## **Electronic supplementary information**

## Demonstration of intramolecular energy transfer in asymmetric bimetallic ruthenium(II) complexes

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## **Experimental section**

Synthesis of [(dipy-Hbzim-tpy)Ru(tpy-PhCH<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (1a). To a suspension of Ru(tpy-PhCH<sub>3</sub>)Cl<sub>3</sub> (100 mg, 0.18 mmol) in 25 mL of Me<sub>2</sub>CO solid AgBF<sub>4</sub> (110 mg, 0.56 mmol) was added and refluxed for 3h with continuous stirring. The resulting mixture was cooled to room temperature and the white precipitate of AgCl was separated out by quick filtration. The filtrate consisting of the solvated complex of the type [(tpv-PhCH<sub>3</sub>)Ru(Me<sub>2</sub>CO)<sub>3</sub>]<sup>3+</sup> was added slowly to an ethanol-chloroform solution of the excess bridging ligand, dipy-Hbzim-tpy (130 mg, 0.25 mmol) and refluxed for 6h under argon protection when the color of the solution gradually changed from violet to orange-red. The reaction mixture was cooled to room temperature and the suspended material was removed by filtration and upon rotary evaporation to a small volume (~10 mL), a red compound deposited. The compound was filtered, washed with chloroform and ether and then dried under vacuum. The compound was dissolved in small acetonitrile and subjected to silica-gel column chromatography (eluent: 1:1 acetonitrile-methanol). The eluent were rotary evaporated to small volume and then anion exchange reaction with NaClO<sub>4</sub> give rise to the desired compound. Further purification of the compound was done by recrystallization from acetonitrile-methanol (1:1 v/v) mixture in presence of a few drops of aqueous 10<sup>-4</sup> M HClO<sub>4</sub>. Yield: 135 mg, 62%. Anal. Calcd. for C<sub>56</sub>H<sub>44</sub>N<sub>10</sub>Cl<sub>2</sub>O<sub>10</sub>Ru: C, 56.57; H, 3.37; N, 11.78. Found: C, 56.42; H, 3.44; N, 11.62. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, δ / ppm): 13.00 (s, 1H, NH imidazole), 9.57 (s, 2H, 2H3'), 9.47 (s, 2H, 2H3'), 9.17-9.13 (m, 6H, 4H6+2H9), 9.74-8.69 (m, 4H, 4H8), 8.62 (d, 2H, J = 8.5 Hz, 2H7), 8.53 (t, 2H, J = 7.9 Hz, 2H11), 8.37 (d, 2H, J = 7.4 Hz, 2H12), 8.11-8.05 (m, 4H, 4H4), 7.91 (t, 2H, J = 6.7 Hz, 2H10), 7.56 (t, 6H, J = 6.4 Hz, 2H7+4H3), 7.31-7.25 (m, 4H, 4H5), 2.48 (s, 3H, CH<sub>3</sub>).

Synthesis of [(dipy-Hbzim-tpy)Ru(H<sub>2</sub>pbbzim)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (1b). A mixture of  $[(H_2pbbzim)RuCl_3]$  (95 mg, 0.18 mmol) and dipy-Hbzim-tpy (110 mg, 0.20 mmol) in 20 mL of ethylene glycol was refluxed for 3h with continuous stirring under argon protection. The resulting solution was then cooled down to room temperature, filtered and poured into an aqueous solution of NaClO<sub>4</sub>·H<sub>2</sub>O (1.0 g in 5 mL of water) to precipitate the complex as the perchlorate salt. The red colored precipitate was filtered, washed with water and then dried under vacuum. The complex was then purified by silica gel column chromatography using CH<sub>3</sub>CN as the eluent. The desired compound was obtained by rotary evaporation of the eluent and

subsequent anion exchange reaction with NaClO<sub>4</sub>·H<sub>2</sub>O. The compound was finally recrystallized from CH<sub>3</sub>CN-H<sub>2</sub>O (2:1) mixture in presence of a few drops of 10<sup>-4</sup> M HClO<sub>4</sub> Yield: 120 mg, 55%. Anal. Calcd. for C<sub>53</sub>H<sub>38</sub>N<sub>12</sub>Cl<sub>2</sub>O<sub>9</sub>Ru: C, 54.92; H, 3.31; N, 14.50 Found: C, 54.84; H, 3.40; N, 14.42. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ /ppm): 15.03 (s, 2H, NH imidazole, H<sub>2</sub>pbbzim), 13.03 (s, 1H, NH imidazole), 9.66 (s, 2H, 2H3'), 9.05 (d, 4H, *J* = 7.6 Hz, 2H6+2H9), 8.79 (t, 5H, *J* = 9.2 Hz, 2H8+H17+2H18), 8.68-8.65 (m, 4H, 2H7+2H12), 8.45-8.43 (m, 2H, 2H11), 7.97 (t, 2H, *J* = 7.6 Hz, 2H5), 7.85-7.82 (m, 2H, 2H10), 7.66 (d, 2H, *J* = 7.9 Hz, 2H3), 7.5 (d, 2H, *J* = 5.0 Hz, 2H19), 7.27-7.25 (m, 4H, 2H5+2H20), 7.01 (t, 2H, *J* = 7.8 Hz, 2H21), 6.08 (d, 2H, *J* = 8.1 Hz, 2H22).

Physical Measurements. Elemental analyses of the compounds were performed with a Vario-Micro V2.0.11 elemental (CHNSO) analyzer. NMR spectra were collected on either a Bruker 300 or Bruker 500 spectrometer in DMSO- $d_6$ , and high resolution mass spectroscopy was performed on a Waters Xevo G2 QTOf mass spectrometer. UV-vis absorption spectra were recorded using a Shimadzu UV 1800 spectrometer at room temperature. Steady state luminescence spectra were obtained by either Perkin-Elmer LS55 or Horiba Fluoromax-4C spectrofluorometer. Luminescence quantum yields were determined using literature method taking [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as the standard. Luminescence lifetime measurements were carried out by using time-correlated single photon counting set up from Horiba Jobin-Yvon. The samples were excited with 450 nm Nanoled. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software. Cyclic and square-wave voltammetric experiments were performed in deaerated acetonitrile with a BAS epsilon electrochemistry system and a three-electrode set up consisting of a platinum or glassy carbon working electrode, a platinum counter electrode, and Ag/AgCl reference electrode. Tetraethylammonium perchlorate (TEAP) was used as background electrolyte. The potentials reported in this study were referenced against the Ag/AgCl electrode, which under the given experimental conditions gave a value of 0.36 V for the Fc/Fc<sup>+</sup> couple.



**Fig. S1** <sup>1</sup>H-<sup>1</sup>H COSY spectra of complex  $[(bpy)_2Ru(tpy-Hbzim-dipy)Ru(H_2pbbzim)](ClO_4)_4$  (4) in DMSO-*d*<sub>6</sub>.



**Fig. S2** <sup>1</sup>H-<sup>1</sup>H COSY spectra of complex  $[(bpy)_2Ru(tpy-Hbzim-dipy)Ru(H_2pbbzim)](ClO_4)_4$  (6) in DMSO-*d*<sub>6</sub>.



**Fig. S3** ESI-MS (positive) for the complex cations of **3**,  $[(bpy)_2Ru(dipy-bzim-tpy)Ru(tpy-PhCH_3)]^{3+}$  (*m/z* = 455.78) in acetonitrile showing the observed and isotopic distribution patterns.



Fig. S4 ESI-MS (positive) for the complex cations of 6,  $[(phen)_2Ru(dipy-Hbzim-tpy) Ru(Hpbbzim)]^{3+}$  (*m/z* = 467.77) and  $[(phen)_2Ru(dipy-Hbzim-tpy)Ru(pbbzim)]^{2+}$  (*m/z* = 701.17) in acetonitrile showing the observed and isotopic distribution patterns.



**Fig. S5** Excited state decay profiles along with their lifetime values for **4** (a) and **5** (b) in MeCN as a function of temperature. The nonlinear fit of the temperature-dependent lifetime data of **4** (c) and **5** (d) using equation 1. Insets of (c) and (d) show the values of different parameters.