Enhancing the Electronic Coupling in Cyclometalated Bisruthenium Complex by Using the 1,3,6,8-Tetra-(pyridin-2-yl)carbazole Bridge

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Synthesis. NMR spectra were recorded in designated solvents on Bruker Avance 400 MHz spectrometer. Spectra are reported in ppm values from residual protons of deuterated solvents. Mass data were obtained with a Bruker Daltonics Inc. ApexII FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement is α-cyano-4-hydroxycinnamic acid. Microanalysis was carried out using Flash EA 1112 or Carlo Erba 1106 analyzer at the Institute of Chemistry, Chinese Academy of Sciences. NMR and MS spectra are provided in the end.

Synthesis of 1,3,6,8-tetra(pyridin-2-yl)-9-butyl-9H-carbazole (N-Bu-tpcaH2). A mixture of 1,3,6,8-tetrabromo-9-butyl-9H-carbazole ¹ (540 mg, 1.0 mmol), 2-(tributylstannyl)pyridine (2.21 g, 6.0 mmol), and Pd(PPh3)4 (140 mg, 0.12 mmol) in toluene was heated to reflux for 48 h at N2 atmosphere. After cooling to rt, the solvent was removed under reduced pressure. The residue was subjected to flash column chromatography on silica gel using CH2Cl2/MeOH (v/v) 100/1 as the eluent to afford 239 mg of N-Bu-tpcaH2 as a yellowish solid in 45% yield. ¹H NMR (400 MHz, CDCl3): δ 8.96 (d, J = 2.0 Hz, 2H), 8.68-8.72 (m, 4H), 8.12 (d, J = 2.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.70-7.80 (m, 4H), 7.68 (d, J = 8.0 Hz, 2H), 7.25-7.31 (m, 2H), 7.15-7.21 (m, 2H), 3.51 (t, J = 8.4 Hz, 2H), 1.26-1.39 (m, 2H), 0.97-0.90 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl3): δ 159.28, 157.78, 149.78, 149.28, 140.35, 136.96, 136.52, 131.41, 128.45, 126.61, 126.36, 125.21, 122.37, 121.68, 120.50, 119.22, 46.75, 31.15, 30.89, 13.45. ESI-MS: 531 for [M]+. ESI-HRMS: calcd for C36H29N5 531.2423, found 531.2416. The assignment of the aromatic signals of the ¹H NMR and ¹³C NMR spectra are delineated in the following table with the aid of HSQC spectrum.

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<tr>
<td>Hα, Hα’</td>
<td>8.96 (d, $J = 2.0$ Hz, 2H), 8.12 (d, $J = 2.0$ Hz, 2H),</td>
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<td>Hβ, Hβ’</td>
<td>7.90 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H),</td>
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<tr>
<td>Hγ, Hγ’, Hδ, Hδ’</td>
<td>7.70-7.80 (m, 4H), 7.25-7.31 (m, 2H), 7.15-7.21 (m, 2H)</td>
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<td>Hε, Hf</td>
<td>8.68-8.72 (m, 4H)</td>
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<tr>
<td>Cα, Cα’</td>
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<td>Cβ, Cβ’</td>
<td>125.21, 120.50</td>
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<tr>
<td>Cγ, Cγ’, Cδ, Cδ’</td>
<td>136.52, 136.96, 121.68, 122.37</td>
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</tr>
<tr>
<td>Cε, Cδ</td>
<td>149.78, 149.28</td>
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<tr>
<td>Cg, Cg’, Ch, Ci, Cj, Ck</td>
<td>159.28, 157.78, 140.35, 131.41, 126.61, 126.36</td>
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Synthesis of [1](PF₆) and [2](PF₆)₂. To 10 mL dry acetone were added [Ru(tpy)Cl₃]₂ (70 mg, 0.16 mmol) and AgOTf (142 mg, 0.55 mmol). The system was heated to reflux for 2 h. After cooling to rt, the mixture was filtered through a pad of Celite. The filtrate was evaporated to dryness. The residue was dissolved in 6.0 mL of DMF, and the solution was transferred to a pressure vessel charged with the above synthesized ligand N-Bu-tpcaH₂ (42 mg, 0.080 mmol) in 6 mL of tBuOH. The mixture was heated under reflux for 20 h at N₂ atmosphere. After cooling to rt, the mixture was filtered and the filtrate was concentrated under vacuum. The residue was dissolved in 3 mL of methanol, followed by the addition of an excess of aq. KPF₆. The resulting precipitate was collected through filtration and washed with water and ethyl ether. This crude product was purified by flash column chromatography on silica gel using CH₂Cl₂/MeOH (v/v) from 50:1 to 20:1 as eluent to afford 11 mg of [1](PF₆) (13%) and 56 mg of [2](PF₆)₂ (48%) as dark brown solids.

[1](PF₆): ¹H NMR (400 MHz, CDCl₃): δ 9.14 (s, 1H), 9.10 (s, 1H), 8.88 (d, J = 4.4 Hz, 1H), 8.76 (d, J = 5.6 Hz, 1H), 8.74 (d, J = 8.0 Hz, 2H), 8.42 (d, J = 8.0 Hz, 2H), 8.38 (s, 1H), 8.23-8.30 (m, 2H), 8.14 (t, J = 8.0 Hz, 2H), 8.02-8.07 (m, 2H), 7.94 (t, J = 8 Hz, 1H), 7.60 - 7.71 (m, 4H), 7.45-7.51 (m, 1H), 7.36 (dd, J = 7.6, 4.8 Hz, 1H), 7.22 (d, J = 5.6 Hz, 2H), 7.10 (d, J = 5.6 Hz, 1H), 6.98 (d, J = 5.2 Hz, 1H), 6.90 (t, J = 6.8 Hz, 2H), 6.63 (t, J = 6.4 Hz, 2H), 4.16 (t, J = 6.8 Hz, 2H), 0.94-1.03 (m, 2H), 0.35-0.47 (m, 2H), 0.33 (t, J = 6.4 Hz, 3H). MALDI-TOF-MS: m/z 865.2 [M – PF₆]⁺. Anal. Calcd for C₅₁H₃₉F₆N₈PRu: C, 60.65; H, 3.89; N, 11.10. Found: C, 60.87; H, 3.46; N, 9.86.

[2](PF₆)₂: ¹H NMR (400 MHz, CDCl₃): δ 9.08-9.24 (br, 2H), 8.81 (t, J = 7.2 Hz, 4H), 8.46 (d, J = 8.0 Hz, 6H), 8.31 (t, J = 8.0 Hz, 2H), 8.20-8.35 (br, 2H), 7.81 (t, J = 7.6 Hz, 2H), 7.65-7.76 (m, 6H), 7.42-7.49 (m, 2H), 7.21-7.28 (m, 2H), 7.14 (d, J = 5.2 Hz, 2H), 6.92-7.20 (br, m, 6H), 6.53-6.74 (br, 4H), 4.68 (t, J = 6.8 Hz, 2H), 1.11-1.17 (m, 2H), 0.66-0.72 (m, 2H), 0.44 (t, J = 7.2 Hz, 3H). MALDI-TOF-MS: m/z 1343.1 [M – PF₆]⁺. Anal. Calcd for C₆₆H₄₉F₁₂N₁₁P₂Ru₂: C, 52.01; H, 3.50; N, 10.11. Found: C, 51.98;

H, 3.33; N, 9.97.

**X-ray Crystallography.** The X-ray diffraction data were collected using a Rigaku Saturn 724 diffractometer on a rotating anode (Mo-K radiation, 0.71073 Å) at 173 K. The structure was solved by the direct method using SHELXS-97\(^3\) and refined with Olex2.\(^4\) The structure graphics were generated using Olex2.

![Figure S1](image_url)

**Figure S1.** CPK models of the single crystal structure of [1](PF\(_6\)).

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\(^3\) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.

**Electrochemical Measurement.** All CV and DPV measurements were taken using a CHI620D potentiostat with one-compartment electrochemical cell under an atmosphere of nitrogen. All measurements were carried out in 0.1 M of ["Bu4N][ClO4] or ["Bu4N][B(C6F5)4] at a scan rate of 100 mV/s. The working electrode was a glassy carbon with a diameter of 0.3 mm. The electrode was polished prior to use with 0.05 μm alumina and rinsed thoroughly with water and acetone. A large area platinum wire coil was used as the counter electrode. All potentials are referenced to a Ag/AgCl electrode in saturated aqueous NaCl without regard for the liquid junction potential.

![Graph](image)

**Figure S2.** CV of compound tpcaH2 in CH3CN containing 0.1 M Bu4NCIO4 as the supporting electrolyte at a scan rate of 100 mV/s.
Figure S3. DPVs of (a) $1^+$ and (b) $2^{2+}$ in CH$_3$CN in the absence (black plots) and presence of ferrocene (red plots) containing 0.1 M Bu$_4$NClO$_4$ as the supporting electrolyte at a scan rate of 100 mV/s. In (a), the Ru$^{II/III}$ wave overlaps with the Fe$^{0/+}$ peak.
Figure S4. DPVs of $2^{2+}$ in CH$_3$CN containing 0.1 M Bu$_4$NClO$_4$ (black plot) or [Bu$_4$N][B(C$_6$F$_5$)$_4$] (red plot) as the supporting electrolyte at a scan rate of 100 mV/s.

**Spectroscopic Measurements.** Spectroelectrochemical measurements were performed in a thin-layer cell (optical length 0.2 cm) in which an ITO glass electrode was set in the indicated solvent containing the compound to be studied (the concentration is around 1 × 10$^{-4}$ M) and 0.1 M Bu$_4$NClO$_4$ as the supporting electrolyte. A platinum wire and Ag/AgCl in saturated aqueous NaCl solution was used as the counter electrode and reference electrode, respectively. The cell was put into a PE Lambda 750 UV/vis/NIR spectrophotometer to monitor spectral changes during electrolysis. During the measurement with chemical oxidation, different equivalent of oxidant (CAN in CH$_3$CN) were added to a solution of the compound in study with constant concentration. The stepwise oxidation process was monitored by the UV/vis/NIR spectrophotometer.
Figure S5. Vis/NIR absorption spectral changes during the (a) $2^{2+} \rightarrow 2^{3+}$ and (b) $2^{3+} \rightarrow 2^{4+}$ process in CH$_3$CN by electrolysis with an ITO glass electrode. The applied potential is +0.10 $\rightarrow$ +0.45 and 0.45 $\rightarrow$ +0.80 V vs Ag/AgCl for (a) and (b), respectively.

Figure S6. A comparison of the IVCT band of $2^{2+}$ obtained by oxidation with CAN (red plot) or by electrolysis (black line).
Figure S7. Vis/NIR absorption spectral changes during the single- and double-oxidation of [(tppy)$_2$Ru$_2$(tpbph)]$^{2+}$ in CH$_3$CN upon stepwise oxidations with CAN.
Figure S8. Vis/NIR absorption spectral changes during the single- and double-oxidation of $2^{2+}$ in CH$_2$Cl$_2$ upon stepwise oxidations with CAN.
Figure S9. Vis/NIR absorption spectral changes during the single- and double-oxidation of $2^{2+}$ in DMF upon stepwise oxidations with CAN.

Figure S10. A comparison of the IVCT band of $2^{3+}$ in different solvents (CH$_2$Cl$_2$, DMF, and CH$_3$CN) obtained by chemical oxidation with CAN.
$^1$H NMR of N-Bu-tpcaH$_2$ in CDCl$_3$: 
$^{13}$C NMR of $N$-Bu-tpeaH$_2$ in CDCl$_3$: 
EI-MS of $N$-Bu-tpcaH$_2$: 

![Graph showing EI-MS data for N-Bu-tpcaH2]
$^1$H NMR of [1](PF₆) in CD₃CN:
MALDI-MS of [1](PF₆):
$^1$H NMR of [2](PF$_6$)$_2$ in CD$_3$CN:

[Graph of NMR spectrum]
MALDI-MS of $[2](\text{PF}_6)_2$: 

MALDI-TOF, CCA, WL-3-92, 2012, 11, 28