Platinum(II) Schiff base as versatile phosphorescent core component in conjugated oligo(phenylene–ethynylene)s†‡

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Novel phosphorescent conjugated oligo(phenylene–ethynylene)s featuring a central tunable platinum(II) Schiff base signalling unit with promising photophysical properties have been investigated to pave their development towards polymeric congeners for sensing applications.

The rapid advancement of poly(phenylene–ethynylene)s (PPEs) as novel functional materials for fluorescent sensing (and optoelectronic) applications has been impressive, and their salient appeal is the enhanced sensitivity arising from the conjugation-mediated amplified quenching effect.[1] The pursuit of phosphorescent relatives of PPEs and other conjugated organic materials, which can potentially transmit the sensing process by visible light without interference from organic/background fluorescence, is a more recent development, and the incorporation of conjugated metal–organic motifs can engender tunability and diverse excited states.[2] The phosphorescent properties and quenching of a conjugated PPE–platinum(II) acetylide polyelectrolyte material[3] and cyclometallated Pt(II) poly(phenylene)s[4] were recently reported, although the anticipated quenching amplification was not detected and design modification of the Pt–acetylide backbone in the former is non-trivial.

We have embarked upon a modular design approach for sensor development based on the controllable integration of functionalised phosphorescent signalling units into well-defined conjugated materials. Our interest in Schiff base–Pt(II) modules stems from the following: (1) phosphorescent multidentate Pt(II) Schiff base materials have recently been examined for OLED applications,[5] and their exceptionally high quantum efficiencies and robustness would facilitate sensing applications in polar (aqueous) media; (2) compared to d^6 octahedral $Ru(bpy)_3^{2+}$ luminophores which exhibit sphere-like coordination, the 'open' unsaturated geometry of square planar d^8 Pt(II) can afford excited states that are sensitive to the micro-environment;[6] (3) the profound impact of Schiff base (salen) complexes upon research areas such as enantioselective organic oxidation has led to tremendous molecular diversity with well-established synthetic methodologies, so that structural modification is readily available and modularity becomes feasible; (4) reports depicting metal–salen derivatives in sensor applications remain sparse in the literature,[7] and development of luminescent versions are very limited.[8] We herein describe novel phosphorescent oligo(phenylene–ethynylene)s (OPEs) conjugated with a Pt(II) Schiff base core module, which constitute the initial step towards the development of phosphorescent salen-based conjugated polymers as tunable sensory materials. Reports on the photophysical studies of luminescent OPEs incorporating octahedral Re–, Ru–, and Ir–bpy moieties have appeared.[9]

The synthetic routes utilized in this work are summarized in Scheme 1. The Pt–diiodosalphen precursor complex **1** was obtained in moderate yield (40–50%) from the gently heated reaction[10] of the tetradentate bis-phenol (generated from typical diamine/salicylaldehyde bis-condensation) with K_2PtCl_4.‡The aldehyde-capped mono- and di(phenylene–ethynylene) ligands **MPE** and **DPE** have been assembled in a stepwise fashion from 2,5-diheptoxy-1,4-diiodobenzene using established procedures or modifications thereof.‡ The desilylation reaction to give **DPE** using KOH followed by HCl was originally unsuccessful (^{13}C NMR characterization indicated conversion of the internal ethynylene group to vinylene), but changing the base to KF in THF/methanol cleanly afforded **DPE** in virtually quantitative yield. The C–C formation step between the terminal phenylene–ethynylenes and Pt–Schiff base **1** was accomplished using conventional Pd-catalysed coupling reactions to afford the monodispersed conjugated oligomers **Pt-n** (n = 2, 4 = no. of PE units) bearing a versatile luminescent Pt–Schiff base interior (*ca.* 55 and 30% yields respectively). The characterisation data[11] for **Pt-2** and **Pt-4**, including the corresponding number of ^{13}C NMR C≡C resonances and excellent agreement between the ES-MS and isotopic distribution simulation for M^+,‡ are entirely consistent with the proposed molecular structures.

The photophysical properties of **Pt-2** and **Pt-4** have been investigated (Table 1). Their UV-vis absorption spectra in CH_2Cl_2 (Fig. 1) feature two highly intense $^1(\pi\pi^*)$ absorption bands at around λ_{max} 300 ($\varepsilon > 4.8 \times 10^4$ mol^{-1} dm^3 cm^{-1}) and 400 ($\varepsilon > 1 \times 10^5$ mol^{-1} dm^3 cm^{-1}) nm. In addition, a moderately intense band that is absent for the ligand **DPE** is observed at λ_{max} 509 and 501 nm (ε = (1.6 and 1.9) × 10^4 mol^{-1} dm^3 cm^{-1} respectively) for **Pt-2** and **Pt-4** respectively, with a shoulder at around 550 nm ($\varepsilon \approx 1 \times 10^4$ mol^{-1} dm^3 cm^{-1}). The influence of solvent polarity upon the UV-vis absorptions of **Pt-4** was probed. While the energies of the absorption maxima at $\lambda < 420$ nm remain relatively unchanged, the low-energy absorption band (and the shoulder in particular) undergoes noticeable red shifts in low-polarity solvents (λ_{max}): 496 (554 sh) nm in THF; 501 (555 sh) nm in CH_2Cl_2; 509 (571 sh) nm in toluene (inset of Fig. 1). Such

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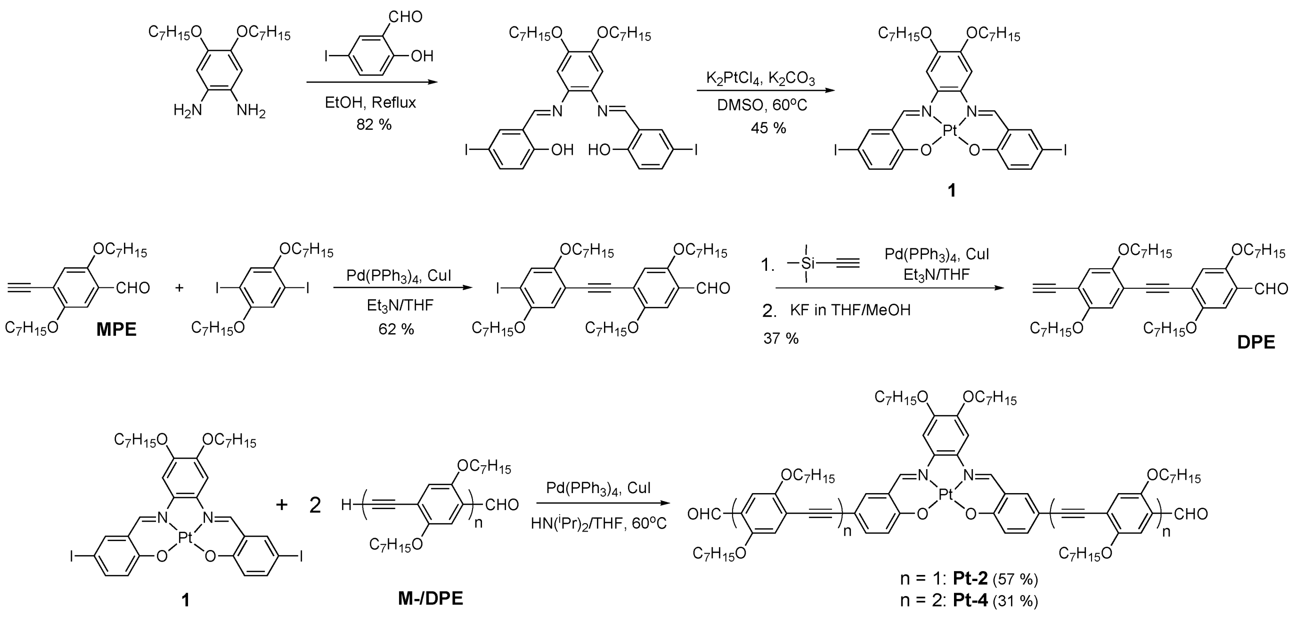
‡ Electronic supplementary information (ESI) available: Experimental details and characterisation, including mono- and di(phenylene-ethynylene) synthesis; ES-MS and calculated isotopic distribution for **Pt-2** and **Pt-4**; solvent effects upon emission of **Pt-4**; 77 K glassy emission and transient absorption–difference spectra. See DOI: 10.1039/b715495j



Scheme 1

Table 1 Photophysical data[a,b]

Complex	UV-vis λ_{max} ($\varepsilon \times 10^4$)	298 K fluid λ_{max}^{em} (τ; Φ)	77 K glass λ_{max}^{em} (τ)[e]	77 K solid λ_{max}^{em} (τ)
Pt-2	292 (4.80), 398 (10.2), 509 (1.56), 553 (sh, 0.87)	596, 658 (max), 727 (1.2; 2.5×10^{-3})	651 (max), 716 (4.2)	671 (max), 745 (1.6)
Pt-4	312 (6.67), 404 (12.8), 501 (1.88), 555 (sh, 1.01)	604, 658 (max), 725 (1.3; 3.1×10^{-3})	646 (max), 714 (2.3)	685 (max), 758 (1.1)
	[c]310 (7.20), 399 (13.9), 496 (2.04), 554 (sh, 1.05)	[c] 601, 653 (max), 720 (1.6; 7.4×10^{-3})		
	[d]304 (6.63), 403 (13.6), 509 (1.80), 571 (sh, 0.93)	[d]608, 659 (max), 727 (2.2; 2.6×10^{-2})		
DPE	304 (2.19), 314 (2.12), 397 (2.99)	457		

[a] λ in nm; ε in dm^3 mol^{-1} cm^{-1}; lifetimes (τ) in μs. [b] In CH_2Cl_2 unless specified. [c] In THF. [d] In toluene. [e] In 2-Me-THF.

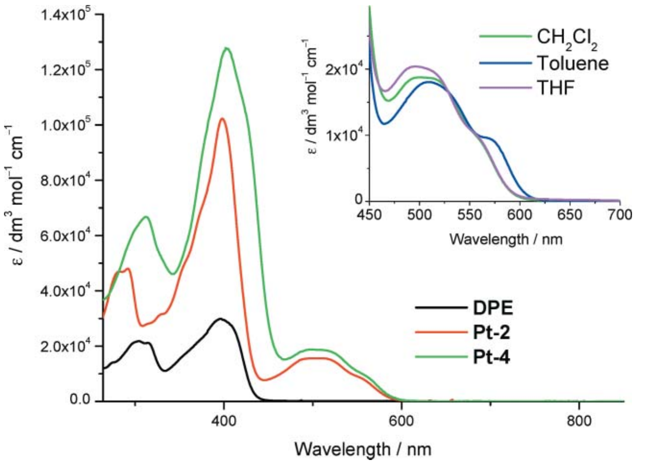


Fig. 1 UV-vis absorption spectra of **Pt-2**, **Pt-4** and **DPE** in CH_2Cl_2 at 298 K. Inset: negative solvatochromic shifts for low-energy absorptions of **Pt-4**.

negative solvatochromic shifts indicate that the ground state is more polar than the excited state and have been previously detected for related Pt–Schiff base derivatives[5,12] such as Ptq_2.[13] We therefore similarly assign this absorption to a charge transfer transition involving the phenoxide lone pair (l) and the imine π* orbital, *i.e.* ^{1}[l(phenoxide) → π*(imine)], mixed with ^{1}[Pt(5d) → π*(Schiff base)] MLCT character.

Complexes **Pt-2** and **Pt-4** display structured phosphorescence in fluid solution (λ_{max} 658 [sh 596 and 604 respectively] nm in CH_2Cl_2; Fig. 2) and the solid state (λ_{max} 660 [sh 725] and 668 [sh 730] nm respectively) at room temperature. Compared with the

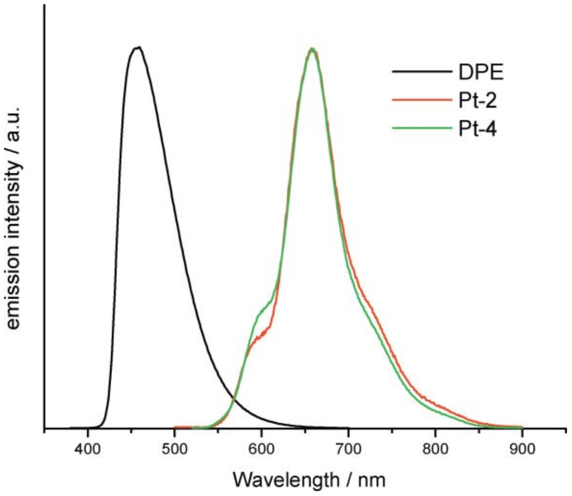


Fig. 2 Normalised emission spectra of **Pt-2**, **Pt-4** and **DPE** in CH_2Cl_2 at 298 K.

absorption data, the fluid emission of **Pt-4** displays less prominent solvatochromic effects (*e.g.* λ_{max} 651 nm in THF is red-shifted by *ca.* 190 cm^{-1} to 659 nm in toluene).‡ Emission lifetimes in the 1–2 μs regime and luminescent quantum yields of up to 2.6×10^{-2} for **Pt-4** in toluene are recorded. The 77 K glassy emission of **Pt-2** and **Pt-4** in 2-Me-THF are partially blue-shifted and highly structured;‡ for example, **Pt-4** exhibits peak maxima at 646 and 714 nm (vibronic progression = 1470 cm^{-1}). As expected, all excitation spectra (monitored at the emission energy) are comparable in shape to the corresponding UV-vis absorption spectra. Upon consideration of the large Stokes shifts, negative solvatochromism and previous assignments,[5,12,13] plus the vibronic progressions of *ca.* 1400–1500 cm^{-1} in the 77 K solid-state and glassy emission spectra, we assign the excited states of **Pt-2** and **Pt-4** to mixed ^{3}MLCT and $^3[l \rightarrow \pi^*(\text{imine})]$ (l = lone pair/phenoxide) parentage.

The transient absorption–difference (TA) spectrum‡ for the excited state of **Pt-4** (900 ns delay) in CH_2Cl_2 at 298 K is characterized by bleaching in the ππ* region ($\lambda < 470$ nm), an excited-state absorption band at *ca.* λ_{max} 505 nm, and additional absorptions extending and rising in the visible region ($\lambda >$ 600 nm) towards the near-IR. While the latter far-red absorptions are not detected in the TA spectra of previously reported Pt–Schiff base analogues[5a,b] and are reminiscent of the OPE ππ* state,[9b,c,14] we suggest further investigations to resolve the detailed contribution and impact of the OPE units upon the excited state. The decay lifetime (τ_{TA}) of 1.4 μs approaches the emission lifetime (1.3 μs), indicating that the observed excited-state absorption can be ascribed to the excited state of **Pt-4**.

Significantly, with regards to sensing applications, the phosphorescent characteristics of the oligomeric **Pt-2** and **Pt-4** derivatives (prominent MLCT component in the excited state; higher quantum yields; low-energy red emission where the human eye is more perceptive) are promising and nevertheless appealing compared with the previously reported Zn/Ni/V-based poly(salphenylene–ethynylene)s[8] (weakly or non-emissive) and Pt–oligo/poly(phenylene)s[4] (dominated by ^{3}LC/ππ* excited state). It is anticipated that the prominent spin–orbit coupling and MLCT character evident in the excited states of **Pt-2** and **Pt-4** can be exploited in due course. Needless to say, we have attempted the Pd-catalysed polymerisation of the diiodo complex **1** with 2,5-diheptyloxy-1,4-diethynylbenzene, but the resultant deep red solid proved intractable and insoluble in organic solvents. Longer alkyl chains are apparently required, and studies dedicated to the fabrication of phosphorescent conjugated polymers featuring Pt–salen moieties are in progress. In conclusion, monodispersed phenylene–ethynylene oligomers linked by a phosphorescent Pt(II) Schiff base unit have been designed and synthesised, and interesting emissive properties have been observed. Based on this work, we envisage that new classes of Pt(II)–Schiff base conjugated materials can be developed for luminescent sensing applications.

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