

# Electronic Supplementary Information

## Heterododecanuclear $\text{Pt}^{\text{II}}_6\text{Ln}^{\text{III}}_6$ (Ln = Nd, Yb) Arrays of 4-Ethynyl-2,2'- Bipyridine with Sensitized Near-Infrared Lanthanide Luminescence by $\text{Pt} \rightarrow \text{Ln}$ Energy Transfer

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## Experimental section

**Material and Reagents.** All manipulations were performed under dry argon atmosphere using Schlenk technique and vacuum-line system. Solvents were dried by standard methods and distilled prior to use. The reagents potassium tetrachloroplatinum ( $K_2[PtCl_4]$ ), bis(diphenylphosphino)methane (dppm), 2,2'-bipyridine (bpy), hexafluoroacetylacetonate (hfac) were commercially available. 5-[2-(Trimethylsilyl)-1-ethynyl]-2,2'-bipyridine ( $bpyC\equiv CSiMe_3$ ),<sup>1</sup>  $PtCl_2(dppm-P,P')$ ,<sup>2</sup>  $Pt(DMSO)_2Cl_2$ ,<sup>3</sup> and  $Ln(hfac)_3(H_2O)_2$  ( $Ln = Nd, Eu, Yb$ )<sup>4</sup> were prepared by the literature procedures.

**Pt( $Me_3SiC\equiv Cbpy$ )( $C\equiv Cbpy$ )<sub>2</sub> (1).**  $Pt(DMSO)_2Cl_2$  (211 mg, 0.5 mmol) and  $bpyC\equiv CSiMe_3$  (126 mg, 0.5 mmol) in acetonitrile (50 mL) was refluxed for 1 d, the solvent was then removed in vacuo and the residue was dissolved in 30 mL of dichloromethane. After filtration, the concentrated dichloromethane solution was layered with ether to afford the desired product as yellow powder. Yield: 78%. ESI-MS ( $CH_3OH-CH_2Cl_2$ ):  $m/z$ : 519  $[M+H]^+$ . IR (KBr,  $cm^{-1}$ ):  $\bar{\nu}$  2162w ( $C\equiv C$ ), 1249s ( $SiMe_3$ ).

To 40 mL of dichloromethane were added  $PtCl_2bpyC\equiv CSiMe_3$  (155 mg, 0.3 mmol),  $HC\equiv Cbpy$  (120 mg, 0.67 mmol),  $CuI$  (5.7 mg, 0.03 mmol), and  $Pr_2^iNH$  (5 mL) and the mixture was refluxed for 1 d. The isolated red crude product was purified by silica gel column chromatography using dichloromethane-methanol ( $v/v = 100 : 1$ ) as an eluent to afford **1** as a yellow product. Yield: 45%. Anal. Calcd. for  $C_{39}H_{30}N_6PtSi$ : C 58.13, H 3.75, N 10.43. Found: C 58.33, H 3.74, N 10.36. ESI-MS ( $CH_3OH-CH_2Cl_2$ ):  $m/z$ : 806  $[M+H]^+$ . IR (KBr,  $cm^{-1}$ ):  $\bar{\nu}$  2114w ( $C\equiv C$ ). <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):  $\delta$  9.79 (s, H,  $bpyC\equiv CSiMe_3$ ), 9.72 (s, H,  $bpyC\equiv CSiMe_3$ ), 8.84 (s, 2H,  $bpyC\equiv C$ ), 8.71 (s, 2H,  $bpyC\equiv C$ ), 8.46 (s, H,  $bpyC\equiv CSiMe_3$ ), 8.38 (s, 3H,  $bpyC\equiv C$  and  $bpyC\equiv CSiMe_3$ ), 8.18 (s, H,  $bpyC\equiv CSiMe_3$ ), 8.10 (s, 2H,  $bpyC\equiv C$ ), 7.96 (s, 2H,  $bpyC\equiv C$ ), 7.86 (s, 2H,  $bpyC\equiv C$ ), 7.67 (s, H,  $bpyC\equiv CSiMe_3$ ), 7.32 (s, 3H,  $bpyC\equiv C$  and  $bpyC\equiv CSiMe_3$ ), 0.31 (s, 9H,  $CH_3$ ).

**{Pt( $Me_3SiC\equiv Cbpy$ )( $C\equiv Cbpy$ )<sub>2</sub>}{Ln(hfac)<sub>3</sub>}<sub>2</sub> (Ln = Nd **2**, Yb **3**).** These compounds were prepared by addition of 2.2 equiv of  $Ln(hfac)_3(H_2O)_2$  to dichloromethane solutions of **1** with stirring for one hour. After filtration, the concentrated dichloromethane solutions were layered with *n*-hexane to afford the desired products as yellow crystals in 55–70% yields.

**2** (Ln = Nd). Anal. Calcd. for C<sub>69</sub>H<sub>36</sub>F<sub>36</sub>N<sub>6</sub>Nd<sub>2</sub>O<sub>12</sub>PtSi: C, 35.47; H, 1.55; N, 3.60. Found: C, 35.79; H, 1.40; N, 3.56. IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  2119w (C≡C), 1653s (C=O).

**3** (Ln = Yb). Anal. Calcd. for C<sub>69</sub>H<sub>36</sub>F<sub>36</sub>N<sub>6</sub>O<sub>12</sub>PtSiYb<sub>2</sub>: C, 34.61; H, 1.52; N, 3.51. Found: C, 34.59; H, 1.40; N, 3.54. IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  2120w (C≡C), 1653s (C=O).

**Pt<sub>6</sub>(μ-dppm)<sub>2</sub>(C≡Cbpy)<sub>12</sub> (4)**. To a dichloromethane (50 mL) solution of **1** (246 mg, 0.30 mmol), were added Pt(dppm-P,P')Cl<sub>2</sub> (100 mg, 0.15 mmol), CuI (5.7 mg, 0.03 mmol), and Pr<sub>2</sub><sup>i</sup>NH (5 mL) with stirring. After the solution was refluxed for 1 d, the solvents were removed in vacuo to give a yellowish-red crude product which was washed thrice with water, methanol, and dichloromethane, respectively. Yield: 58%. Anal. Calcd. for C<sub>194</sub>H<sub>128</sub>N<sub>24</sub>Pt<sub>6</sub>P<sub>4</sub>: C 56.98, H 3.15, N 8.22. Found: C 57.08, H 3.33, N 8.46. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ 8.80–7.06 (m, 124H, Ph and bpy), 4.67 (m, 4H, PCH<sub>2</sub>P). IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  2110w (C≡C).

**Pt<sub>6</sub>Ln<sub>6</sub>(dppm)<sub>2</sub>(C≡Cbpy)<sub>12</sub>(hfac)<sub>18</sub> (Ln = Nd **5**, Gd **6**, Yb **7**)**. To suspended dichloromethane solutions of **4** were added 8.8 equiv of Ln(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> with stirring at room temperature for one hour to give yellow solutions. After filtration, the concentrated dichloromethane solutions were layered with *n*-hexane to afford the desired products as orange crystals in 65–80% yields. Elemental analyses were satisfactory for all of the complexes. The Pt<sub>6</sub>Yb<sub>6</sub> Compound **7** was characterized by X-ray crystallography.

**5** (Ln = Nd). Anal. Calcd. for C<sub>284</sub>H<sub>146</sub>F<sub>108</sub>N<sub>24</sub>Nd<sub>6</sub>O<sub>36</sub>P<sub>4</sub>Pt<sub>6</sub>: C, 39.29; H, 1.69; N, 3.87. Found: C, 39.41; H, 1.47; N, 3.56. IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  2115w (C≡C), 1651s (C=O).

**6** (Ln = Gd). Anal. Calcd. for C<sub>284</sub>H<sub>146</sub>F<sub>108</sub>N<sub>24</sub>Gd<sub>6</sub>O<sub>36</sub>P<sub>4</sub>Pt<sub>6</sub>: C, 38.94; H, 1.68; N, 3.84. Found: C, 38.89; H, 1.77; N, 3.86. IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  2116w (C≡C), 1651s (C=O).

**7** (Ln = Yb). Anal. Calcd. for C<sub>284</sub>H<sub>146</sub>F<sub>108</sub>N<sub>24</sub>Yb<sub>6</sub>O<sub>36</sub>P<sub>4</sub>Pt<sub>6</sub>: C 38.52; H 1.66; N 3.80. Found: C, 38.79; H, 1.60; N, 3.74. IR (KBr, cm<sup>-1</sup>):  $\bar{\nu}$  2116w (C≡C), 1651s (C=O).

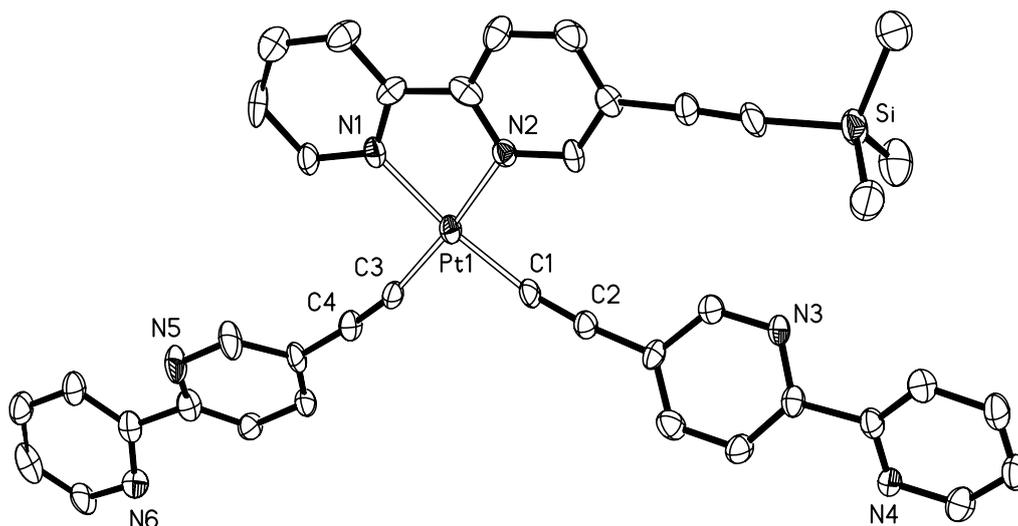
**Crystal Structural Determination.** Data collection was performed on a RIGAKU MERCURY CCD diffractometer by  $\omega$  scan technique using graphite-monochromated Mo/K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. An absorption correction by multi-scan was applied to the intensity data. The structures 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, and 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.<sup>[5]</sup>

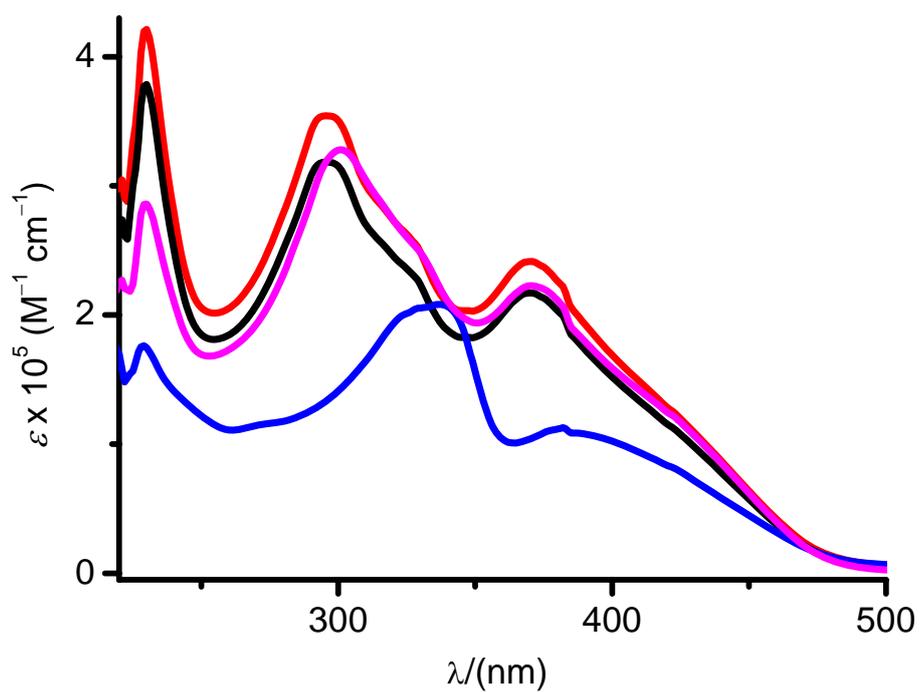
**Physical Measurements.** Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240C automatic instrument. Electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as mobile phase. UV-vis absorption spectra were measured on a Perkin-Elmer Lambda 25 UV-Vis spectrometer. Infrared spectra were recorded on a Magna750 FT-IR spectrophotometer with KBr pellet. <sup>1</sup>HNMR spectra were measured on a Varian UNITY-500 spectrometer using SiMe<sub>4</sub> as the internal reference. 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. The emission quantum yields of compounds **1**, **4** and **6** were measured in degassed dichloromethane solutions at 298 K and estimated relative to [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> in acetonitrile as the standard ( $\Phi_{em} = 0.062$ ) and calculated by  $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)(D_s/D_r)$ , where the subscripts *s* and *r* refer to the sample and reference standard solution, respectively, *n* is the refractive index of the solvents; *d* is the integrated intensity, and  $\Phi$  is the luminescence quantum yield. The quantity *B* is calculated by  $B = 1 - 10^{-AL}$ , where *A* is the absorbance at the excitation wavelength and *L* is the optical path length.

## References

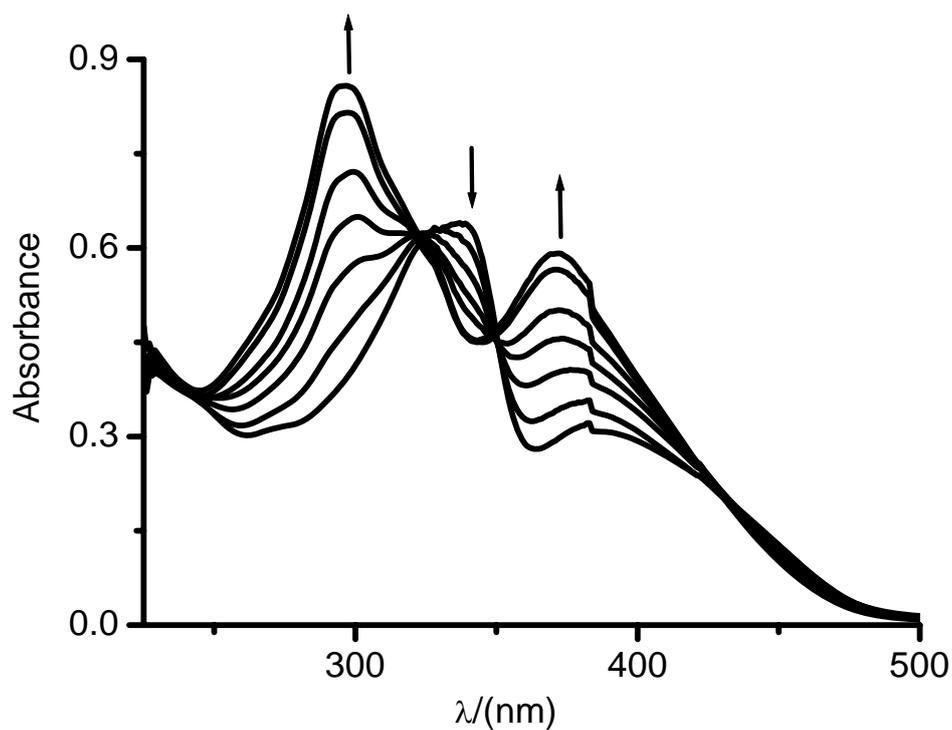
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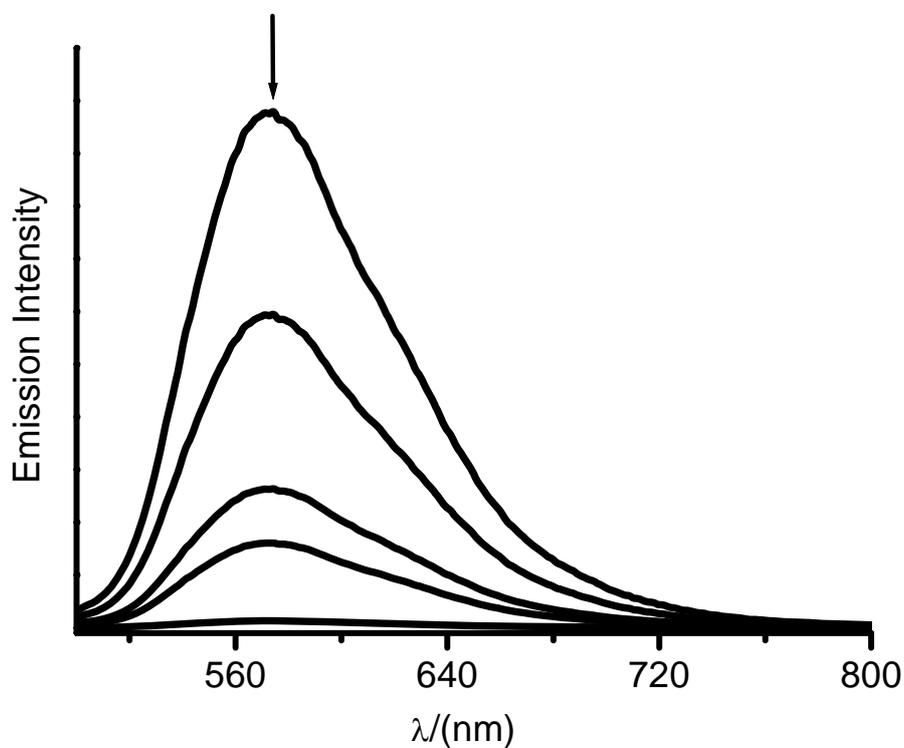
**Fig. S1.** ORTEP drawing of **1**, showing 30% thermal ellipsoid.



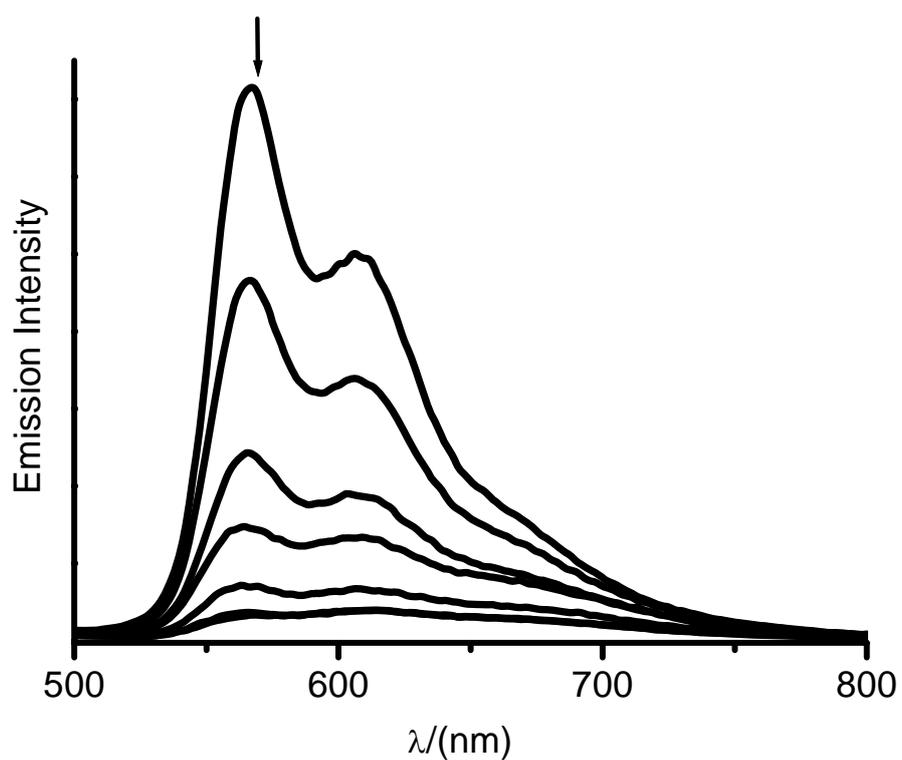
**Fig. S2.** UV-vis electronic absorption spectra of **4** (blue), **5** (black), **6** (red) and **7** (magenta) in dichloromethane.



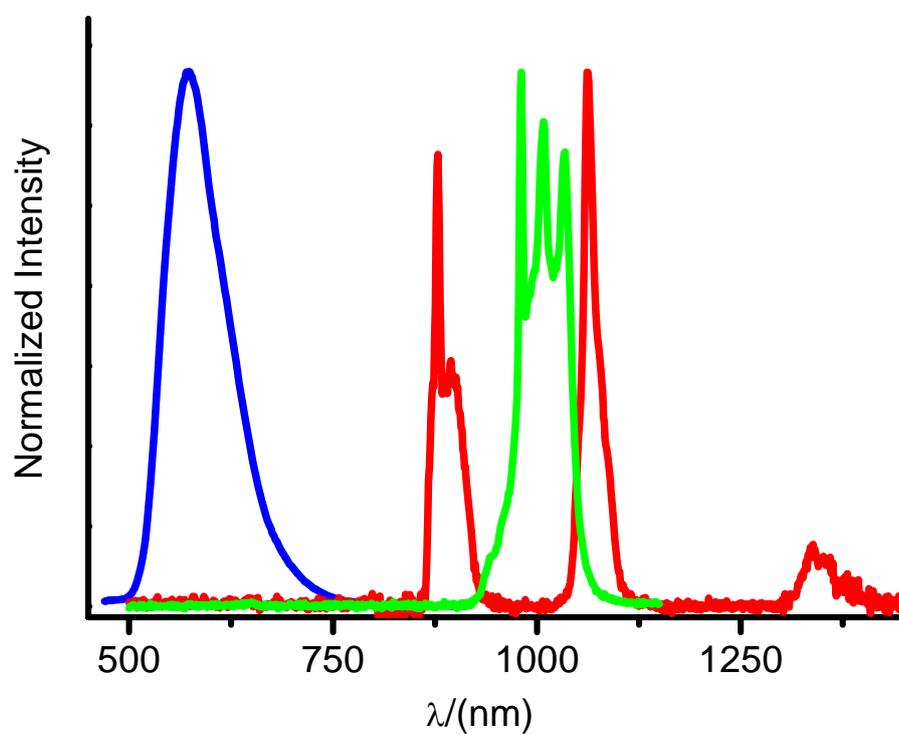
**Fig. S3.** Titration of **4** with Yb(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in dichloromethane solution, showing a blue shift of the MLCT absorption band in Pt<sup>II</sup>(bpy)(acetylide)<sub>2</sub> chromophore.



**Fig. S4.** Titration of **1** with Yb(hfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in dichloromethane solution, showing the quenching of the Pt<sup>II</sup>(bpy)(acetylide)<sub>2</sub>-based emission.



**Fig. S5.** Titration of **4** with  $\text{Yb}(\text{hfac})_3(\text{H}_2\text{O})_2$  in dichloromethane solution, showing the quenching of the Pt-based emission.



**Fig. S6.** Emission spectra of **1** (blue), **2** (red), and **3** (green) in dichloromethane at 298 K.