platinum(II) served as a starting material [58]. This dione was then manipulated along the established reaction sequence toward quinoline-annulated porphyrin *N*-oxide [54]: formation of oxime **7Pt**, followed by DDQ-induced oxidative ring-closure to quinoline-annulated porphyrin *N*-oxide platinum(II) complex **8Pt** [54]. All platinum complexes possessed the expected spectroscopic properties. Most ^{1}H NMR spectroscopic data of the platinum complexes are comparable to those of the corresponding nickel(II) or palladium(II) complexes, for some of which X-ray crystal structure data have become known [54], thereby suggesting that the platinum complexes also assume the non-planar conformations of their congeners.

Optical properties of the quinoline-annulated porphyrin platinum(II) complexes

As previously shown for select zinc(II), nickel(II), and palladium(II) complexes of the quinoline-annulated porphyrins [54], the much red-shifted and broadened spectra of the free-base parent chromophores are also maintained in their platinum(II) complexes. Metallation simplifies somewhat the Soret and Q-band regions. The much broadened NIR absorbance already present in dione **6Pt** (or the near-identical spectrum of mono-oxime **7Pt**) are slightly intensified and broadened by a single annulation reaction, but the overall characteristics of the spectrum of the dione are not altered. The formal *N*-oxidation of mono-quinoline **9Pt** to form **8Pt** leads to a general increase in the absorptivity and a slight red-shift, a trend also observed in their free bases (Fig. 1a) [54]. Bis-annulation (**11Pt**), on the other hand, results in a reduction of the absorptivity by about a factor of three, a split Soret band feature appears, and the Q-band region becomes, relative to the intensity of the Soret region, much more intense (Fig. 1b). Like in the



(a)



(b)

Fig. 1. UV-vis spectra in CH_2Cl_2 of the compounds indicated

previous examples of bis-annulated quinolines [54], we attribute this to a combination of the effect of the removal of the β-ketone functionality from conjugation with the porphyrinic π system [63] and conformational effects. Compared to the λ_{max} band of, for example **1Pt** (λ_{max} = 538 nm [64]), the λ_{max} bands for the quinoline annulated platinum porphyrins are much broadened and above 700 nm, clearly showing the effects of the annulation. The absorbance λ_{max} bands are comparable to other π-extended metalloporphyrins [36], including, for example, indaphyrin platinum complex **4Pt** (λ_{max} = 677 nm) [33].

A comparison of the phosphorescence spectra of dione complex **6Pt** with those of the mono-quinoline-annulated derivatives **8Pt** and **9Pt** belie the similarity of their UV-vis spectra (Fig. 2). The emission bands for **6Pt** (733, 809, 824 nm) are much red-shifted from those of porphyrin complex **1Pt** (657, 721 nm) or various fluorinated derivatives [64], but in character and position much different from the much more red-shifted mono-quinolines **8Pt** (1004, 1154 nm) and **9Pt** (950, 1068 nm). The vibrational spacing of 1282 cm^{-1} in **6Pt**, 1351 cm^{-1} in **1Pt**, 1295 cm^{-1} in **8Pt**, and 1163 cm^{-1} in **9Pt** suggests a similar origin of the bands. As predicted by the energy gap law, accompanying the wavelength shift is a significantly decreasing phosphorescence yield and lifetime (τ) (Fig. 3) [8, 65]. The decrease of the lifetime by about two orders to about 0.5 μs makes those chromophores unsuitable for time-delayed measurements [17].

The bis-quinoline-annulated complex **11Pt** exhibits phosphorescent emission bands (943, 1076 nm) at similar wavelengths as the mono-quinoline-annulated congeners, but the bands are associated with a slightly longer excited state lifetime, bringing this probe into the realm of gated measurements [17].

EXPERIMENTAL

Materials and instrumentation

All reagents and solvents were from commercial sources and used without prior purification. Dione **6Pt** [58] and oxime **7Pt** [58], free-base dione **6** [59, 66], and free-base annulated quinolines **9** and **11** [54] were prepared as described previously (Scheme 1). Aluminum-backed, silica gel 60, 250 μm thickness analytical plates were used for analytical TLC; 20 × 20 cm, glass-backed, silica gel 60, 500 μm thickness preparative TLC plates, and standard grade, 60 Å, 32 × 63 μm flash column silica gel were used for preparative chromatography.

^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument in the solvents indicated, and were referenced to residual solvent peaks. High- and low-resolution mass spectra were provided by the Mass Spectrometry Facility, Department of Chemistry, University of Connecticut.

The microwave synthesizer used was a Discover SP model manufactured by CEM Corporation, USA.

***Synthesis of* [*meso*-tetraphenyl-2-hydroxyimino-3-oxo-porphyrinato]platinum(*II*) (7*Pt*).** [*meso*-Tetraphenyl-2,3-dioxoporphyrinato]platinum(II) **6Pt** (98 mg, 117 μmol) was dissolved in pyridine (25 mL) in a round-bottom flask equipped with a magnetic stir bar and N_2 gas inlet. Solid H_2N-OH·HCl (407 mg, ~50 equiv) was added and the mixture was stirred for 24 h at room temperature. Once the starting material was consumed (reaction was monitored by TLC), the reaction mixture was evaporated to dryness by rotary evaporation, the residue was taken up in CH_2Cl_2 and filtered through a glass frit (M). The volume of the filtrate was reduced and the mixture was separated by column chromatography (CH_2Cl_2–petroleum ether 30–60, 3 : 1), allowing the isolation of **7Pt** in 89% yield (88.8 mg) as a dark green powder. R_f (silica-CH_2Cl_2) = 0.77; ^1H NMR (400 MHz, $CDCl_3$): δ 15.9 (s, 1H, exchangeable with D_2O), 8.62 (d, ^3J = 5.0 Hz, 1H), 8.56 (d, ^3J = 5.0 Hz, 1H), 8.53 (two overlapping d, ^3J = 5.2 Hz, 5.0 Hz, 2H), 8.43 (d, ^3J = 5.2 Hz, 1H), 8.38 (d, ^3J = 5.0 Hz, 1H), 8.04 (two overlapping d, ^3J = 7.8 Hz, 4H), 7.85–7.83 (m, 4H), 7.76–7.62 (m,

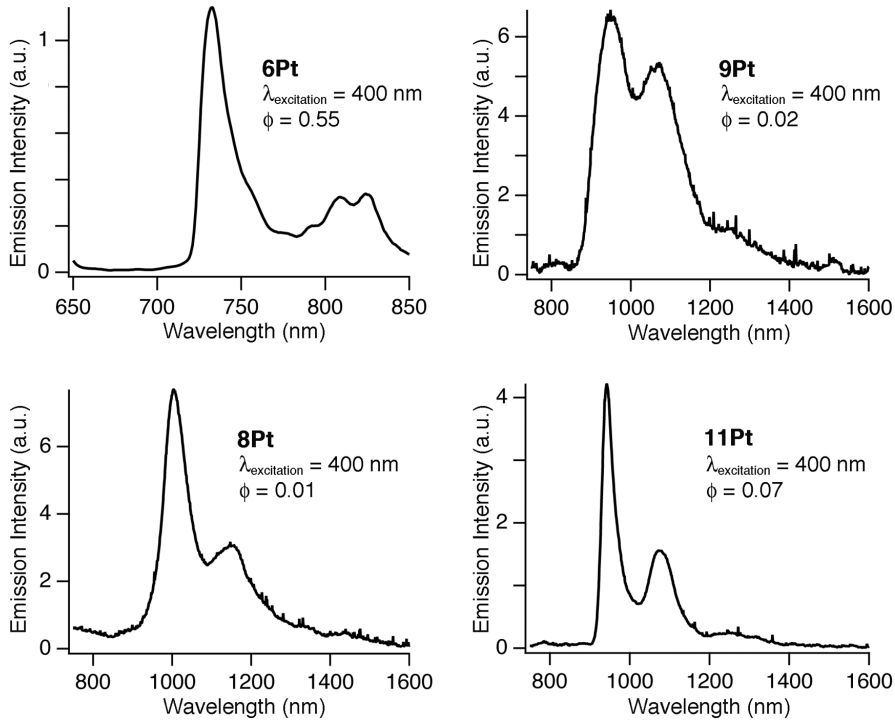


Fig. 2. Phosphorescence spectra (EtOH glass at 77 K) of the compounds indicated

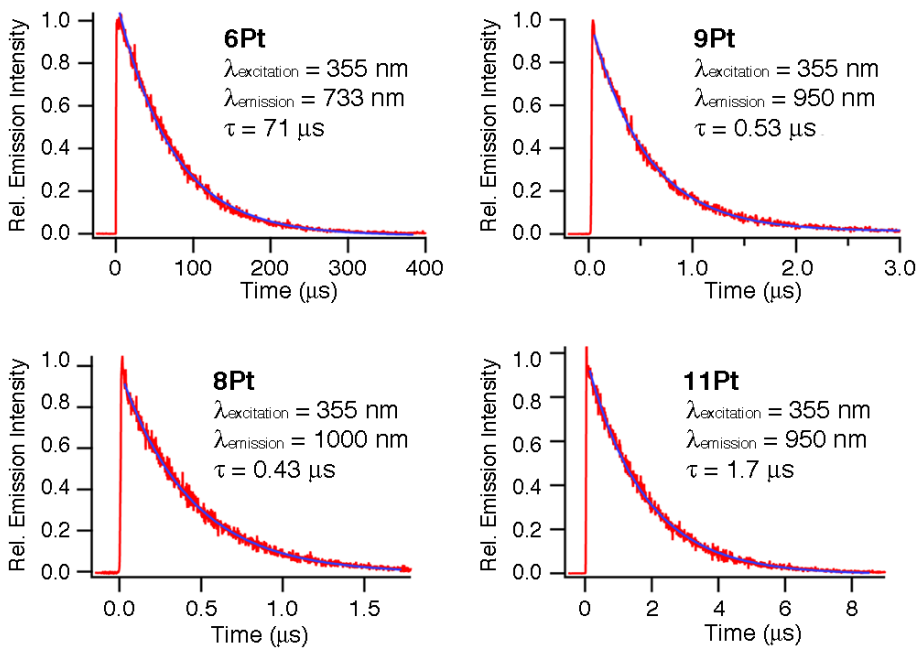


Fig. 3. Phosphorescence lifetimes of the compounds indicated (in a EtOH glass at 77 K)

12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.0, 151.9, 145.9, 143.2, 140.9, 140.8, 140.6, 140.5, 140.3, 140.0, 139.5, 139.2, 138.7, 138.4, 134.5, 134.4, 133.6, 133.5, 133.4, 133.3, 133.2, 132.7, 132.6, 132.1, 131.9, 130.1, 129.7, 129.5, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 127.5, 127.3, 127.2, 127.1, 125.7, 120.2, 115.6 ppm. UV-vis (CH_2Cl_2): λ_{max} (log ε) 391 (5.19), 457 (4.37), 493 (4.16), 535–713 (very broad band) nm. IR (neat, diamond ATR): $\nu_{C=O}$ = 1728.4 cm^{-1}. MS (DART$^+$, orifice voltage = 20 V, 100% CH_3CN) *m/z* calcd for $C_{44}H_{28}N_5O_2Pt$ ($[M \cdot H]^+$) 853.1894, found 853.1869.

***Synthesis of* [*meso*-triphenyl-mono-quinoline-annulated 3-oxo-porphyrinato-*N*-oxide]platinum(*II*) (8*Pt*).** Monooxime **7Pt** (20.2 mg, 23.7 μmol) was dissolved in CH_2Cl_2 (10.0 mL) in a round-bottom flask equipped with

a magnetic stir bar. DDQ (11 mg, 47 μmol, 2 equiv) was added and the mixture was stirred for 30 min at room temperature. When the starting material was consumed (reaction control by TLC), the reaction mixture was filtered through a short plug of silica gel to remove excess DDQ/the corresponding hydroquinone. The filtrate was washed with water (2 × 10 mL), dried over anhydrous Na_2SO_4, evaporated to dryness by rotary evaporation, and the residue was purified by preparative TLC (CH_2Cl_2/2% MeOH). After solvent exchange of the extracted main green band with MeOH, **8Pt** was isolated by filtration in 82% yield (16.5 mg) as a green powder. R_f (silica-CH_2Cl_2/5% MeOH) 0.55. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (d, ^3J = 5.2 Hz, 1H), 8.88, (d, ^3J = 8.5 Hz, 1H), 8.70 (d, ^3J = 8.1 Hz, 1H), 8.57 (d, ^3J = 5.0 Hz, 1H), 8.36, 8.33, 8.31 (three overlapping d, ^3J = 5.0 Hz, 3H), 8.21 (d, ^3J = 5.0 Hz, 1H), 8.04 (dd, ^3J = 6.3 Hz, ^4J = 1.5 Hz, 2H), 7.99 (dd, ^3J = 6.2 Hz, ^4J = 1.6 Hz, 2H), 7.83 (t, ^3J = 7.8 Hz, 1H) 7.77–7.66 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.7, 147.5, 141.4, 141.1, 140.1, 140.0, 139.9, 138.2, 137.5, 136.2, 134.9, 134.6, 133.6, 133.4, 133.1, 131.9, 131.7, 130.9, 130.0, 129.9, 129.7, 129.5, 129.0, 128.7, 128.6, 128.4, 128.1, 127.9, 127.7, 127.5, 125.9, 121.6, 118.4, 103.4 ppm. UV-vis (CH_2Cl_2): λ_{max} (log ε) 408 (5.33), 475 (4.59), 650 (sh), 702 (4.33) nm. phosphorescence (EtOH glass at 77 K) λ_{max} (rel. I) 1004 (1.0), 1154 (0.4) nm; IR (neat, diamond ATR): $\nu_{C=O}$ = 1695.4 cm^{-1}. MS (DART$^+$, orifice voltage = 20 V, 100% CH_3CN) *m/z* calcd for $C_{44}H_{26}N_5O_2Pt$ ($[M \cdot H]^+$) 851.1738, found 851.1719.

***Synthesis of* [*meso*-triphenyl-mono-quinoline-fused oxoporphyrinato]platinum(*II*) (9*Pt*).** Free-base mono-quinoline-fused oxoporphyrin **9** (17.7 mg, 27.6 μmol) was dissolved in benzonitrile (5.0 mL) and added to a hot solution of PhCN (15 mL) and platinum(II) chloride ($PtCl_2$ 29.3 mg, 110 μmol, 4.0 equiv) in a round-bottom flask equipped with a magnetic stir bar and N_2 gas inlet. The mixture was refluxed and stirred for 2 h. When the starting material was consumed (reaction monitored by UV-vis and TLC), the resulting mixture was allowed to cool to room temperature, the solvent was removed *in vacuo* and taken up in CH_2Cl_2. The main product was isolated and purified by flash column chromatography (CH_2Cl_2/0.5% MeOH), followed by recrystallization *via* solvent exchange into MeOH, to provide **9Pt** as a light green powder in 93% yield (21.4 mg). R_f (silica-CH_2Cl_2) 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (d, ^3J = 4.7 Hz, 1H), 8.65, (d, ^3J = 8.2 Hz, 1H), 8.42 (t, 2H), 8.24–8.19 (overlapping s and d, ^3J = 5.0 Hz, 3H), 8.10 (d, ^3J = 5.0 Hz, 1H), 8.00 (d, ^3J = 7.0 Hz, 2H), 7.93 (d, ^3J = 6.7 Hz, 2H), 7.74–7.60 (m, 13H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 150.0, 148.6, 145.2, 141.4, 140.5, 140.0, 139.9, 139.5, 138.0, 137.3, 135.5, 134.5, 134.1, 133.9, 133.3, 133.2, 133.1, 133.0, 132.8, 132.1, 131.8, 129.8, 129.4, 129.3, 129.1, 128.7, 128.6, 128.3, 128.1, 127.9, 127.8, 127.5, 127.3, 127.1, 125.3, 117.3, 110.8 ppm. UV-vis (CH_2Cl_2): λ_{max} (log ε) 399 (5.07), 462 (4.38), 492 (4.24), 668 (sh), 720 (4.05) nm. phosphorescence (EtOH glass at 77 K) λ_{max} (rel. I) 950 (1.0), 1068 (0.8) nm. IR (neat, diamond ATR): $\nu_{C=O}$ = 1714.7 cm^{-1}. MS (DART$^+$, orifice voltage = 20 V, 100% CH_3CN) *m/z* calcd for $C_{44}H_{26}N_5OPt$ ($[M \cdot H]^+$) 835.1788, found 835.1779.

***Synthesis of* [*meso*-diphenyl-bis-quinoline-fused porphyrinato]platinum(*II*) (11*Pt*).** Free-base bisquinoline-annulated porphyrin **11** (11.6 mg, 18 μmol) was dissolved in PhCN (2.7 mL) in a thick-walled glass tube equipped with a magnetic stir bar. $Pt(acac)_2$ (22 mg, 54 μmol, 3 equiv) was added, and the vessel was sealed and placed in a microwave cavity. Using an initial microwave power of 300 W, the contents of the reaction vessel were heated to 250 °C where it was held for 20 min. Upon completion the vessel was cooled to ambient temperature. The solvent was evaporated and the residue was separated on a preparative TLC plate (CH_2Cl_2/5% MeOH) to provide **11Pt** as a dark green solid in 60% yield (9.1 mg). R_f (silica-CH_2Cl_2/5% MeOH) = 0.51. ^{1}H NMR (400 MHz; CD_2Cl_2): δ 8.29 (d, ^3J = 4.0 Hz, 1H), 8.21 (two overlapping d, ^3J = 6.7 Hz, 2H), 7.83 (s, 1H), 7.76–7.61 (m, 8H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 149.6, 143.9, 143.7, 139.3, 139.0, 134.3, 134.1, 133.0, 132.0, 131.4, 129.8, 129.0, 128.1, 127.5, 127.0, 126.9, 125.7, 124.3, 124.2, 108.6 ppm. UV-vis (CH_2Cl_2): λ_{max} (log ε) 399 (4.46), 455 (4.20), 658 (3.66), 717 (3.99) nm. phosphorescence (EtOH glass at 77 K) λ_{max} (rel. I) 943 (1.0), 1076 (0.36) nm. HR-MS (ESI$^+$, 100% CH_3CN, TOF) *m/z* calcd for $C_{44}H_{25}N_6Pt$ ($[M \cdot H]^+$) 832.1792, found 832.1769.

Photophysical measurements

All UV-vis spectra were recorded on a Cary 50 UV-vis spectrometer (Varian). For NIR emission measurements, microcrystalline samples prepared by diffusion of MeOH into a CH_2Cl_2 solution were dissolved in minute quantities of CH_2Cl_2 and then diluted with EtOH to reach an absorbance of 0.2. The sample solutions were placed in 5-mm-diameter Pyrex NMR tubes and NIR emission spectra at 77 K (using a liquid nitrogen Dewar with optical window) were recorded with a modified SPEX Fluorolog 3 spectrometer (J. Y. Horiba, Edison, NJ), equipped with a liquid N_2-cooled Ge diode detector (EO817L; North Coast Scientific Corp.). A 450 W Xe lamp (Osram), in conjunction with a double-grating monochromator, served as the excitation source. The emission spectra reported were not corrected for the wavelength-dependent sensitivity of the detector. Excitation emission spectra demonstrating the validity of the emission spectral assignments are provided in the supporting information. Phosphorescence lifetimes were measured at 77 K using the pulses from a Spectra Physics Nd:YAG laser (GCR-150-30). The phosphorescence was collected and isolated using lenses and monochromators (H10 for visual spectral range and 1681B for NIR spectral range; Jobin-Yvon Inc.) and focused into Hamamatsu photomultiplier tubes (PMT; R928 for visual spectral range and H10330A-45

for NIR spectral range). The photocurrent from the PMT was amplified (SR 560, Stanford Research Systems) and stored on a digital oscilloscope (TDS 360, Tektronix).

CONCLUSIONS

Quinoline-annulated porphyrins are NIR-absorbing, essentially non-fluorescing derivatives accessible along complementary pathways [53, 54]. The platinum(II) complexes of mono- and bis-quinoline-annulated porphyrins are phosphorescent in, depending on the derivative, the wavelength range between ~950 to 1200 nm. This adds an additional example to the portfolio of π-extended platinum porphyrins, again highlighting that π-extension of a porphyrinic chromophore is a powerful approach toward the red-shifting of their optical spectra, particularly when the annulation strategy involves the *meso*-aryl groups. In terms of shifts that can be achieved, this approach is more powerful than what can be achieved with, for example, platinum chlorins [5]. This is presumably because of the severe non-planarization of the chromophores these annulations cause. The emission wavelengths of the mono-annulated derivatives are within the optical window of tissue. However, the annulation-induced shifts come with a major trade-off: the emission yields of the mono-quinoline-annulated porphyrins are low and their lifetimes short. Even though the bis-annulated derivative recovers some of the lifetime and emission yield, both values are only just within a range that would make them practical oxygen sensors for biological systems. On the other hand, we have shown previously how to solubilize quinoline-annulated porphyrins for use in *in vivo* imaging applications [57].

Acknowledgments

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Supporting information

A reproduction of the experimental data (such as ^{1}H, ^{13}C NMR spectra, FT-IR, MS spectra, and excitation emission spectra) of all novel platinum complexes described is given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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