Supplementary Materials

Diplatinum Alkynyl Chromophores as Sensitisers for Lanthanide Luminescence in Pt_2Ln_2 and Pt_2Ln_4 (Ln = Eu, Nd, Yb) Arrays with Acetylide-functionlized Bipyridine/Phenanthroline

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Experimental Section

[Pt_2(μ-dppm)$_2$(bpyC≡C)$_4$] (**1**). 5-[2-(Trimethylsilyl)-1-ethynyl]-2,2'-bipyridine (220 mg, 0.87 mmol) and [$PtCl_2$(dppm-p,p')] (270 mg, 0.42 mmol) were dissolved in dichloromethane (30 mL) with stirring. To the solution were added a methanol (5 mL) solution of potassium fluoride (52 mg, 0.90 mmol) and copper(I) iodide (5 mg, 0.026 mmol) suspended in acetonitrile (2 mL). The mixture was stirred at room temperature for five days to afford yellow muddy solution. The solvents were removed in vacuo and the crude product was purified by silica gel column chromatography. Elution with dichloromethane-methanol (v/v = 100 : 2) afforded 220 mg of the pure product. Yield: 56%. Anal. Calcd for $C_{98}H_{72}N_8P_4Pt_2$: C, 62.75; H, 3.87; N, 5.97. Found: C, 62.41; H, 4.07; N, 5.96. ESI-MS: *m/z* 1876 $[M+H]^+$, 1696 [M–(bpyC≡C)]$^+$, 758 [M–2(bpyC≡C)]$^{2+}$. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 8.47 (m, 4H, bpy), 8.05 (m, 4H, bpy), 7.87 (m, 16H, Ph), 7.74 (m, 8H, Ph), 7.58 (t, 8H, bpy), 7.19 (m, 16H, Ph), 7.13 (m, 8H, bpy), 6.74 (d, 4H, bpy), 4.77 (m, 4H, PC*H*$_2$P). ^{31}P NMR (202.3 MHz, $CDCl_3$, H_3PO_4): δ 1.14 (t, $J_{\text{Pt-P}}$ = 1385 Hz). IR (KBr): $\bar{\nu}$ 2110 cm^{-1} (w, C≡C).

{Pt_2(μ-dppm)$_2$(bpyC≡C)$_4$}{Ln(hfac)$_3$(H_2O)}$_2$ (Ln = Nd **2**, Eu **3**, Yb **4**). Compound **1** and 4 equiv of Ln(hfac)$_3$(H_2O)$_2$ were stirred in dichloromethane for one hour to give a yellow solution. After filtration, layering hexane onto the concentrated dichloromethane solution gave the Pt_2Ln_2 products as yellow crystals.

2. Yield: 82%. Anal. Calcd for $C_{128}H_{82}F_{36}N_8Nd_2O_{14}P_4Pt_2$: C, 44.66; H, 2.40; N, 3.25. Found: C, 44.31; H, 2.65; N, 3.23. IR (KBr): $\bar{\nu}$ 2107 (C≡C), 1651 (C=O).

3. Yield: 87%. Anal. Calcd for $C_{128}H_{82}Eu_2F_{36}N_8O_{14}P_4Pt_2$: C, 44.46; H, 2.39; N, 3.24. Found: C, 44.68; H, 2.56; N, 3.02. IR (KBr): $\bar{\nu}$ 2108 (C≡C), 1654 (C=O).

4. Yield: 89%. Anal. Calcd for $C_{128}H_{82}F_{36}N_8O_{14}P_4Pt_2Yb_2{\cdot}3CH_2Cl_2$: C, 41.90, H, 2.36; N, 2.98. Found: C, 41.55; H, 2.44; N, 2.88. IR (KBr): $\bar{\nu}$ 2108 (C≡C), 1653 (C=O).

[Pt$_2$(μ-dppm)$_2$(phenC≡C)$_4$] (**5**). 5-ethynyl-1,10-phenanthroline (110 mg, 0.54 mmol) and [PtCl$_2$(dppm)] (160 mg, 0.25 mmol) were dissolved in dichloromethane (30 mL) with stirring. To the solution were added 2 mL of iso-dipropylamine and copper(I) iodide (5 mg, 0.026 mmol) suspended in 2 mL of acetonitrile. The mixture was stirred at room temperature for five days to afford pale-yellow muddy solution. The solvents were removed in vacuo and the crude product was washed with water, acetonitrile and methanol for three times to afford 137 mg of the product. As the product is only slightly soluble in dichloromethane, purification by chromatography is difficult. Yield: 55%. Anal. Calcd for $C_{106}H_{72}N_8P_4Pt_2$: C, 64.56; H, 3.68; N, 5.69. Found: C, 64.41; H, 3.91; N, 5.76. ESI-MS: *m/z* 1973 $[M+H]^+$, 1768 $[M-(bpyC{\equiv}C)]^+$. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 8.52–6.45 (m, 68H, Ph and phen), 4.21 (m, 4H, PC*H*$_2$P). IR (KBr): $\bar{\nu}$ 2090 (C≡C).

{Pt$_2$(μ-dppm)$_2$(phenC≡C)$_4$}{Ln(hfac)$_3$}$_4$ (Ln = Nd **6**, Eu **7**, Yb **8**)**.** The Pt$_2$Ln$_4$ complexes were prepared by addition of 4.2 equiv of Ln(hfac)$_3$(H$_2$O)$_2$ to a dichloromethane solution of **5** with stirring for one hour. After filtration, the concentrated dichloromethane solution was layered with hexane or diethyl ether to give the product as yellow crystals in a few days.

6. Yield: 68%. Anal. Calcd for $C_{166}H_{84}F_{72}N_8Nd_4O_{24}P_4Pt_2$: C, 39.61, H, 1.68; N, 2.23. Found: C, 40.05; H, 2.01; N, 2.24. IR (KBr): $\bar{\nu}$ 2095 (C≡C), 1654 (C=O).

7. Yield: 72%. Anal. Calcd for $C_{166}H_{84}Eu_4F_{72}N_8O_{24}P_4Pt_2$: C, 39.37, H, 1.67; N, 2.21. Found: C, 39.65; H, 1.79; N, 2.30. IR (KBr): $\bar{\nu}$ 2095 (C≡C), 1650 (C=O).

8. Yield: 76%. Anal. Calcd for $C_{166}H_{84}F_{72}N_8O_{24}P_4Pt_2Yb_4$: C, 38.73, H, 1.64; N, 2.18. Found: C, 38.63; H, 1.84; N, 2.14. IR (KBr): $\bar{\nu}$ 2096 (C≡C), 1652 (C=O).

Crystal Structural Determination. Single crystals coated with epoxy resin for **2**·CH_2Cl_2, **3**·CH_2Cl_2, and **7**·1.5Et_2O were measured on a RIGAKU MERCURY CCD diffractometer by the ω scan technique at room temperature using graphite-monochromated Mo/Kα (λ = 0.71073 Å) radiation. An absorption correction by multi-scan was applied to the intensity data. The structures were solved by direct method and the heavy atoms were located from E-map. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically with isotropic thermal parameters. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package. Full crystallographic data are provided in CIF files as Supporting Information.

Physical Measurements. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240C automatic instrument. Electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. UV-vis absorption spectra were measured on a Perkin-Elmer Lambda 25 UV-Vis spectrometer. Infrared spectra were recorded on a Magna750 FT-IR spectrophotometer with KBr pellet. ^{31}P NMR spectra were measured on a Varian UNITY-500 spectrometer using 85% H_3PO_4 as external standard. Emission and excitation spectra in the UV-vis region were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a red-sensitive photomultiplier type R928. The steady-state near-infrared (NIR) emission spectra were measured on an Edinburgh FLS920 fluorescence spectrometer equipped with a Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM300 emission monochromator with NIR grating blazed at 1000 nm. Corrected spectra were obtained via a calibration curve supplied with the instrument. The emission lifetimes above

10 μs were obtained by using an Edinburgh Xe900 450 W pulse xenon lamp as the excitation light source. The emission lifetimes below 10 μs were determined using LED laser at 397 nm excitation.

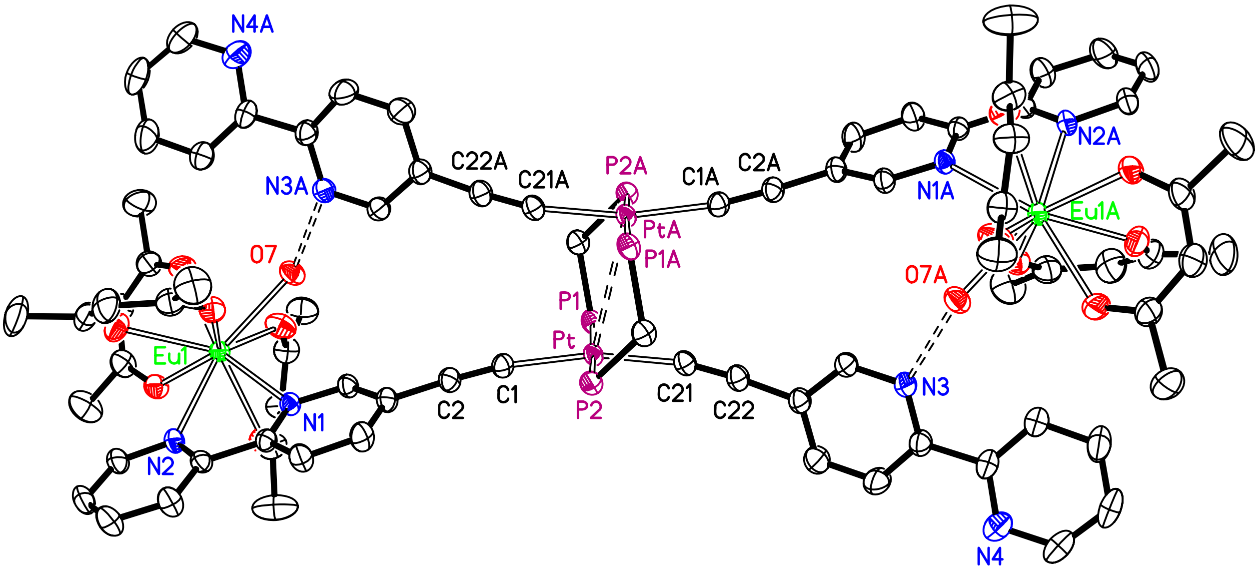

Fig. S1. ORTEP drawings of **3** with 30% thermal ellipsoids. Phenyl rings and F atoms are omitted for clarity.

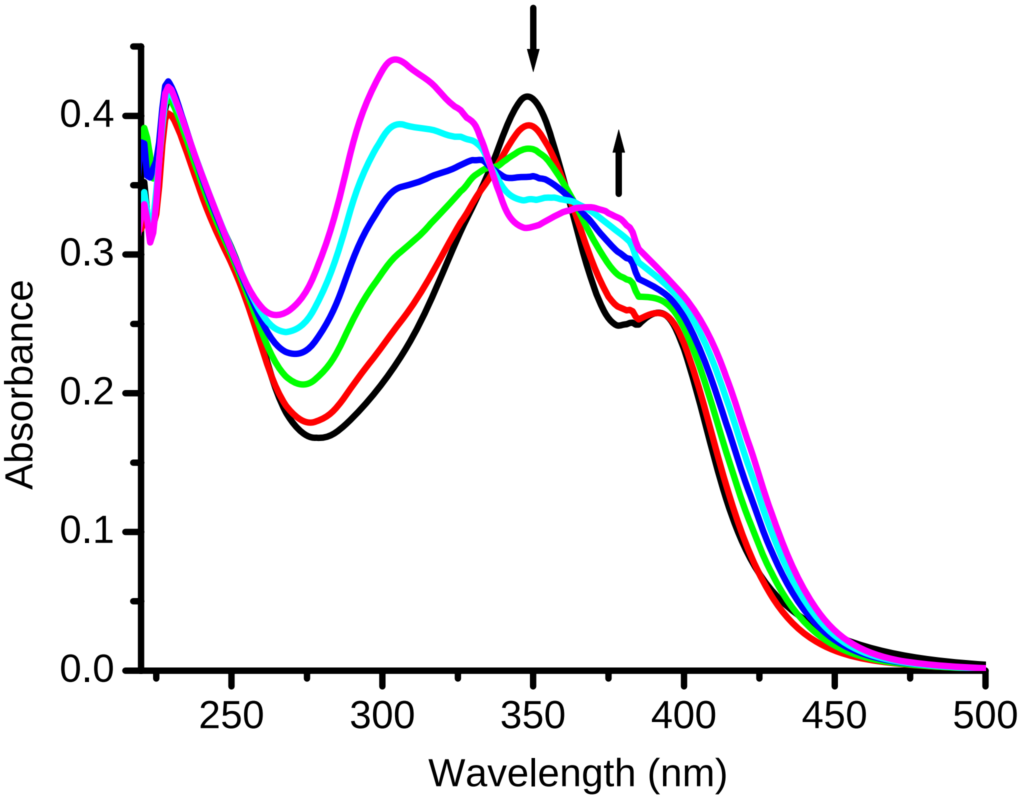

Fig. S2. Titration of **1** with Eu(hfac)$_3$(H$_2$O)$_2$ in dichloromethane solution, showing red shift of the MLCT absorption band from Pt^{II} alkynyl chromophore.

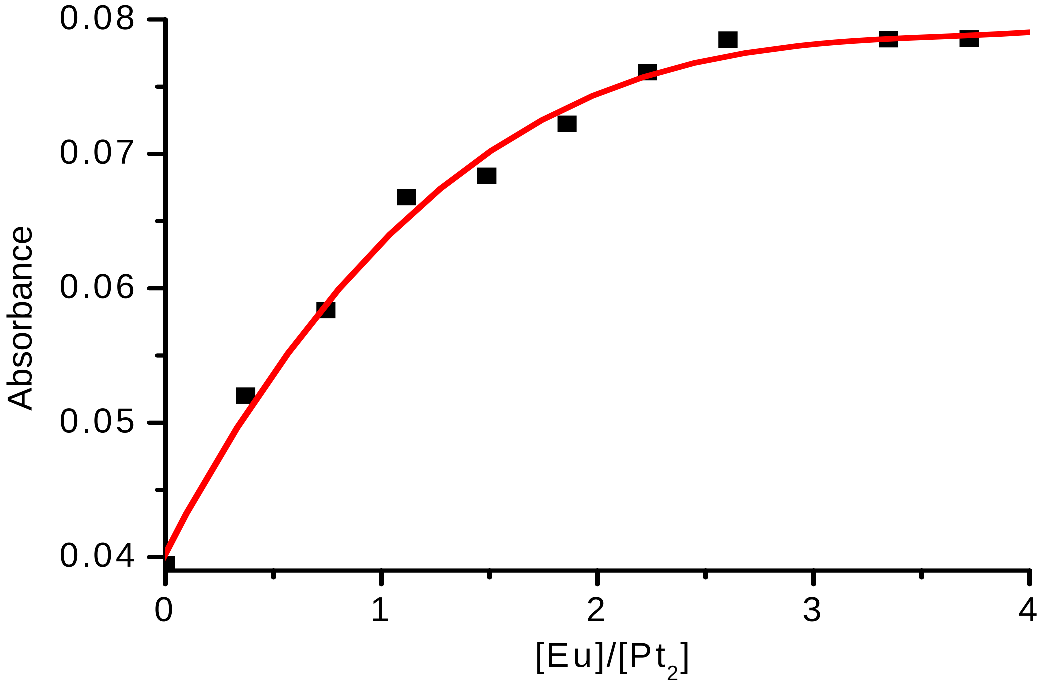

Fig. S3. Absorbance values at 412 nm during titration of **1** with Eu(hfac)$_3$(H$_2$O)$_2$ in dichloromethane solution fitted to 1 : 2 binding ratio.

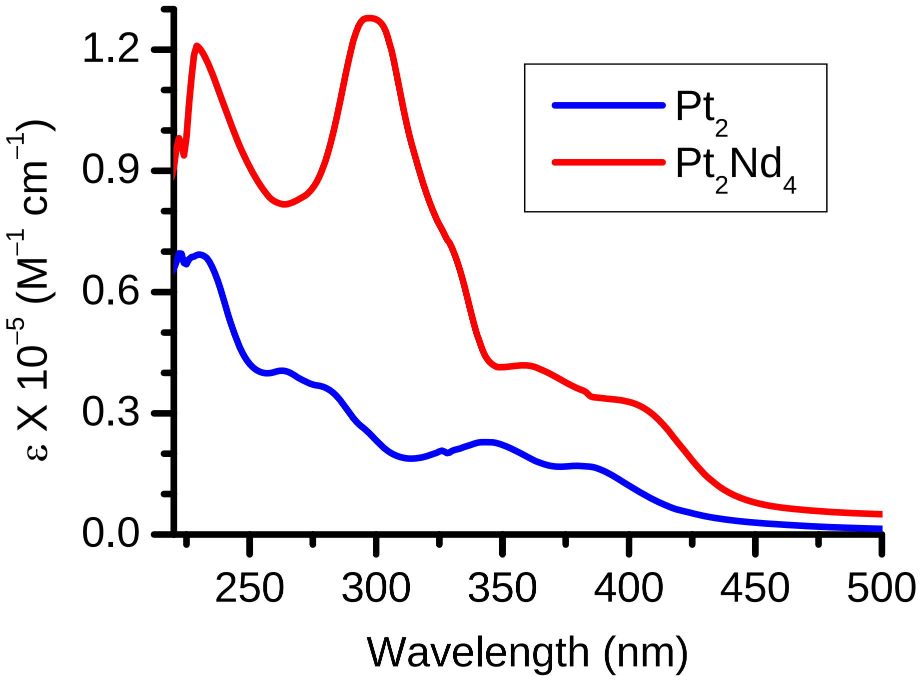

Fig. S4. UV-vis absorption spectra of Pt$_2$ complex **5** (blue line) and Pt$_2$Nd$_4$ complex **6** (red line)**,** showing red shift of the MLCT absorption bands of the Pt^{II} alkynyl chromophore from **5** to **6**.

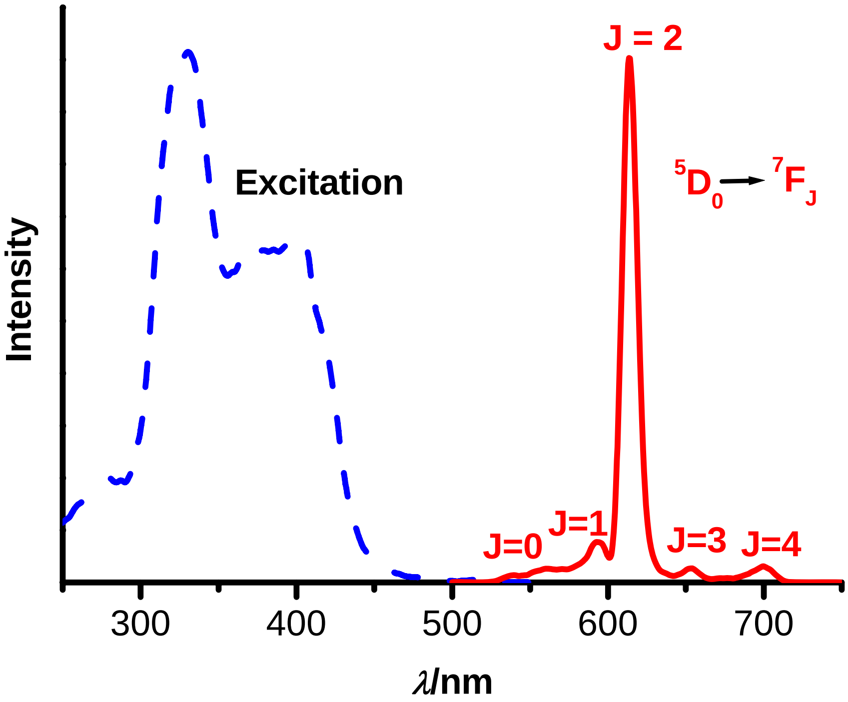

Fig. S5. Excitation (blue) and emission (red) spectra of $Pt^{II}_2Eu^{III}_4$ complex **7** in dichloromethane at 298 K.

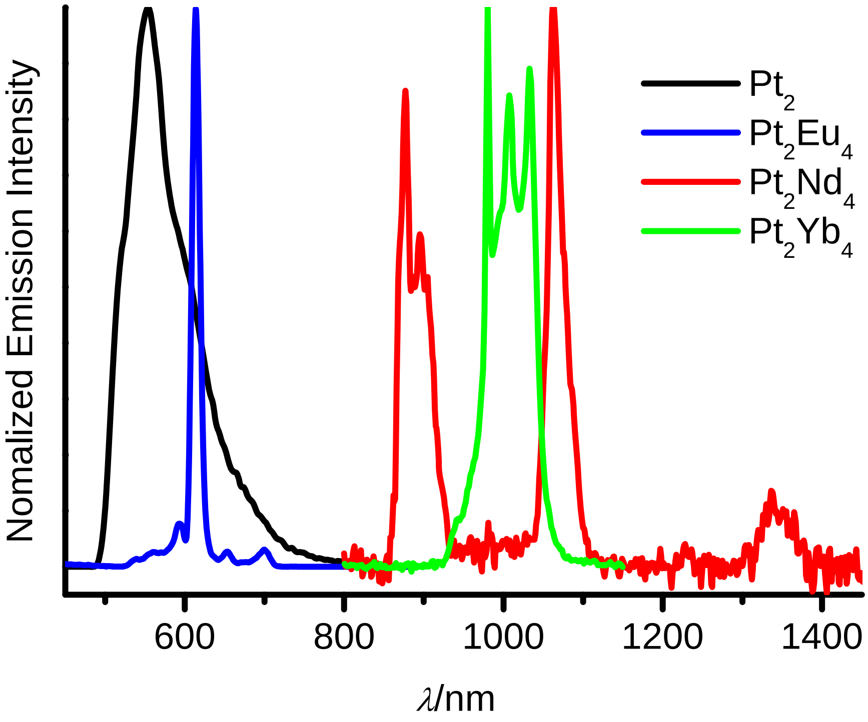

Fig. S6. Emission Spectra of **5** (black), **6** (red), **7** (blue), and **8** (green) in dichloromethane at 298 K.