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Platinum(II) Schiff Base as Versatile Phosphorescent Core Component in Conjugated Oligo(phenylene-ethynylene)s

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ESI available: experimental details and characterisation, including mono- and di(phenylene-ethynylene) synthesis; ES-MS and calculated isotopic distribution (M⁺) for Pt-2 and Pt-4; solvent effects upon fluid emission of Pt-4 at 298 K; 77 K glassy emission and transient absorption-difference spectra.

General Considerations

All reactions were performed under a nitrogen atmosphere and solvents for syntheses (analytical grade) were used without further purification. Solvents for photophysical measurements were purified according to conventional methods. ¹H and ¹³C NMR spectra were obtained on Bruker DRX 300, 400 and 500 FT-NMR spectrometers (ppm) using Me₄Si as internal standard. ESI mass spectra were measured on a Perkin-Elmer Sciex API 365 mass spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer. Elemental analyses were performed on an Elementar Analysensysteme GmbH Vario EL elemental analyzer. UV-vis absorption spectra were obtained on an Agilent 8453 diode array spectrophotometer.
Steady-state emission spectra were recorded on a SPEX FluoroLog 3-TSCPC spectrophotometer equipped with a Hamamatsu R928 PMT detector, and emission lifetime measurements were conducted using NanoLed sources in the fast MCS mode. Sample and standard solutions were degassed with at least three freeze-pump-thaw cycles. Low-temperature (77 K) emission spectra for glasses and solid-state samples were recorded in 5-mm diameter quartz tubes which were placed in a liquid nitrogen Dewar equipped with quartz windows. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability. The emission quantum yield was measured (J. N. Demas, G. A. Crosby, *J. Phys. Chem.* 1971, 75, 991) by using [Ru(bpy)3](PF6)2 in degassed acetonitrile as the standard (Φr = 0.062) and calculated by:

\[
\Phi_s = \Phi_r \left(\frac{B_r}{B_s}\right) \left(\frac{n_s}{n_r}\right)^2 \left(\frac{D_s}{D_r}\right)
\]

where the subscripts s and r refer to sample and reference standard solution respectively, n is the refractive index of the solvents, D is the integrated intensity, and Φ is the luminescence quantum yield. The quantity B is calculated by the equation: 

\[
B = 1 - 10^{-\Delta L};
\]

where A is the absorbance at the excitation wavelength and L is the optical path length. Errors for λ (± 1 nm), τ (± 10 %), and Φ (± 10 %) are estimated.

**Synthesis**


**Scheme S1**

![Scheme S1](image)

Synthetic method for DPE (Scheme S2) also employed the procedure described by Nierengarten at al. (*Helv. Chim. Acta*, 2004, 87, 2948) using 4-[2,5-bis(heptoxy)-4-
iodophenyl)ethynyl]-2,5-bis(heptoxy)benzaldehyde [62 %; $^1$H NMR (300 MHz, CDCl$_3$): 10.45 (s, 1H), 7.32 (s, 1H), 7.31 (s, 1H), 7.10 (s, 1H), 6.91 (s, 1H), 4.06-3.94 (m, 8H), 1.86-1.80 (m, 8H), 1.49-1.25 (m, 32H), 0.92-0.84 (m, 12H)], and 4-[2,5-bis(heptoxy)-4-[(trimethylsilyl)ethynyl]phenyl]ethynyl]-2,5-bis(heptoxy)benzaldehyde [39 %; $^1$H NMR (300 MHz, CDCl$_3$): 10.45 (s, 1H), 7.32 (s, 1H), 7.10 (s, 1H), 6.97 (s, 1H), 6.96 (s, 1H), 4.07-3.95 (m, 8H), 1.87-1.79 (m, 8H), 1.52-1.26 (m, 32H), 0.92-0.84 (m, 12H), 0.27 (s, 9H)].

**Scheme S2**

DPE. A 50 mL flask charged with the Me$_3$Si-protected precursor (0.1 g, 0.132 mmol) and KF (0.115 g, 1.98 mmol) in THF (5 mL) and methanol (5 mL) was stirred at room temperature for 20 hours. The mixture was concentrated under vacuum and re-dissolved in CH$_2$Cl$_2$. The resulting yellow solution was filter through a pad of silica gel with copious washing of CH$_2$Cl$_2$. The concentrated product was obtained as a yellow solid which required no further purification (0.086 g, 96 %). $^1$H NMR (300 MHz, CDCl$_3$): 10.45 (s, 1H), 7.32 (s, 1H), 7.10 (s, 1H), 7.00 (s, 1H), 6.99 (s, 1H), 4.07-3.97 (m, 8H), 3.37 (s, 1H), 1.84-1.79 (m, 8H), 1.56-1.27 (m, 32H), 0.92-0.84 (m, 12H).

**Scheme S3**

The diiodo Schiff base ligand (Scheme S3) was prepared by a typical bis-condensation reaction between 1,2-bis-heptoxy-4,5-diaminobenzene and 2 equivalents of...
2-hydroxy-5-iodo-benzaldehyde in ethanol (82 % yield). \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): 13.21 (s, 2H), 8.52 (s, 2H), 7.68 (d, \( J = 2.2 \) Hz, 2H), 7.60-7.57 (dd, \( J = 8.6, 2.2 \) Hz, 2H), 6.85 (d, \( J = 8.9 \) Hz, 2H), 6.78 (s, 2H), 4.07 (t, \( J = 6.5 \), 4H), 1.86 (m, 4H), 1.57-1.25 (m, 16H). Synthesis of complex 1 was based on a literature report (C. M. Che, S. C. Chan, H. F. Xiang, M. C. W. Chan, Y. Liu and Y. Wang, Chem. Commun., 2004, 1484) and a red shiny product was obtained (45% yield). \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): 8.00 (s, 2H), 7.53(d, \( J = 9.2 \) Hz, 2H), 7.45 (s, 2H), 6.90 (d, \( J = 9.6 \) Hz, 2H), 6.77 (s, 2H), 3.78 (t, \( J = 6.6 \) Hz, 4H), 1.70 (m, 4H), 1.36 (m, 16H), 0.95 (t, \( J = 6.7 \) Hz, 6H). ESI-MS (+ve mode): \( m/z \) 990 [M + H]\(^+\).

### Scheme S4

\[
\begin{align*}
\text{Pt-n (n = 2, 4). A similar procedure was employed for both complexes. For Pt-4, a} \\
\text{50 mL flask was charged with 1 (0.1 g, 0.146 mmol), DPE (0.07 g, 0.069 mmol), CuI (0.3} \\
\text{mg, 0.0014 mmol) and Pd(PPh\(_3\))\(_4\) (1.6 mg, 0.0014 mmol) under a nitrogen atmosphere.} \\
\text{Dry THF (10 mL) and diisopropylamine (10 mL) were successively added by syringe, and} \\
\text{the mixture was stirred at 70 °C for 3 days. The mixture was allowed to cool and was} \\
\text{filtered through a pad of silica gel with copious washing of CH\(_2\)Cl\(_2\). After removal of} \\
\text{volatiles under vacuum, the crude product was purified by SiO\(_2\) column chromatography} \\
\text{(diethyl ether/hexane) to afford a deep red solid (0.045 g, 31 %). Found: C, 70.89; H, 7.85;} \\
\text{N, 1.48. C\(_{124}\)H\(_{170}\)N\(_2\)O\(_{14}\)Pt (2107.79) requires C, 70.66; H, 8.13; N, 1.33.} \\
\text{\( ^1 \)H NMR (300 MHz, CDCl\(_3\)): 10.44 (s, 2H), 8.43 (s, 2H), 7.72 (d, \( J = 1.8 \) Hz, 2H), 7.62} \\
\text{(dd, \( J = 1.9 \) Hz, 2H), 7.32 (d, \( J = 9.2 \) Hz, 2H), 7.31 (s, 2H), 7.17 (s, 2H), 7.09 (s, 2H), 7.00} \\
\text{(s, 2H), 6.97 (s, 2H), 4.08-4.01 (m, 20H), 1.91-1.78 (m, 20H), 1.56-1.29 (m, 40H), 0.94-0.86} \\
\text{(m, 30H). \( ^{13} \)C NMR (126 MHz, CDCl\(_3\)): 189.2 (C=O), 165.2, 155.6, 153.8, 153.5, 153.4, 149.5, 147.0, 138.5, 137.9, 124.8, 123.0, 121.9, 120.9, 117.5, 117.3, 116.9, 115.2, 113.2, 111.7, 110.1, 99.0, 94.8 (C=C), 94.1 (C≡C), 90.8 (C≡C), 84.8 (C≡C), 69.9, 69.7, 69.4, 69.2, 31.9–31.8} \\
\text{(4 peaks), 29.4–29.0 (7 peaks), 26.1–25.9 (4 peaks), 22.6, 14.1–14.0 (3 peaks). ES-MS} \\
\text{(+ve mode): \( m/z \) 2107 [M + H]\(^+\).}
\end{align*}
\]
For **Pt-2**, the mixture was stirred at 60 °C for 24 hours, and a deep red solid was obtained in 57 % yield. Found: C, 66.84; H, 7.20; N, 1.85. C₈₀H₁₀₆N₂O₁₀Pt·(C₆H₁₄)₀.₃ (1476.66) requires C, 66.53; H, 7.52; N, 1.90. ¹H NMR (300 MHz, CDCl₃) 10.27 (s, 2H), 7.63 (s, 2H), 7.32 (s, 2H), 7.08-7.01 (m, 6H), 6.84 (s, 2H), 6.58 (s, 2H), 3.98 (m, 8H), 3.70 (br, 4H), 1.94 (br, 4H), 1.75 (br, 8H), 1.40-1.28 (m, 48H), 0.97-0.86 (m, 18H). ¹³C NMR (126 MHz, CDCl₃): 188.9 (C=O), 163.8, 155.9, 152.8, 152.7, 149.3, 145.8, 143.2, 138.6, 138.4, 136.9, 124.0, 122.3, 121.5, 116.4, 111.4, 111.1, 100.2, 97.2 (C≡C), 84.9 (C≡C), 70.3, 68.6, 32.0, 31.9, 31.8, 29.6–29.1 (6 peaks), 26.2, 26.1–26.0 (2 peaks), 22.8–22.7 (2 peaks), 22.6, 14.1, 14.0. ESI-MS (+ve mode): m/z 1452 [M + H]^+. 
Figure S1. ESI mass spectrum of [M + H]^+ in CH₂Cl₂ (upper) and calculated isotopic distribution (lower) for Pt-2.
Figure S2. ESI mass spectrum of \([M + H]^+\) in CH\(_2\)Cl\(_2\) (upper) and calculated isotopic distribution (lower) for Pt-4.
Table S1. UV-Vis Absorption Data in CH$_2$Cl$_2$ at 298 K

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-2</td>
<td>292 (48040), 398 (102280), 509 (15630), 553 (sh, 8680)</td>
</tr>
<tr>
<td>Pt-4</td>
<td>312 (66730), 404 (127590), 501 (18770), 555 (sh, 10110)</td>
</tr>
<tr>
<td>Pt-4$^a$</td>
<td>310 (72020), 399 (138940), 496 (20410), 554 (sh, 10470)</td>
</tr>
<tr>
<td>Pt-4$^b$</td>
<td>304 (66310), 403 (136190), 509 (18040), 571 (sh, 9310)</td>
</tr>
<tr>
<td>DPE</td>
<td>304 (21860), 314 (21190), 397 (29900)</td>
</tr>
</tbody>
</table>

$^a$ In THF. $^b$ In toluene

Table S2. Emission Data

<table>
<thead>
<tr>
<th>Fluid (CH$_2$Cl$_2$)</th>
<th>$\lambda_{\text{ex}}$/nm</th>
<th>298 K: $\lambda_{\text{max}}$/nm; $\tau_o$/µs; $\Phi_o$</th>
<th>77K: $^c$ $\lambda_{\text{max}}$/nm; $\tau_o$/µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-2</td>
<td>509</td>
<td>596, 658 (max), 727; 1.2; 2.5 × 10$^{-3}$</td>
<td>651 (max), 716; 4.2</td>
</tr>
<tr>
<td>Pt-4</td>
<td>503</td>
<td>604, 658 (max), 725; 1.3; 3.1 × 10$^{-3}$</td>
<td>646 (max), 714; 2.3</td>
</tr>
<tr>
<td>Pt-4$^a$</td>
<td>493</td>
<td>601, 653 (max), 720; 1.6; 7.4 × 10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Pt-4$^b$</td>
<td>509</td>
<td>608, 659 (max), 727; 2.2; 2.6 × 10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>DPE</td>
<td>314</td>
<td>457</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid state</th>
<th>$\lambda_{\text{ex}}$/nm</th>
<th>298 K: $\lambda_{\text{max}}$/nm</th>
<th>77K: $\lambda_{\text{max}}$/nm; $\tau_o$/µs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-2</td>
<td>509</td>
<td>660 (max) 725</td>
<td>671 (max), 745; 1.6</td>
</tr>
<tr>
<td>Pt-4</td>
<td>502</td>
<td>668 (max) 730</td>
<td>685 (max), 758; 1.1</td>
</tr>
</tbody>
</table>

$^a$ In THF. $^b$ In toluene. $^c$ In 2-Me-THF.
Figure S3. Emission spectra of Pt-4 in different solvent at 298 K.

Figure S4. Emission spectra of Pt-2 and Pt-4 in 2-Me-THF at 77 K.
Figure S5. Transient absorption difference spectrum of Pt-4 (conc. = 1.025 × 10⁻⁵ M) recorded 900 ns after 355 nm excitation in degassed CH₂Cl₂ at 298 K.