Purification and characterization of the complexes.

All compounds were systematically purified by column chromatography on alumina as solid phase and CH$_2$Cl$_2$/CH$_3$OH as mobile phase. Recrystallization in adequate solvents afforded the analytically pure samples. Selected data for Pt: ESI-MS (CH$_3$CN) $m/z$ 822.3 ([M+H]$^+$, 100); FT-IR 2109.7 cm$^{-1}$ ($v_{C≡C}$); elemental analysis Found: C, 61.19, H, 4.42, N, 10.02. C$_{42}$H$_{38}$N$_6$Pt requires: C, 61.38; H, 4.66; N, 10.23; for PtRu: ESI-MS (CH$_3$CN) $m/z$ 1380.2 ([M-PF$_6$]$^+$, 100), 617.5 ([M-2PF$_6$]$^{2+}$, 40); FT-IR 2109.3 cm$^{-1}$ ($v_{C≡C}$); elemental analysis C, 48.52, H, 3.23, N, 8.87. C$_{62}$H$_{54}$F$_{12}$N$_{10}$P$_2$PtRu requires C, 48.82; H, 3.57; N, 9.18. $^1$H NMR in d$_6$-acetone $\delta$ 9.58 (1H, d, $^3J$ = 6.8 Hz), 9.36 (1H, d, $^3J$ = 6.0 Hz), 8.86-8.79 (4H, 4 line m), 8.73 (1H, d, $^3J$ = 8.5 Hz), 8.67-8.66 (4H, 2 line m), 8.57 (1H, s), 8.49 (1H, d, $^3J$ = 7.6 Hz), 8.42 (1H, d, $^3J$ = 8.0 Hz), 8.23-8.11 (8H, 8 line m.), 8.05 (1H, d, $^3J$ = 5.0 Hz), 8.01-7.93 (4H, 8 line m), 7.82-7.79 (3H, 5 line m), 7.63-7.50 (5H, 9 line m), 7.41 (1H, t, $^3J$ = 6.6 Hz), 1.46 ppm (18H, s.).for PtRu$_2$: ESI-MS (CH$_3$CN) $m/z$ 2083.2 ([M-PF$_6$]$^+$, 100), 969.0 ([M-2PF$_6$]$^{2+}$, 80); 598.1 ([M-3PF$_6$]$^{3+}$, 50); FT-IR 2114.4 cm$^{-1}$ ($v_{C≡C}$); elemental analysis C, 43.78, H, 2.93, N, 8.49. C$_{82}$H$_{70}$F$_{24}$N$_{14}$P$_4$PtRu$_2$ requires: C, 44.19; H, 3.17; N, 8.80. $^1$H NMR in d$_6$-acetone $\delta$ 9.18 (2H, d, $^3J$ = 5.8 Hz), 8.84-8.69 (13H, 11 line m), 8.21-7.98 (22H, 13 line m), 7.84 (2H, s), 7.72-7.50 (13H, 12 line m), 1.46 ppm (18H, s).

Electrochemistry.

With reference to the Table below, to notice the following.

1) The oxidation on the PtRu and PtRu$_2$ complexes is Ru based due to the clear reversibility compared to the irreversible oxidation of the Pt precursor at higher potential.

2) The first reduction on the PtRu and PtRu$_2$ complexes is based on the Ru part, i.e., on the ethynylbpy ligand. A second very close reversible reduction is likely localized on the Pt part, the third reduction is localized on the Ru-unsubstituted bpy.

3) The third reduction of the unsubstituted bpy is not observed, as usually for [Ru(bpy)$_3$]$^{2+}$, or the Ru complex which has a second two electron reduction wave.
Table. Electrochemical data for the Pt/Ru complexes.α

<table>
<thead>
<tr>
<th>Cmpds</th>
<th>E₀'(ox, soln) (V), ΔE (mV)</th>
<th>E₀'(red, soln) (V), ΔE (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>+1.37 (irrev, Ia/Ic ≈ 0) -1.43 (70)</td>
<td></td>
</tr>
<tr>
<td>Pt(bpy)Cl₂</td>
<td>+1.38 (irrev, Ia/Ic ≈ 0) -1.38 (80)</td>
<td></td>
</tr>
<tr>
<td>PtRu</td>
<td>+1.32 (70)* -1.33 (60), -1.38 (70), -1.61 (60)</td>
<td></td>
</tr>
<tr>
<td>PtRu₂</td>
<td>+1.32 (70)* -1.34 (60), -1.39 (60), -1.63 (60)</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>+1.40 (60) -1.17 (60), -1.55 (100)**</td>
<td></td>
</tr>
</tbody>
</table>

αPotentials determined by cyclic voltammetry in deoxygenated CH₃CN solution, containing 0.1 M TBAPF₆, at a solute concentration of ca. 1.5 mM and at rt. Potentials were standardized versus ferrocene (Fc) as internal reference and converted to the SCE scale assuming that E₁/₂ (Fc/Fc⁺) = +0.38 V (ΔEp = 60 mV) vs SCE. Error in half-wave potentials is ±15 mV, all potential correspond to single electron transfer processes unless otherwise noticed. For irreversible processes the peak potentials (Eap or Ecp) are quoted. (*) The visibility is perturbed by adsorption of the complex on the electrolyte surface. (**) Two-electron process.

Pt→Ru energy transfer in PtRu and PtRu₂

From the luminescence properties of Pt and Ru, Pt→Ru energy transfer is exothermic by ca. 0.4 eV. For PtRu and PtRu₂, the electronic interaction between the partners is likely weak, as suggested by the fact that the Ru-based unit largely keeps its individual electronic properties in the MLCT absorption region. On this basis, we tentatively discard the dual electron exchange (i.e., through-bond) Dexter energy transfer. ¹ For the dipole-dipole Förster mechanism, ² evaluation of the spectral overlap Jₓ between the luminescence profile of Pt and the absorption profile of bound Ru (which overlaps that of the Ru-based unit in PtRu, Figure 1 of main text), allows the estimate of the Pt→Ru energy transfer rate constant, kₓ,F, at an intermetal separation dₓc ≅ 9 Å, eqs. 1-3,

\[ J_F = \frac{\int F(\nu) \epsilon(\nu) \nu^{-4} d\nu}{\int F(\nu)} \]  \hspace{1cm} (1)

\[ k_{\text{en}} F = \frac{8.8 \times 10^{-25} K^2 \phi_{\text{em}}}{n^4 \tau_{\text{em}} d_{\text{xc}}^6} J_F \]  \hspace{1cm} (2)

\[ R_{\phi}(\text{Å}) = 9.79 \times 10^3 \left( K^2 n^{-4} \phi_{\text{em}} J_F \right)^{1/6} \]  \hspace{1cm} (3)
where $F(\nu)$ and $\varepsilon(\nu)$ are the luminescence and absorption profiles on an energy scale (cm$^{-1}$) of Pt and Ru, respectively, $K^2$ is a geometric factor (taken as $2/3$); $\phi_{em}$ and $\tau_{em}$ are the luminescence quantum yield and lifetime, respectively, of Pt (the excitation energy donor), $n$ is the refractive index of the solvent, the intermetal distance $d_{cc}$ is estimated 9 Å from molecular modeling, and $R_o$ is the critical transfer radius. Results were $J_F = 8.2 \times 10^{-15}$ cm$^3$ M$^{-1}$, $k_{en}^F = 1.04 \times 10^8$ s$^{-1}$ (at 9 Å), and $R_o = 25.2$ Å. Figure SI_1 provides a schematic layout for the Pt- and Ru-based energy levels involved.

**SI References**


Figure SI_1. Energy layout for the Pt- and Ru-based levels in PtRu and PtRu$_2$. ILCT levels are not indicated.