

Intramolecular excimers based on rigidly-linked platinum(II) complexes: an alternative approach to highly luminescent, deep-red triplet emitters

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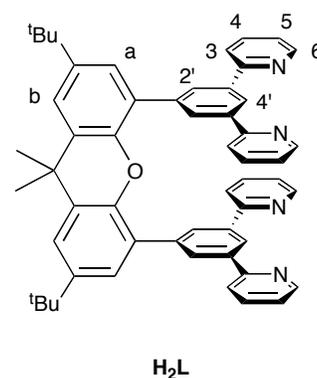
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A. Details of synthetic procedures

NMR spectra were recorded on a Varian Mercury-400 operating at 400 MHz, and were referenced to residual solvent resonances. All chemical shifts listed below are quoted in ppm and coupling constants J are in Hertz. Electrospray ionisation mass spectra were recorded in +ve ion mode with a Micromass LCT spectrometer with methanol or acetonitrile as the carrier solvent. In the case of charge-neutral platinum(II) complexes based on the $[\text{Pt}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Cl}]$ structure, dissociation of the chloride ligand and its substitution by solvent is commonly observed in the mass spectrometer when MeCN is used as the carrier, leading to a cationic species that is detectable by +ve ion electrospray. The key starting material 3,5-di(2-pyridyl)-1-bromobenzene (dpybH-Br) was prepared by a palladium-catalysed Stille cross-coupling of 1,3,5-tribromobenzene and 2-tributylstannyl pyridine, as described previously [S.J. Farley, D.L. Rochester, A.L. Thompson, J.A.K. Howard and J.A.G. Williams, *Inorg. Chem.*, 2005, **44**, 9690].

1. Synthesis of 4,5-bis(3,5-di-(2-pyridyl)-phenyl)-2,7-di-tert-butyl-9,9-dimethylxanthene, H_2L

Butyl lithium (1.2 mL of a 3 M solution in hexanes, 3.0 mmol) was added dropwise at -78°C to a solution of 3,5-di(2-pyridyl)-1-bromobenzene (dpybH-Br, 770 mg, 2.5 mmol) in dry THF (10 mL). After stirring for 30 min, trimethoxyborate (312 mg, 3.0 mmol) was added dropwise to the mixture and stirring continued for a further 1 h at -78°C . After allowing the solution to warm to room temperature, water was added (50 mL), and the mixture then extracted into ethyl acetate (3×50 mL). The solution was dried over sodium sulfate and the solvent evaporated under reduced pressure to give crude 1,3-di(2-pyridyl)benzene-5-boronic acid (dpybH-B), which was used directly in the next step without further purification. A mixture of the crude dpybH-B and 4,5-dibromo-2,7-di-tert-butyl-9,9-dimethylxanthene, (Br-xnth-Br, 207 mg, 0.43 mmol) in dimethoxyethane was degassed via three

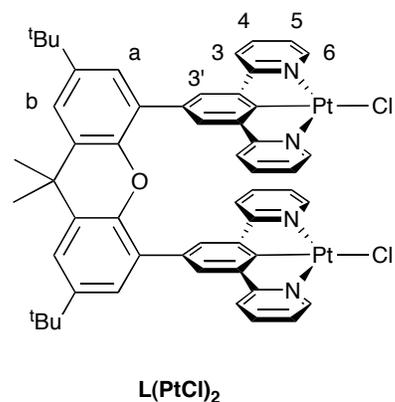


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freeze-pump-thaw cycles and placed under nitrogen. Tetrakis(triphenylphosphine)palladium (50 mg, 0.04 mmol) and sodium carbonate dissolved in water (137 mg in 0.5 mL) were added under a flow of nitrogen, and the mixture was heated at reflux for 3 days. The residue obtained upon removal of solvent was taken up into a mixture of dichloromethane (50 mL) and water (50 mL), and the organic layer was separated and washed with more water (3 × 50 mL). After drying of the organic phase over anhydrous sodium sulfate, the solvent was removed under reduced pressure. The yellow residue was purified by column chromatography on silica gel, gradient elution from hexane to 20% hexane / 80% ethylacetate, to give H₂L as a colourless solid (270 mg, 80%). ¹H NMR (CDCl₃, 400MHz): δ = 8.51 (4H, d, ³J = 5.0, H⁶), 8.14 (2H, d, ⁴J = 1.5, H⁴), 8.00 (4H, d, ⁴J = 1.5, H^{2'}), 7.49 (2H, d, ⁴J = 2.0, H^a or H^b), 7.39 (4H, td, ³J = 6.5, ⁴J = 1.5, H⁴), 7.37 (4H, overlapping with H⁴, H³), 7.29 (2H, d, ⁴J = 2.0, H^a or H^b), 6.90 (4H, ddd, ³J = 6.5, 5.0, ⁴J = 1.5, H⁵), 1.83 (6H, s, Me), 1.38 (18H, s, *t*-Bu). MS (ES⁺): *m/z* = 783 (M+H⁺), 1565 (2M+H⁺), 1587 (2M+Na⁺). HRMS = 783.4071 (M+H⁺); calc. for C₅₅H₅₁N₄O, 783.4063.

2. Preparation of L(PtCl)₂

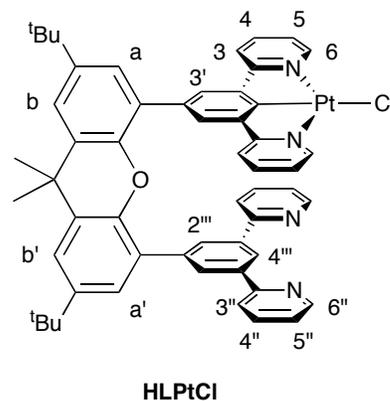
The ligand H₂L (62 mg, 0.08 mmol) was dissolved in de-aerated acetonitrile (3 mL), and an aqueous solution of K₂PtCl₄ (115 mg, 0.28 mmol in 1 mL water) was added under a nitrogen atmosphere via cannula. The mixture was heated at reflux under nitrogen for 11 days. Upon cooling, the orange precipitate that had formed was separated by centrifugation, and washed with water (4 × 5 mL), ethanol (4 × 5 mL), and diethyl ether (4 × 5 mL). The solid was extracted into dichloromethane, the solution separated from a small amount of beige



solid residue by centrifugation, and the solvent removed under reduced pressure to give the desired dinuclear complex L(PtCl)₂; (30 mg, 30%). ¹H NMR (400 MHz, CDCl₃): δ 9.37 (4H, d, ³J = 5.0, ³J(¹⁹⁵Pt) = 36, H⁶), 7.52 (2H, d, ⁴J = 2.0, H^a or H^b), 7.35 (8H, overlapping m, H⁴ and H^{3'}), 7.25 (2H, d, ⁴J = 2.0, H^a or H^b), 7.22 (4H, d, ³J = 7.0, H³), 7.09 (4H, dd, ³J = 6.5, 5.0, H⁵), 1.83 (6H, s, Me), 1.83 (6H, s, *t*-Bu), 1.41 (6H, s). MS (ES⁺): *m/z* = 1245 [M-Cl⁻ + MeCN]⁺, with isotope match consistent with C₅₅H₄₈N₄OPt₂Cl·CH₃CN. HRMS (ES⁺) = 1246.3066; calc. for C₅₇H₅₁N₅O¹⁹⁵Pt₂³⁵Cl, 1246.3078. Anal. calc. for C₅₅H₄₈N₄OPt₂Cl₂: C, 53.2, H, 3.9, N, 4.5 %. Found: C, 53.8, H, 4.2, N, 5.0 %.

3. Preparation of HLPtCl

The mononuclear complex was obtained in a similar manner upon reaction of H₂L (60 mg, 0.08 mmol) with 1.1 equiv. of K₂PtCl₄ (36 mg, 0.09 mmol) for a period of 3 days at reflux. The product was isolated as a yellow solid (65 mg, 80%). ¹H NMR (400 MHz, CDCl₃): δ 9.18 (2H, d, ³J = 5.0, ³J(¹⁹⁵Pt) = 42, H⁶), 8.48 (2H, d, ³J = 5.0, H^{6''}), 8.10 (2H, s, H^{2'''}), 7.98 (1H, s, H^{4'''}), 7.65 (1H, s, xanthene H), 7.61 (1H, s, xanthene H), 7.46 (8H, overlapping m), 7.23 (4H, two overlapping m and overlapped CHCl₃), 6.95 (2H, t, ³J = 5.0, H⁵ or H^{5''}), 6.85 (2H, t, ³J = 5.0, H⁵ or H^{5''}), 1.81 (6H, s, Me), 1.38 (9H, s, *t*-Bu), 1.36 (9H, s, *t*-Bu). MS (ES⁺): *m/z* = 976 [M-Cl]⁺, with isotope match consistent with C₅₅H₄₉N₄OPt. HRMS (ES⁺) = 975.8232; calc. for C₅₅H₄₉N₄O¹⁹⁵Pt³⁵Cl, 975.8243.



B. Details of procedures and instrumentation for photophysical measurements

UV-visible absorption spectra were recorded using a Biotech Instruments XS spectrometer in quartz cuvettes of 1 cm pathlength, against a reference of pure solvent contained within a matched cuvette. Steady-state luminescence spectra were recorded using an Instruments S.A. Fluoromax-2 spectrometer, equipped with a Hamamatsu R928 photomultiplier tube. Room temperature measurements were made in quartz fluorescence cuvettes of 1 cm pathlength, modified to allow degassing via a vacuum line. Samples were degassed via three freeze-pump-thaw cycles to a base pressure < 10⁻² mbar as monitored using a Pirani gauge connected to the line. Emission spectra shown have been corrected for the spectral response of the detector; quoted values of λ_{max} refer to the corrected spectra. The standards used in the measurement of luminescence quantum yields were fluorescein in 0.1 M NaOH_(aq), Φ_{lum} = 0.90 [J. N. Demas and G.A. Crosby, *J. Am. Chem. Soc.*, 1970, **92**, 7262], and Ru(bpy)₃Cl₂ in H₂O, Φ_{lum} = 0.90 [K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697].

Low temperature (77 K) measurements were obtained using a home-built liquid-nitrogen Dewar. Samples were contained within 4 mm external-diameter glass tubes, and the spectra were recorded as described above.

Luminescence lifetimes were measured by time-correlated single-photon counting (TCSPC) following excitation at 374.0 nm with an EPL-375 pulsed diode laser. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator.