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Development of bright NIR-emitting pressure-sensitive paints using benzoporphyrin luminophores†

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Pressure-sensitive paints (PSPs) are an optical surface pressure sensor for aerodynamic measurements that operates through the oxygen dependent luminescence of a luminophore molecule. The luminophore has remained relatively consistent over the past 20 years, with platinum(II)/palladium(II)-5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorphenyl)-porphyrin (Pt/PdTFPP) being popular choices due to their well-known photostability. In this work, NIR-emitting Pt(II) and Pd(II) complexes of tetraphenyl tetrabenzoporphyrins and new *para* CF$_3$ substituted tetraphenyl tetrabenzoporphyrins have been investigated as improved luminophores in PSP formulations for the first time. The red shifted NIR emission spectra of the benzoporphyrins offer a wider and more conveniently placed spectral window than Pt/PdTFPP, creating more of a spectral gap for a secondary temperature-sensitive luminophore to be used in future binary PSPs. The *para* CF$_3$ substituted Pt(II) and Pd(II) benzoporphyrins exhibited substantially increased luminescent brightness over PtTFPP and PdTFPP (5× higher), resulting in signficantly brighter PSP formulations. The benzoporphyrins greatly improved the performance of polystyrene based-PSPs, increasing pressure sensitivity by 20% and decreasing temperature sensitivity by 50%, compared to the current gold standard PtTFPP and PdTFPP.

Introduction

Singlet oxygen photosensitisers have found widespread use in a variety of fields, for example: photodynamic therapy (PDT),[1,2] biomedical imaging,[3] chemical synthesis,[4,5] water treatment[6,7] and optical oxygen sensors.[8,9] A notable and unique application of optical oxygen sensors is pressure-sensitive paints (PSPs), which are a powerful tool for measuring full-field surface pressure distributions and visualising aerodynamic phenomena in model-based wind tunnel testing. PSPs are formulations of a photoactive molecule, known as a luminophore, and an oxygen permeable binder which are applied to a model's surface.[10] Upon illumination the luminophore molecule is excited into the triplet (T$_1$) state, which is long enough lived (typically μs lifetime), to be quenched through collisional quenching by dissolved O$_2$ in the binder matrix. The luminophore emission can be imaged during wind tunnel operation, and full-field surface pressure maps of the test model, in a given flow, can be generated.[11–14] PSPs are relatively easy to apply (*via* spraying) and have distinct advantages over traditional pressure taps, which are expensive to implement and only provide low-resolution spatial measurements.

Despite the myriad benefits that PSPs provide, several key features limit their widespread industrial use. A crucial limitation is the inherent temperature sensitivity associated with PSP measurements, which is due to two components: the temperature-dependency of the non-radiative decay of the luminophore and of oxygen diffusion through the binder matrix.[10,15] Models in wind tunnel experiments often experience large surface temperature gradients and thus this temperature sensitivity can result in inaccurate surface pressure sensing.

Binary PSP formulations attempt to solve this problem, by introducing a secondary luminophore that is normally temperature-sensitive but pressure-insensitive.[16–19] However, many of these formulations suffer from significant spectral cross-talk and overlap between the two luminophores, causing major performance loss.[16,20] Many PSP formulations also suffer from low brightness, especially at higher pressures, where the luminescent signal can become challenging to measure, rendering accurate pressure determination difficult, due to the decreased signal-to-noise ratio (SNR).

There has been extensive development on the binder and data acquisition methods for PSPs, which have led to significant

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improvements in the technology;[20–25] however, the chemistry of the pressure-sensitive luminophore has been left curiously undeveloped since the early 2000s. In terms of porphyrin-based PSPs, platinum(II) octaethylporphyrin (PtOEP) was first used due to its large quantum yield.[12] However, PtOEP is very sensitive to concentration dependant self-quenching at higher dye loadings and suffers from severe photodegradation over prolonged exposure.[26] Therefore, platinum(II)-*meso*-tetra(pentafluorophenyl) porphyrin (**PtTFPP**) quickly replaced PtEOP due to its greater photostability and lower sensitivity to concentration quenching.[27] **PtTFPP** has since become the predominant luminophore in the majority of PSP formulations.

For binary PSP formulations, the broad red emission of **PtTFPP** (roughly 650 nm), causes significant spectral overlap with many desirable secondary luminophores, reducing overall performance. Khalil *et al.* synthesised and successfully used platinum(II)-*meso*-tetra(pentafluorophenyl)porpholactone (PtTFPL), in a binary PSP formulation.[17,28] PtTFPL possessed a red shifted emission band (733 nm), compared to **PtTFPP** making it the first NIR-emitting PSP. However, PtTFPL still suffers from a low overall brightness, especially at high pressures.

In this work, we aim to develop new and improved NIR-emitting PSPs, with the goal of making a brighter PSP that has a larger spectral window for insertion of secondary luminophores to avoid spectral overlap and cross talk in binary formulations. The NIR-emitting luminophores investigated in this work are Pt(II) and Pd(II) benzoporphyrins. Benzoporphyrins have found great success in other oxygen-sensing platforms due to their large quantum yields and oxygen sensitivities.[29–31] We have synthesised Pt(II) and Pd(II) tetraphenyl tetrabenzoporphyrin, called **PtBP** and **PdBP** in this study, as well as the

novel para CF$_3$ substituted derivatives denoted as **Pt-pCF3-BP** and **Pd-pCF3-BP** (Fig. 1). These benzoporphyrins will then be benchmarked against **PtTFPP** and **PdTFPP** (the standard PSP luminophores), to investigate their efficacy as luminophores in new NIR-emitting polymer-based PSPs.

Results and discussion

Synthesis

The reference luminophores **PtTFPP** and **PdTFPP** were synthesised previously.[32,33] The unsubstituted and *para* CF$_3$ substituted benzoporphyrins were synthesised using the multi-step synthesis developed by Finikova *et al.* (see ESI† for full details).[34] This synthesis involved the formation of tetrahydroisoindole, and the subsequent Lindsey reaction with benzaldehyde/4-trifluoromethyl benzaldehyde to form the respective tetraphenyl cyclohexenoporphyrins (TPCHPs). These compounds were isolated as dark green cationic salts that were deprotonated to form the corresponding purple freebase species, which were then subsequently metalated with PtCl$_2$ and PdCl$_2$ to afford the metalated TPCHPs. The metalated TPCHPs were then converted to the benzo derivatives by aromatization with excess DDQ, giving yields of approximately 30% for the Pt(II) benzoporphyrins and roughly 90% for Pd(II) benzoporphyrins.

UV-Vis electronic absorption spectroscopy

The UV-Vis electronic absorption spectra are characteristic of metalloporphyrins, with an intense feature in the near-UV, called the Soret band and weaker visible region features, called Q bands (Fig. 2) (Table S1†). The higher energy Q band is denoted as $Q_{abs}(1,0)$ and the lower in energy as $Q_{abs}(0,0)$.[35] These spectral features can be assigned according to Gouterman's four-orbital model, with the Soret band being comprised of a pair of symmetry-matched excited states; each being formed predominantly of a one-electron transition from the HOMO−1 to one of the degenerate LUMOs.[36] Correspondingly, the $Q_{abs}(0,0)$ feature is formed of a pair of symmetry-matched excited states that are predominantly formed of a one-electron transitions from the HOMO to the one of the degenerate LUMOs. The $Q_{abs}(1,0)$ feature is a vibronic satellite that is allowed *via* a Herzberg-Teller coupling pathway.[37] A key distinction of the spectra of the benzoporphyrins compared to the tetraphenyl porphyrins, is the overall red shift of absorption features; as well as the greatly increased intensity of the $Q_{abs}(0,0)$ feature, which is commonly found throughout the literature.[31]

Emission spectroscopy

The emission spectra of the porphyrin luminophores possess two distinct characteristic bands, a higher in energy electronic origin band denoted as $Q_{em}(0,0)$ and a lower in energy vibronic satellite, denoted as $Q_{em}(0,1)$ (Fig. 3) (Table 1).[35] The lifetimes of emission, $\tau_{(Ar)}$ and quantum yields $\Phi_{(Ar)}$ were measured in argon saturated solutions. Lifetime mono-exponential decay fits and
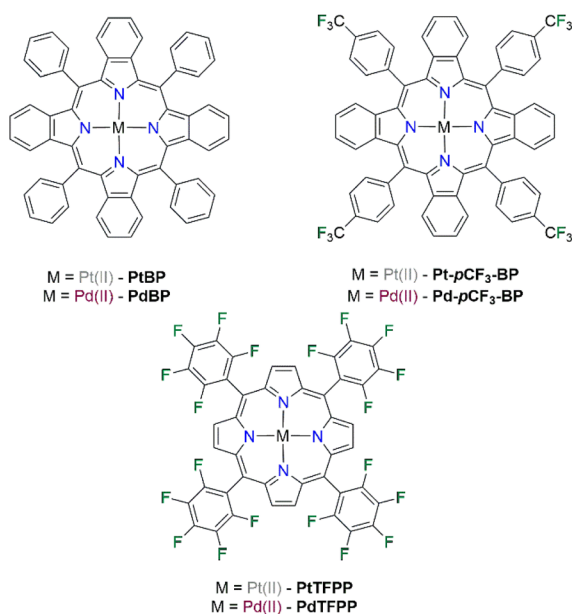

Fig. 1 The chemical structures of the Pt(II) and Pd(II) benzoporphyrin luminophores used in this study. **PtTFPP** and **PdTFPP** are the standard PSP luminophores and are the reference compounds in this study.
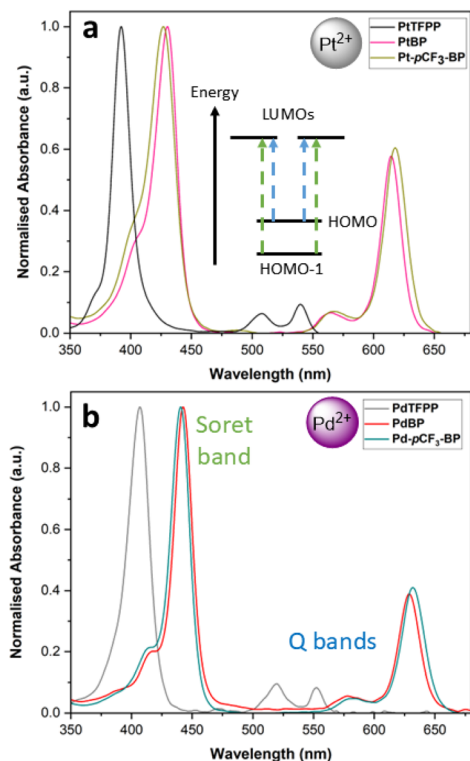
Fig. 2 The UV-Vis electronic absorption spectra of (a) PtTFPP,[32] PtBP and Pt-pCF$_3$-BP and (b) PdTFPP,[33] PdBP and Pd-pCF$_3$-BP in chloroform. Accompanying this, is a typical energy level diagrams showing the four frontier MOs found in tetraphenyl porphyrins and the electronic transitions that form the Soret and Q band features.
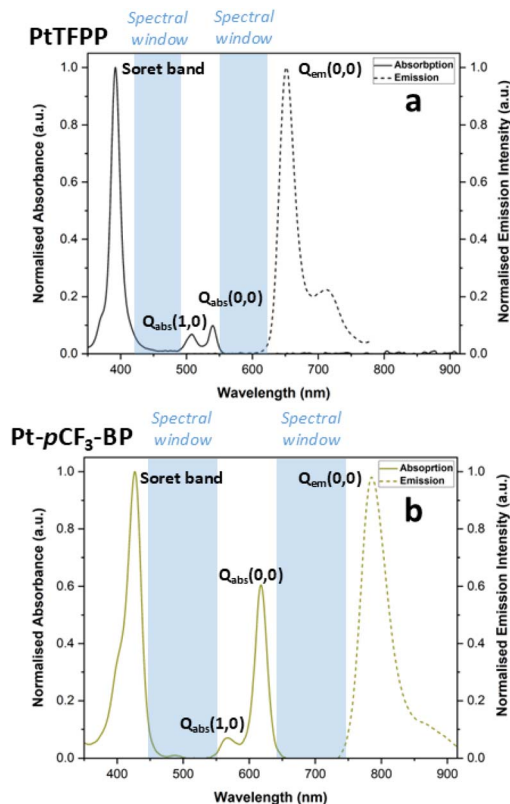

Fig. 3 The normalised absorption and emission spectra of (a) PtTFPP and (b) Pt-pCF$_3$-BP showing the 'spectral windows' where a secondary luminophore's emission spectrum could viably occur.

the emission spectra for all the luminophores can be found in the accompanying ESI.

The Pd(II) benzoporphyrins exhibit the typical spectral red shift (roughly 27 nm) relative to the Pt(II) analogues. A large red shift (roughly 134 nm) is present for the emission spectra of the benzoporphyrins when compared to their TFPP derivatives. This red shift of the emission features into the NIR region makes the benzoporphyrins viable luminophores for new and improved binary PSP formulations. There are two ideal 'spectral windows' in which a secondary temperature-sensitive luminophore could emit to avoid significant spectral overlap with the pressure-sensitive luminophore, the Soret band to the $Q_{abs}(1,0)$ feature and the $Q_{abs}(0,0)$ feature to the $Q_{em}(0,0)$ feature. For the benzoporphyrins, these spectral windows are much wider; for example, for Pt-pCF$_3$-BP, they are 25 nm and 57 nm wider when compared to PtTFPP. Although this increase in spectral window appears small, using the sharp emission features of lanthanide temperature-sensitive luminophores, this could significantly decrease performance-reducing spectral overlap with the pressure-sensitive luminophore signal. Additionally, the red shifted spectra of the benzoporphyrins recentres the Soret band to $Q_{abs}(1,0)$ spectral window to roughly 508 nm, putting it in the spectral range of the emission spectrum of the desirable temperature-sensitive luminophore coumarin 6.[19]

Compared to the TFPP complexes, the benzoporphyrins exhibit increases in $\Phi_{(Ar)}$ (roughly 7× larger for the Pt(II) and 4×

larger for the Pd(II) benzoporphyrins). Incorporation of the *para* CF$_3$ group further increases $\Phi_{(Ar)}$, with PtBP and Pt-pCF$_3$-BP possessing $\Phi_{(Ar)}$ values of 0.55 and 0.63 respectively. This increase in $\Phi_{(Ar)}$ matches well with Borisov *et al.* who found that *para* fluorination can increase the $\Phi_{(Ar)}$ of benzoporphyrins, whilst *meta* substitution was found to decrease $\Phi_{(Ar)}$.[31] PdBP and Pd-pCF$_3$-BP follow a similar trend. The brightness (BS) of a given luminophore can be determined using the product of the molar absorption coefficient and the quantum yield of emission (BS = $\Phi_{(Ar)} \times \varepsilon$). For the benzoporphyrins, the larger quantum yields result in much brighter luminophores when compared to the TFPP complexes; for example, the BS of PtTFPP, PtBP and Pt-pCF$_3$-BP is 23 700, 115 800 and 136 400 M^{-1} cm^{-1} respectively.

Therefore, the benzoporphyrins are roughly 5× brighter than the TFPP complexes, rendering them attractive new luminophores for PSP formulations.

The lifetimes of emission, $\tau_{(Ar)}$ for the Pt(II) benzoporphyrins show a slight decrease from that of PtTFPP; however, the Pd(II) benzoporphyrins show a much larger reduction in $\tau_{(Ar)}$ (roughly 2–3× lower) compared to PdTFPP. This large reduction for the Pd(II) benzoporphyrins, is likely due to their longer lived T$_1$ state being more sensitive to the increase in T$_1 \rightarrow$ S$_0$ non-radiative decay associated with the large out-of-plane structural distortions adopted by the benzoporphyrins.[38]

Table 1 Emission peak maxima, select spectral window, lifetimes of emission, quantum yields of emission and brightness values in deoxygenated chloroform for the porphyrins

Porphyrin	$Q_{em}(0,0)$ maximum (nm)	$Q_{em}(0,1)$ maximum (nm)	Soret band to $Q_{abs}(1,0)$ spectral window width^c (nm)	$Q_{abs}(1,0)$ to $Q_{em}(0,0)$ spectral window width^c (nm)	Lifetime of emission in argon $\tau_{(Ar)}$ (µs)	Quantum yield of emission in argon $\Phi_{(Ar)}$	Brightness BS $\Phi_{(Ar)} \times \varepsilon$ (M^{-1} cm^{-1})
PtTFPP^a	651	710	115	111	49.6	0.08	23 700
PtBP	775	—	134	161	48.7	0.55	115 800
Pt-pCF$_3$-BP	786	—	140	168	47.5	0.63	136 400
PdTFPP^b	672	739	112	120	748.2	0.04	10 900
PdBP	806	—	135	175	258.7	0.17	44 900
Pd-pCF$_3$-BP	816	—	142	180	234.3	0.19	52 900

^{a} Data previously published.[32] ^{b} Data previously published.[33] ^{c} Calculated as the difference between the respective features' maxima.
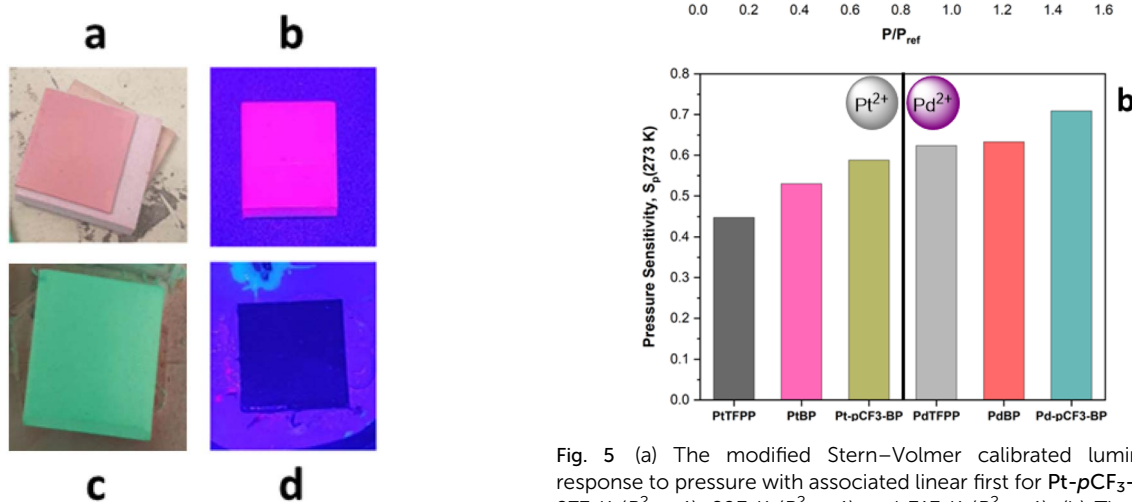
Polystyrene PSP performance studies

The benzoporphyrins and **Pt/PdTFPP** were trialled in simple polystyrene PSPs, using an *a priori* calibration method described in our previous work.[32] The polystyrene formulation was used in our previous studies and is effective for direct luminophore comparison (see ESI† for full details).[32] These samples are denoted as luminophore (PS). One noteworthy feature of the benzoporphyrin-based PSPs is their unique green colour, in contrast to the pink colour of Pt/PdTFPP based PSPs, along with their black appearance under 430 nm light excitation (Fig. 4).

A crucial performance metric for PSPs is the pressure sensitivity (S_p). A large S_p allows smaller pressure changes to be more accurately resolved; however, too high a pressure sensitivity can result in excessive quenching and therefore a loss of performance at higher pressures. S_p is governed by two factors, the oxygen permeability of the binder matrix, and the lifetime of the luminophore excited state, $\tau_{(Ar)}$ (from the Stern–Volmer constant ($K_{SV} = k_q\tau_0$). If the binder is kept the same the effect of the luminophore species on S_p can be isolated. In general, a longer-lived luminophore excited state has a higher chance of undergoing collisional quenching with oxygen and therefore, affords an increased S_p.

For all the polystyrene PSPs, a linear modified Stern–Volmer fit (eqn S(1)†) (Fig. 5a) was used to determine S_p; however, some non-linearity is present in the Pd(ii) porphyrin polystyrene-based PSPs due their longer phosphorescence lifetimes.

The individual modified Stern–Volmer calibrated plots for each polystyrene PSP at 273, 293 and 313 K and the S_p at each temperature can be found in the accompanying ESI. The Pt(ii) benzoporphyrin polystyrene-based PSPs exhibit remarkable linearity in their Stern–Volmer response ($R^2 = 1$), even at higher temperatures where non-linear behaviour is typical for **PtTFPP**. Focusing on the Pt(ii) porphyrins first, the S_p at 273 K denoted as

Fig. 5 (a) The modified Stern–Volmer calibrated luminescence response to pressure with associated linear first for **Pt-pCF$_3$-BP(PS)** at 273 K ($R^2 = 1$), 293 K ($R^2 = 1$) and 313 K ($R^2 = 1$). (b) The pressure sensitivity at 273 K, S_p (273 K), for the porphyrin polystyrene PSPs. The S_p is calculated using the linear form of the modified Stern–Volmer (eqn S(1)†). The data for **PtTFPP** and **PdTFPP** is previously published.[33]

Fig. 4 Images of select PSP samples. (a) Traditional **PtTFPP**-based PSP. (b) **PtTFPP**-based PSP under light excitation. (c) Benzoporphyrin based PSP. (d) Benzoporphyrin based PSP under light excitation.

S_p(273 K) (Fig. 5b) increases from 0.448 for **PtTFPP(PS)**[33] to 0.530 for **PtBP(PS)** and then to 0.588 for **Pt-pCF$_3$-BP(PS)**. The same trend occurs for the Pd(II) analogues with S_p(273 K) increasing from 0.624 for **PdTFPP(PS)** to 0.633 for **PdBP(PS)** and then to 0.709 for **Pd-pCF$_3$-BP(PS)**; however, the Pd(II) porphyrins exhibited a larger S_p, owing to their significantly longer $\tau_{(Ar)}$.

Overall, the benzoporphyrin polystyrene-based PSPs are more sensitive to pressure than **Pt/PdTFPP(PS)**. The highest S_p(293 K) is found for the *para* CF$_3$ substituted benzoporphyrins, **Pt/Pd-pCF$_3$-BP(PS)**, agreeing with our previous study on tetraphenyl porphyrins, which suggested that CF$_3$ groups on the luminophore can increase S_p in polymer-based PSPs.[32] The relative emission lifetimes of the luminophores are similar in polystyrene and solution (Table S2†) – implying a large increase in emission lifetime does not correlate with the much higher pressure sensitivities of the benzoporphyrin-based polystyrene PSPs. At 293 K and 313 K the trends in S_p break down as the individual temperature sensitivities of each luminophore start to increasingly influence the S_p of the PSPs. The increased brightness of emission, wider spectral windows and higher-pressure sensitivities of the benzoporphyrin polystyrene-based PSPs, make them attractive options as new luminophores in PSP formulations.

PSPs also have an inherent temperature sensitivity (S_T), experiencing a reduction in luminescence intensity with increasing temperature. Ideally, a PSP formulation should have zero temperature dependence. A large S_T can make accurate determination of pressure challenging or even impossible when surface temperature gradients are also present. Recently, we demonstrated that the extent, pattern and nature of phenyl halogenation for tetraphenyl porphyrin luminophores can have a significant effect on the S_T of polymer-based PSPs.[32] Consequently, we then investigated the effect of the nature of the central metal ion for TFPP luminophores on polymer-based PSP performance, finding that **PtTFPP(PS)** had a lower S_T at higher pressures and **PdTFPP(PS)** had a lower S_T at lower pressures.[33] The S_T for a given PSP is calculated using eqn (S3).† Focusing on the S_T at 100 kPa (Fig. 6a), denoted as S_T(100 kPa); for **PtBP(PS)** (1.27%/K) and **Pt-pCF$_3$-BP(PS)** (0.79%/K), they both possess a lower S_T(100 kPa) than that of **PtTFPP(PS)** (1.56%/K).[33] The same trend occurs for the Pd(II) benzoporphyrin polystyrene-based PSPs, but S_T is generally higher when compared to the Pt(II) analogues. For example, for **PdBP(PS)** (1.33%/K) and **Pd-pCF$_3$-BP(PS)** (0.81%/K), they both have a lower S_T(100 kPa) than that of **PdTFPP(PS)** (1.71%/K).[33] Overall, the unsubstituted benzoporphyrins reduce S_T by 20% and the *para* CF$_3$ substituted benzoporphyrins by 50% from that of the **Pt/PdTFPP(PS)**. This significantly decreased S_T makes the *para* CF$_3$ substituted benzoporphyrins excellent candidates for improved PSPs.

The change in S_T with pressure, for a given PSP, is also important to consider (Fig. 6b). S_T increases with increasing pressure because of the increasing concentration of the quencher oxygen molecules. An ideal PSP would have a low S_T that remains constant with pressure. S_T is observed to change most drastically (steeper gradient) with pressure for **PtTFPP(PS)** and **PdTFPP(PS)**.[33] For the *para* CF$_3$ substituted benzoporphyrins, S_T increases at a slower rate (shallower gradient) with
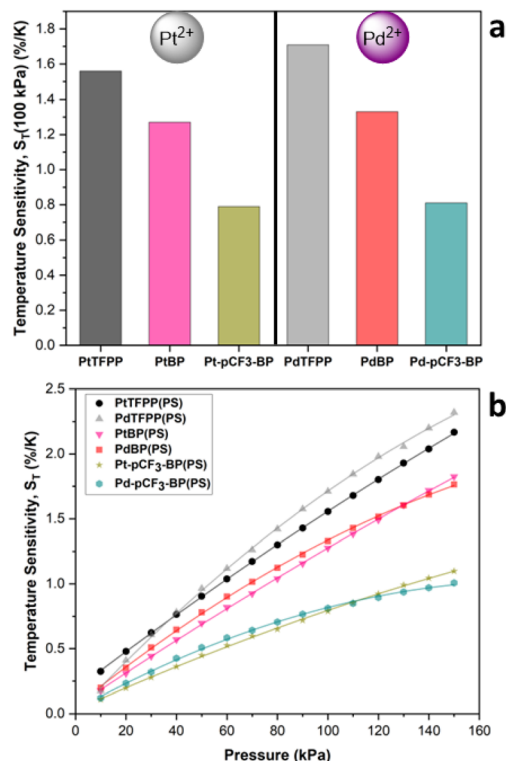

Fig. 6 (a) The S_T at 100 kPa, S_T(100 kPa) for the polystyrene-based PSPs. (b) The change in S_T with pressure for PtTFPP, PdTFPP, PtBP, PdBP, Pt-pCF$_3$-BP and Pd-pCF$_3$-BP polystyrene-based PSPs. The data for PtTFPP and PdTFPP is previously published.[33]

increasing pressure than the unsubstituted benzoporphyrins and the TFPP derivatives, resulting in better sensor performance. The reason for the lower sensitivity of S_T to pressure may be due to increased luminophore compatibility with the polystyrene matrix for **Pt/Pd-pCF$_3$-BP**, because of the increased solubility afforded by the CF$_3$ substituents. The increased pressure sensitivity of the **Pt/Pd-pCF$_3$-BP** PSPs, compared to the **Pt/PdBP** PSPs, supports this conclusion. For the Pd(II) luminophores, S_T is more sensitive to increasing pressure, with a highly non-linear response, when compared to their Pt(II) analogues. The highly non-linear behaviour of S_T for the Pd(II) analogues, is likely due to the longer lived excited state of the Pd(II) benzoporphyrins being more sensitive to increasing pressure. Eventually, at higher pressures, S_T for the Pd(II) benzoporphyrin PSPs begins to plateau (possibly due to excess quenching) and drop below that of their corresponding Pt(II) luminophores. This plateauing occurs at increasingly higher pressures, for example: **Pd-pCF$_3$-BP(PS)** at 110 kPa, **PdBP(PS)** at 130 kPa and then at >150 kPa for **PdTFPP(PS)** – aligning well with the increasing luminescence lifetime across this series. The initial rise in S_T at lower pressures is greatest for **PdTFPP(PS)** and is again most likely due to the longer $\tau_{(Ar)}$ of **PdTFPP** > **PdBP** > **Pd-pCF$_3$-BP**.

FIB PSP performance studies

To explore the efficacy of benzoporphyrin luminophores in PSP further, **Pt-pCF$_3$-BP** and **Pd-pCF$_3$-BP** were made into fluoro/iso/butyl polymer (FIB polymer) formulations denoted as **Pt-pCF$_3$-**

BP(amount of dye FIB) and **Pd-*p*CF₃-BP**(amount of dye FIB). FIB polymer was first introduced by Puklin *et al.* as a low temperature sensitivity polymer for PSP, due to its low energy barrier to oxygen diffusion.[39] The CF₃ substituted benzoporphyrins were chosen as they are higher performing than the unsubstituted benzoporphyrins. Additionally, it was anticipated that the CF₃ groups would induce more compatibility between the highly polar FIB polymer binder and the luminophore. The S_p at each temperature and the S_T(100 kPa) for each FIB PSP can be found in the accompanying ESI (Tables S3 and S4†).

Initially an in-house FIB recipe was used as a trial for FIB-based benzoporphyrin PSP that was optimised for tetra-aryl metalloporphyrins in our previous work. This involved using 3.2% w/w dye to FIB polymer and 3.2% w/v FIB polymer to tri-fluorotoluene (TFT).[32] A smooth coating was acquired after 10 light coats of spray brushing, which was subsequently cured in an oven for two hours to reach the T_g of FIB at 75 °C. However, when the samples were placed into the calibration chamber and illuminated under 430 nm light, no signal could be detected. After increasing the exposure time of the camera to 400 000 μs for **Pt-*p*CF₃-BP**(3.2% w/w FIB) and 800 000 μs for **Pd-*p*CF₃-BP**(3.2% w/w FIB), a weak signal was observed. For comparison, the benzoporphyrin polystyrene PSPs displayed an excellent signal at 4000 μs exposure time on the same camera. The
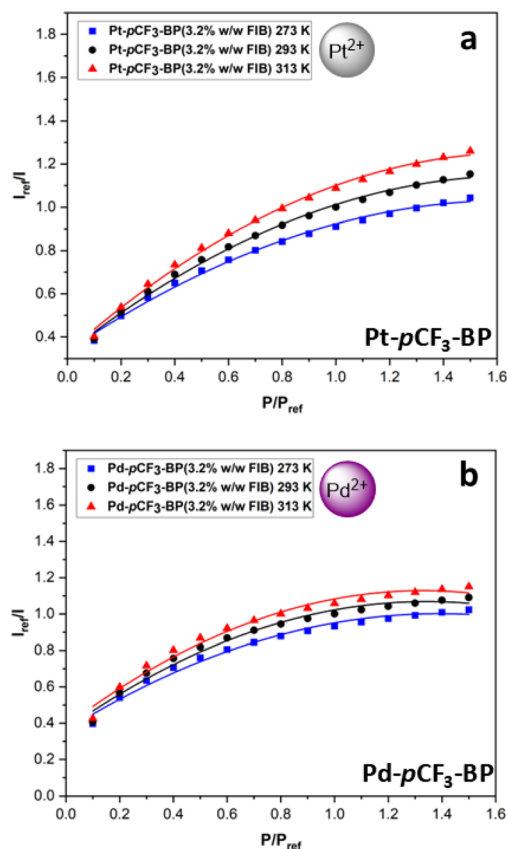

Fig. 7 The modified Stern–Volmer calibrated luminescent response to pressure with 2nd order polynomial fits (eqn S(2)†) at 273 K, 293 K and 313 K for (a) Pt-*p*CF₃-BP(3.2% w/w FIB) (average $R^2 = 0.995$). (b) Pd-*p*CF₃-BP(3.2% w/w FIB) (average $R^2 = 0.980$). The average R^2 is across the fits for the three temperatures.

performance of the PSPs (Fig. 7) was similarly poor with low pressure sensitivities (especially at higher pressures) that are highly non-linear compared to the polystyrene PSPs (the non-linear Stern–Volmer eqn (S2)† better fits the data).

The poor performance of **Pt/Pd-*p*CF₃-BP** in FIB could be due to several reasons. The low luminescence signal implies too high a concentration of luminophore was used and therefore, significant self-quenching is occurring (sensor deactivation). Grenoble *et al.* observed an increased susceptibility of PtOEP to undergo self-quenching over **PtTFPP**.[26] As previously mentioned, we used an in-house recipe developed for platinum(II)-5,10,15,20-tetrakis-(3,5-bis(trifluoromethyl)phenyl)-porphyrin and therefore, the benzoporphyrins appear to be more sensitive to concentration quenching. Additionally, the highly non-linear response of **Pt/Pd-*p*CF₃-BP**(3.2% w/w FIB) to pressure, implies a low level of luminophore-polymer compatibility. Therefore, this low level of luminophore-polymer compatibility, results in the **Pt/Pd-*p*CF₃-BP** being potentially unsuitable for FIB-based PSP formulations

To eliminate the observed self-quenching in benzoporphyrin FIB-based PSPs, a lower luminophore loading was examined. A formulation of 0.8% w/w luminophore to FIB polymer and 3.2% w/v FIB polymer to TFT was used. These samples were sprayed in 10 light coats and cured in an oven for two hours to reach the T_g of FIB at 75 °C. The samples are denoted as **Pt-*p*CF₃-BP**(0.8% w/w FIB)/**Pd-*p*CF₃-BP**(0.8% w/w FIB). An intense signal with a 10 000 μs camera exposure time could be achieved for both **Pt-*p*CF₃-BP**(0.8% w/w FIB) and **Pd-*p*CF₃-BP**(0.8% w/w FIB). This significant increase in brightness compared to the higher luminophore loading samples, suggests that self-quenching had effectively been reduced by using the lower luminophore loading. The performance of the benzoporphyrin FIB-based PSPs, using the lower luminophore loading, was also significantly improved (Fig. 8). For example, the S_p(293 K) of **Pt-*p*CF₃-BP**(0.8% w/w FIB) is 0.501 and the response to pressure was much more linear ($R^2 = 0.998$ using the linear Stern–Volmer eqn S(1)†) when compared to **Pt-*p*CF₃-BP**(3.2% w/w FIB). However, the pressure response of **Pt-*p*CF₃-BP**(0.8% w/w FIB) is still less linear than **Pt-*p*CF₃-BP(PS)**. The S_T(100 kPa) of **Pt-*p*CF₃-BP**(0.8% w/w FIB) compared to **Pt-*p*CF₃-BP(PS)** is higher (0.89%/K and 0.79%/K respectively). The FIB polymer has a low energy barrier to oxygen diffusion and thus is expected to reduce the S_T of a given PSP.[39] Additionally, the S_T of **Pt-*p*CF₃-BP**(0.8% w/w FIB) is much more sensitive to pressure (Fig. 8c) when compared to **Pt-*p*CF₃-BP(PS)**. Overall, these factors result in **Pt-*p*CF₃-BP**(0.8% w/w FIB) exhibiting reduced performance compared to **Pt-*p*CF₃-BP(PS)**, which suggests a level of incompatibility between the partially fluorinated **Pt-*p*CF₃-BP** and the highly polar FIB polymer. For example, the heavily fluorinated platinum(II)-5,10,15,20-tetrakis-(3,5-bis(trifluoromethyl)phenyl)-porphyrin luminophore we recently trialled in FIB, displayed excellent linearity in its response to pressure and much higher performance metrics.[32] The performance of **Pd-*p*CF₃-BP**(0.8% w/w FIB) was still poor, compared to **Pd-*p*CF₃-BP**(3.2% w/w FIB), with a highly non-linear pressure response and low pressure sensitivities. The long $\tau_{(Ar)}$ of **Pd-*p*CF₃-BP** is probably too sensitive for the FIB binder, resulting in an over-
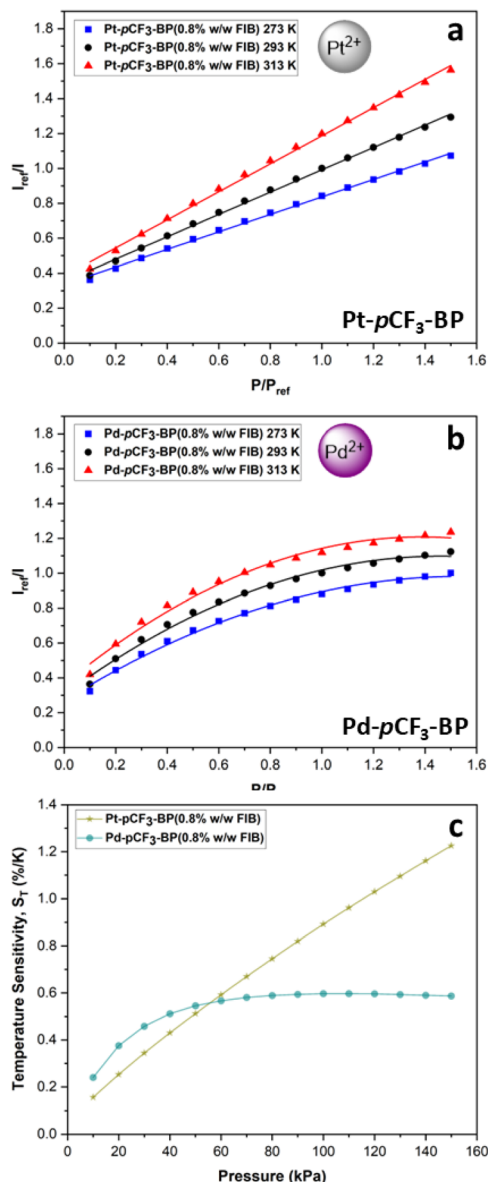
Fig. 8 The modified Stern–Volmer calibrated luminescent response to pressure at 273, 293 and 313 K for (a) Pt-pCF$_3$-BP(0.8% w/w FIB) with linear fits (eqn S(1)†) (average R^2 = 0.998). (b) Pd-pCF$_3$-BP(0.8% w/w FIB) with 2nd order polynomial fits (eqn S(2)†) (average R^2 = 0.990). (c) The change in S_T with increasing pressure for Pt-pCF$_3$-BP(0.8% w/w FIB) and Pd-pCF$_3$-BP(0.8% w/w FIB). The average R^2 is across the fits for the three temperatures.

sensitivity to pressure. The low activation energy of oxygen diffusion for the FIB polymer results in higher concentrations of oxygen dissolved in the polymer, which will affect Pd-pCF$_3$-BP more than Pt-pCF$_3$-BP due to the much longer $\tau_{(Ar)}$ of the former.

Conclusions

Benzoporphyrins are an attractive class of luminophore for a new and improved generation of NIR-emitting polymer-based PSP formulations, which exhibit more desirable properties over

PSPs utilising Pt/PdTFPP. In particular, the wider and red shifted spectral windows in the benzoporphyrin's absorption and emission spectra allow more spectral room for a secondary temperature sensitive luminophore, thus potentially decreasing performance reducing spectral overlap and crosstalk in future binary PSPs. The benzoporphyrin luminophores offer increased luminescent brightness; in particular, the *para* CF$_3$ substituted benzoporphyrins exhibited a roughly 5× higher brightness compared to the traditional Pt/PdTFPP luminophores. Initial polystyrene PSP trials, using *para* CF$_3$ substituted benzoporphyrins, afforded PSPs with significantly higher performance metrics. For example, the benzoporphyrins increased pressure sensitivity, S_p, by 20% and reduced temperature sensitivity, S_T, by 50% when compared to Pt/PdTFPP polystyrene-based PSPs. The *para* CF$_3$ substituted benzoporphyrins were examined in the higher performing fluoro/Iso/butyl (FIB) polymer. The benzoporphyrins were found to be concentration sensitive which reduced brightness and PSP performance at higher luminophore loadings. Using a lower luminophore loading, the benzoporphyrin FIB-based PSPs exhibited a reasonable performance; however, some performance loss was observed when compared to the polystyrene PSPs. This performance loss is theorized to be caused by a lower luminophore-polymer compatibility between the partially fluorinated benzoporphyrin and the highly fluorinated FIB polymer.

In general, the benzoporphyrins present a significant performance improvement over the traditional Pt/PdTFPP luminophores in polystyrene PSPs and thus are attractive candidates for new brighter NIR-emitting PSP formulations. We plan to test the benzoporphyrins presented here, in a range of PSP formulations, including binary systems, to fully explore their efficacy as new NIR-emitting luminophores for improved PSP formulations in wind tunnel tests. We hope this investigation inspires further development of NIR-emitting luminophores as they offer distinct advantages over the widely used traditional luminophores, particularly in the development of higher performing binary PSPs.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article and/or its ESI.

Author contributions

Elliott J Nunn: writing – review and editing, writing – original draft, visualization, methodology, data curation, conceptualization. Dimitrios Tsioumanis: visualization, methodology, data curation. Tom B. Fisher: writing – review and editing, supervision, funding acquisition, conceptualization. David. A. Roberts: writing – review and editing, supervision, funding acquisition, conceptualization. Mark K. Quinn: writing – review and editing, validation, supervision, project administration, funding acquisition, conceptualization. Louise S. Natrajan: writing – review and editing, validation, supervision, project administration, funding acquisition.

Conflicts of interest

There are no conflicts of interest to declare

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