

**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

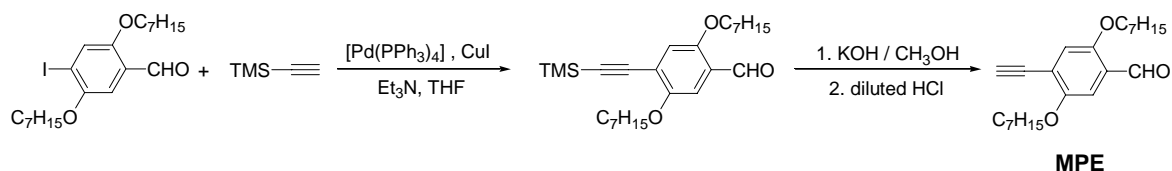
All reactions were performed under a nitrogen atmosphere and solvents for syntheses (analytical grade) were used without further purification. Solvents for photophysical measurements were purified according to conventional methods. ^1H and ^{13}C NMR spectra were obtained on Bruker DRX 300, 400 and 500 FT-NMR spectrometers (ppm) using Me_4Si 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 $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in degassed acetonitrile as the standard ($\Phi_r = 0.062$) and calculated by: $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$, 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: $B = 1 - 10^{-AL}$; 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

Published procedures or minor modifications thereof were used for the preparation of the following compounds: 4-iodo-2,5-di(heptoxy)benzaldehyde and 2,5-di(heptoxy)-4-ethynylbenzaldehyde (**MPE** according to Scheme S1: J-F. Nierengarten, T. Gu, G. Hadziioannou, D. Tsamouras and V. Krasnikov, *Helv. Chim. Acta*, 2004, **87**, 2948); 1,2-bis-heptoxy-4,5-diaminobenzene (C. W. Ong, S. C. Liao, T. H. Chang and H. F. Hsu, *J. Org. Chem.*, 2004, **69**, 3181).

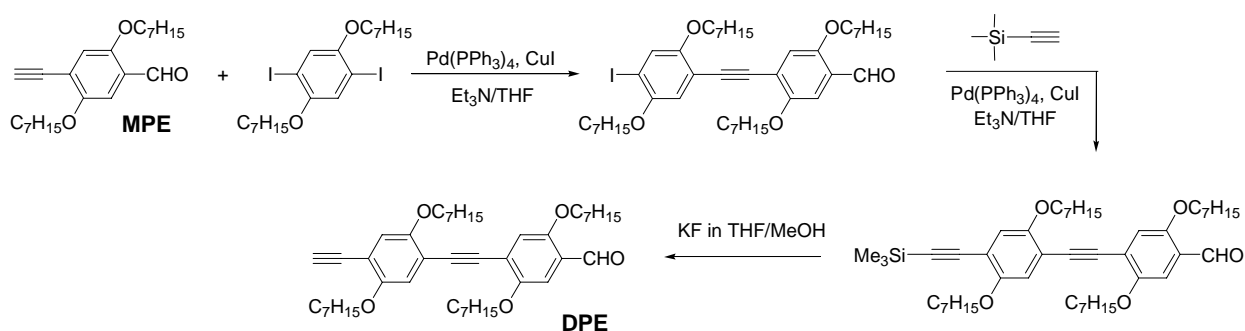
Scheme S1



Synthetic method for **DPE** (Scheme S2) also employed the procedure described by Nierengarten et al. (*Helv. Chim. Acta*, 2004, **87**, 2948) using 4- $[\{2,5\text{-bis(heptoxy)-4-}$

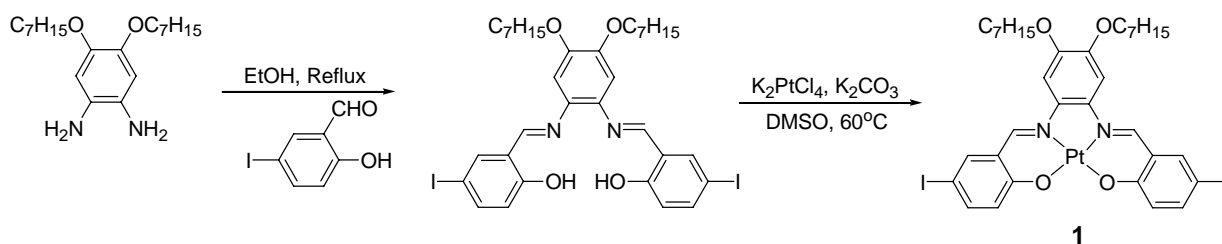
iodophenyl}ethynyl]-2,5-bis(heptoxy)benzaldehyde [62 %; ^1H NMR (300 MHz, CDCl_3): 10.45 (s, 1H), 7.32 (s, 1H), 7.31 (s, 1H), 7.10 (s, 1H), 6.91 (s, 1H), 4.06-3.94 (m, 8H), 1.86-1.80 (m, 8H), 1.49-1.25 (m, 32H), 0.92-0.84 (m, 12H)], and 4-[(trimethylsilyl)ethynyl]-phenyl}ethynyl]-2,5-bis(heptoxy)benzaldehyde [39 %; ^1H 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_3Si -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_2Cl_2 . The resulting yellow solution was filter through a pad of silica gel with copious washing of CH_2Cl_2 . The concentrated product was obtained as a yellow solid which required no further purification (0.086 g, 96 %). ^1H 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).

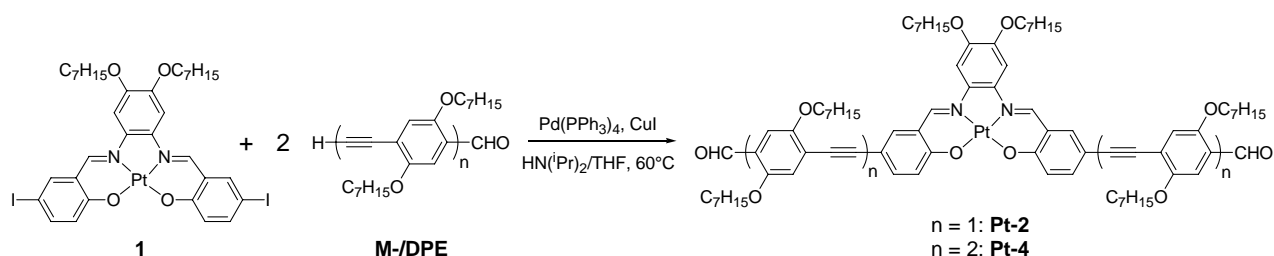
Scheme S3



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). $^1\text{H NMR}$ (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). $^1\text{H NMR}$ (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 $[\text{M} + \text{H}]^+$.

Scheme S4



Pt-n ($n = 2, 4$). A similar procedure was employed for both complexes. For **Pt-4**, a 50 mL flask was charged with **1** (0.1 g, 0.146 mmol), **DPE** (0.07 g, 0.069 mmol), CuI (0.3 mg, 0.0014 mmol) and Pd(PPh_3)₄ (1.6 mg, 0.0014 mmol) under a nitrogen atmosphere. Dry THF (10 mL) and diisopropylamine (10 mL) were successively added by syringe, and the mixture was stirred at 70 °C for 3 days. The mixture was allowed to cool and was filtered through a pad of silica gel with copious washing of CH_2Cl_2 . After removal of volatiles under vacuum, the crude product was purified by SiO_2 column chromatography (diethyl ether/hexane) to afford a deep red solid (0.045 g, 31 %). Found: C, 70.89; H, 7.85; N, 1.48. $\text{C}_{124}\text{H}_{170}\text{N}_2\text{O}_{14}\text{Pt}$ (2107.79) requires C, 70.66; H, 8.13; N, 1.33. $^1\text{H NMR}$ (300 MHz, CDCl_3): 10.44 (s, 2H), 8.43 (s, 2H), 7.72 (d, $J = 1.8$ Hz, 2H), 7.62 (dd, $J = 1.9$ Hz, 2H), 7.32 (d, $J = 9.2$, 2H), 7.31 (s, 2H), 7.17 (s, 2H), 7.09 (s, 2H), 7.00 (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 (m, 30H). $^{13}\text{C NMR}$ (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 \equiv C), 94.1 (C \equiv C), 90.8 (C \equiv C), 84.8 (C \equiv C), 69.9, 69.7, 69.4, 69.2, 31.9–31.8 (4 peaks), 29.4–29.0 (7 peaks), 26.1–25.9 (4 peaks), 22.6, 14.1–14.0 (3 peaks). ES-MS (+ve mode): m/z 2107 $[\text{M} + \text{H}]^+$.

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. $C_{80}H_{106}N_2O_{10}Pt \cdot (C_6H_{14})_{0.3}$ (1476.66) requires C, 66.53; H, 7.52; N, 1.90. 1H NMR (300 MHz, $CDCl_3$) 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). ^{13}C NMR (126 MHz, $CDCl_3$): 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 CH_2Cl_2 (upper) and calculated isotopic distribution (lower) for **Pt-2**.

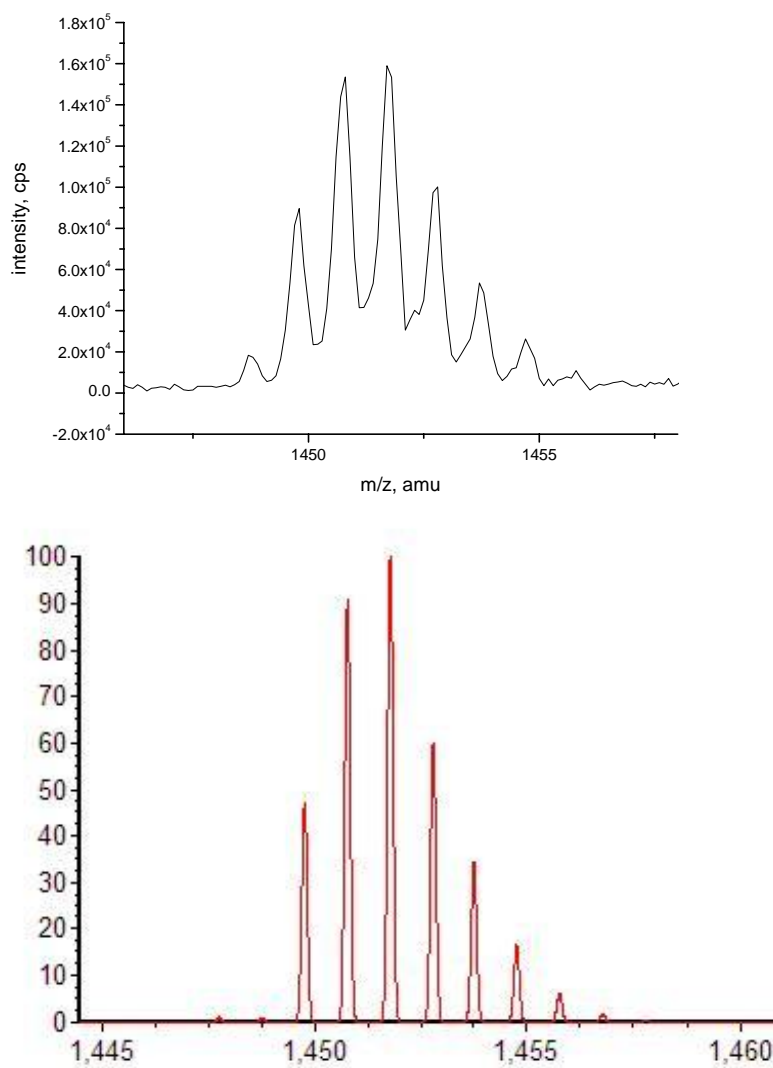


Figure S2. ESI mass spectrum of $[M + H]^+$ in CH_2Cl_2 (upper) and calculated isotopic distribution (lower) for **Pt-4**.

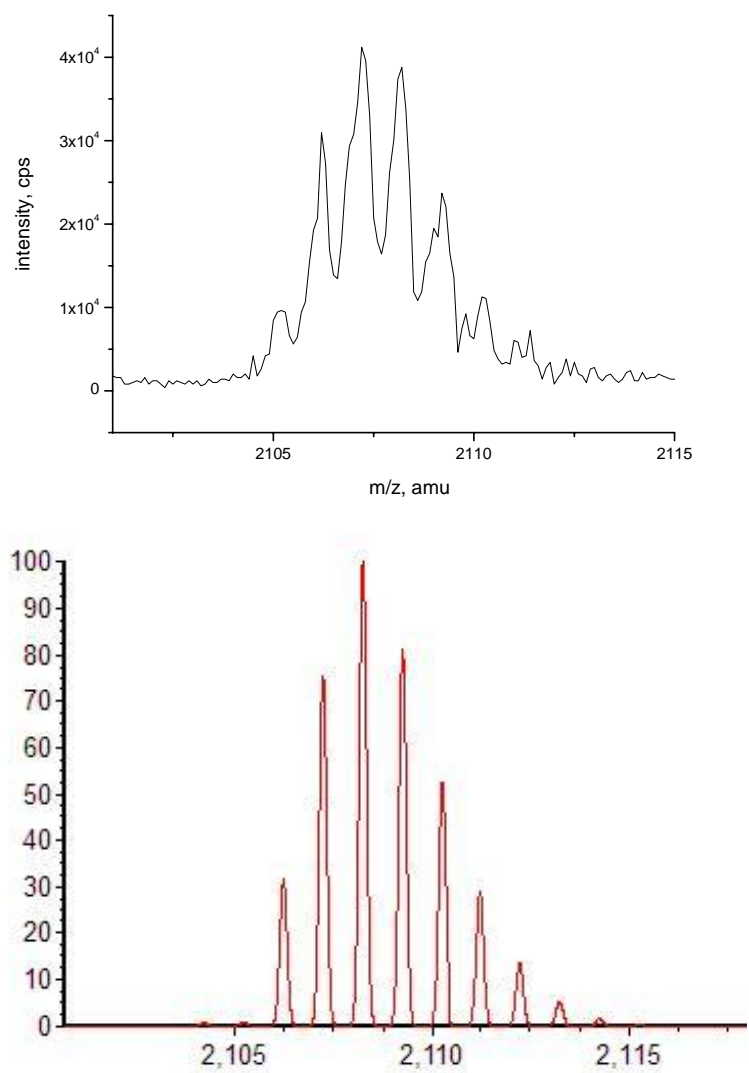


Table S1. UV-Vis Absorption Data in CH₂Cl₂ at 298 K

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

^a In THF. ^b In toluene**Table S2.** Emission Data

Fluid (CH ₂ Cl ₂)	$\lambda_{\text{ex}}/\text{nm}$	298 K: $\lambda_{\text{max}}/\text{nm}$; $\tau_0/\mu\text{s}$; Φ_0	77K: ^c $\lambda_{\text{max}}/\text{nm}$; $\tau_0/\mu\text{s}$
Pt-2	509	596, 658 (max), 727; 1.2; 2.5×10^{-3}	651 (max), 716; 4.2
Pt-4	503	604, 658 (max), 725; 1.3; 3.1×10^{-3}	646 (max), 714; 2.3
Pt-4 ^a	493	601, 653 (max), 720; 1.6; 7.4×10^{-3}	
Pt-4 ^b	509	608, 659 (max), 727; 2.2; 2.6×10^{-2}	
DPE	314	457	

Solid state	$\lambda_{\text{ex}}/\text{nm}$	298 K: $\lambda_{\text{max}}/\text{nm}$	77K: $\lambda_{\text{max}}/\text{nm}$; $\tau_0/\mu\text{s}$
Pt-2	509	660 (max) 725	671 (max), 745; 1.6
Pt-4	502	668 (max) 730	685 (max), 758; 1.1

^a In THF. ^b In toluene. ^c In 2-Me-THF.

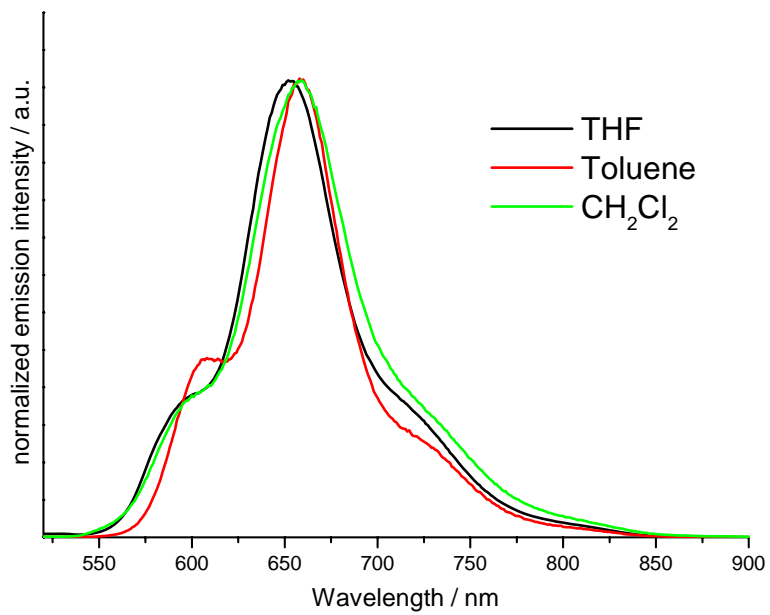


Figure S3. Emission spectra of **Pt-4** in different solvent at 298 K.

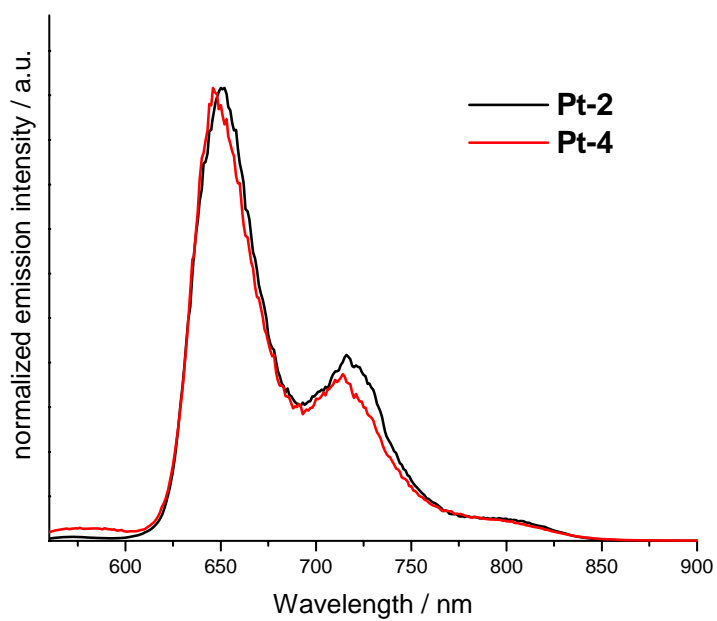


Figure S4. Emission spectra of **Pt-2** and **Pt-4** in 2-Me-THF at 77 K.

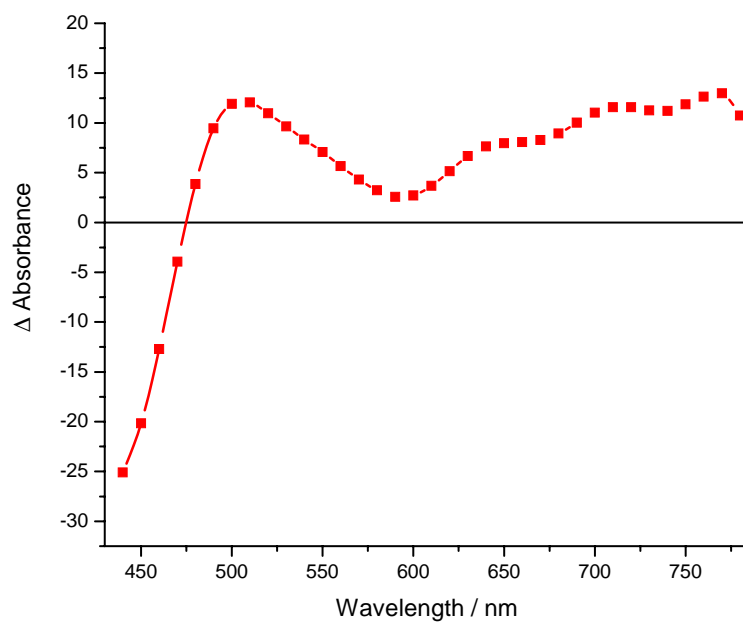


Figure S5. Transient absorption difference spectrum of **Pt-4** (conc. = 1.025×10^{-5} M) recorded 900 ns after 355 nm excitation in degassed CH_2Cl_2 at 298 K.