

## Electronic Supplementary Information

### **Tuning visible-light absorption properties of Ru-diacetylide complexes: a simple access to colorful efficient dyes for DSSC.**

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**Figure S6.** IPCE action spectra of a co-sensitized DSSC device including **[Ru]1&[Ru]3** in a [4:1] molar ratio (black plain line), and single-dye devices including **[Ru]1** (red dotted line) or **[Ru]3** (blue dotted line).

**Figure S7.** Molecular structure of the commercial dye N3 and  $J(V)$  curves (plain: light; dashed: dark) of DSSC based on this benchmark-dye.

## 1. Materials and methods

The reactions were carried out under inert atmosphere using the Schlenk techniques. Solvents were dried from appropriate drying agents (sodium for pentane, diethyl ether and THF; calcium hydride for dichloromethane, chloroform and methanol) and freshly distilled under nitrogen before use. All reagents were obtained from commercially available sources and used without further purification. [RuCl(dppe)<sub>2</sub>][TfO] (**[1][TfO]**),<sup>[1]</sup> 4-trimethylsilylethynylbenzaldehyde (**(III)**)<sup>[2]</sup> and 5'-ethynyl-[2,2']bithiophene-5-carbaldehyde<sup>[3]</sup> were synthesized according to literature procedures. 9-(4-Ethynylphenyl)carbazole (**(2)**), 2-trimethylsilylethylcyanoethanoate, **[3][TfO]** and **[Ru]1** were prepared as previously reported.<sup>[4]</sup>

<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR analyses were performed on Bruker Avance III 200 MHz, Avance I 300 MHz, Avance II 400 MHz and Avance III 600 MHz spectrometers. Chemical shift values are given in ppm with reference to solvent residual signals.

HR-MS analyses were performed by the CESAMO (Bordeaux, France). Electrospray (ESI): the measurements were carried out on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source and spectra were recorded in the positive mode. The electrospray needle was maintained at 4500 V and operated at room temperature. Samples were introduced by injection through a 20 µL sample loop into a 400 µL/min flow of methanol from the LC pump. Field desorption (FD): the measurements were carried out on a TOF mass spectrometer AccuTOF GCv using an FD emitter with an emitter voltage of 10 kV. One to two microliters solution of the compound were deposited on a 13µm emitter wire.

Elemental analyses were performed on a Thermo Scientific Flash 2000 Elemental Analyser.

FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer using KBr pellets.

UV-visible absorption and emission fluorescence spectra were recorded on a UV-1650PC SHIMADZU spectrophotometer and on a FluoroMax-4 HORIBA spectrofluorometer, respectively.

Cyclic voltammetry analyses were performed using a potentiostat/galvanostat Autolab PGSTAT100 and a three-electrode system (working electrode: Pt disc; reference electrode: Ag/AgCl, calibrated with decamethylferrocene as internal reference; counter electrode: Pt) with 0.1M Bu<sub>4</sub>NPF<sub>6</sub> as salt support at a scan rate of 100 mV.s<sup>-1</sup>.

The method used for dye-loading amount determination is as follows: a solution of dye (0.3 mM) and cheno-deoxycholic acid (1 mM) in dichloromethane was prepared and used to sensitize a nanoparticulate TiO<sub>2</sub> thin-film (thickness = 9 µm ; surface area = 1 cm<sup>2</sup>) as described in the experimental section. UV-visible absorption spectrum of the dye solution was recorded prior to and after sensitization. The amount of dye loaded onto TiO<sub>2</sub> was deduced from the difference between the two sets of data.

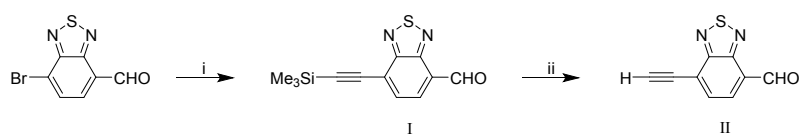
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[2] C. Teng, X. Yang, C. Yang, S. Li, M. Cheng, A. Hagfeldt and L. Sun, *J. Phys. Chem. C*, 2010, **114**, 9101.

[3] J.-L. Fillaut, J. Perruchon, P. Blanchard, J. Roncali, S. Golhen, M. Allain, A. Migalsaka-Zalas, I. V. Kityk and B. Sahraoui, *Organometallics*, 2005, **24**, 687.

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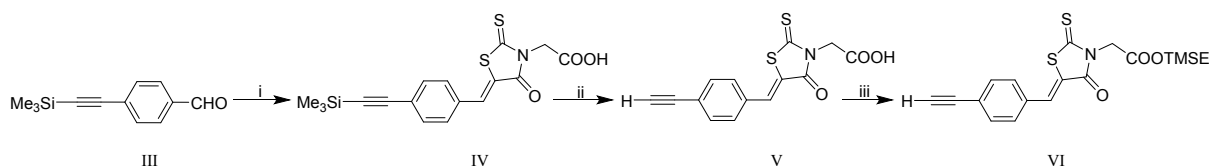
## 2. Synthesis of organic precursors



**Scheme S1.** Synthetic route to 7-ethynyl-2,1,3-benzothiadiazole-4-carbaldehyde (**II**): i) TMSA, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, Et<sub>3</sub>N, THF; ii) K<sub>2</sub>CO<sub>3</sub>, MeOH.

*Synthesis of 7-(trimethylsilylethynyl)-2,1,3-benzothiadiazole-4-carbaldehyde (I):* To a solution of 7-bromo-2,1,3-benzothiadiazole-4-carbaldehyde (1.0 g, 4.1 mmol, 1 equiv.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (140 mg, 0.20 mmol, 5%) and CuI (19 mg, 0.10 mmol, 2.5%) in dry THF (15 mL) under inert atmosphere, were added distilled Et<sub>3</sub>N (15 mL) and trimethylsilylacetylene (0.75 mL, 5 mmol, 1.2 equiv.). The suspension was stirred for 24 h at room temperature. After removal of the solvent, the resulting solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered. The crude product was purified on silica gel column chromatography (petroleum ether/ethyl acetate (90:10, v/v)) to afford **I** as a yellow solid in 63 % yield (0.67 g, 2.6 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.75 (s, 1H), 8.17 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 12 Hz), 7.90 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 12 Hz), 0.35 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 191.9 (C<sub>q</sub>(C=O)), 155.3 (C<sub>q</sub>(C=N)), 152.8 (C<sub>q</sub>(C=N)), 142.8 (C<sub>q</sub>), 133.6 (CH), 128.3 (CH), 117.1 (C<sub>q</sub>), 103.0 (C<sub>q</sub>), 100.2 (C<sub>q</sub>), 0.08 (CH<sub>3</sub>(SiMe<sub>3</sub>)).

*Synthesis of 7-ethynyl-2,1,3-benzothiadiazole-4-carbaldehyde (II):* To a solution of **I** (0.65 g, 2.5 mmol, 1 equiv.) in dry MeOH (20 mL) and under inert atmosphere, was added K<sub>2</sub>CO<sub>3</sub> (35 mg, 0.25 mmol, 0.1 equiv.). The suspension was stirred for 24 h at room temperature. The reaction mixture was poured into water (300 mL) and extracted with Et<sub>2</sub>O. The organics were washed with brine, dried over MgSO<sub>4</sub> and evaporated to dryness. The crude product was recrystallized from hot pentane and dried to afford **II** as a yellow solid in 72 % yield (0.34 g, 1.8 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 10.78 (s, 1H), 8.20 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 12 Hz), 7.96 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 12 Hz), 3.92 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 192.1 (C<sub>q</sub>(C=O)), 155.1 (C<sub>q</sub>(C=N)), 151.6 (C<sub>q</sub>(C=N)), 142.9 (C<sub>q</sub>), 134.2 (CH), 128.5 (CH), 123.6 (C<sub>q</sub>), 84.4 (CH), 79.6 (C<sub>q</sub>).



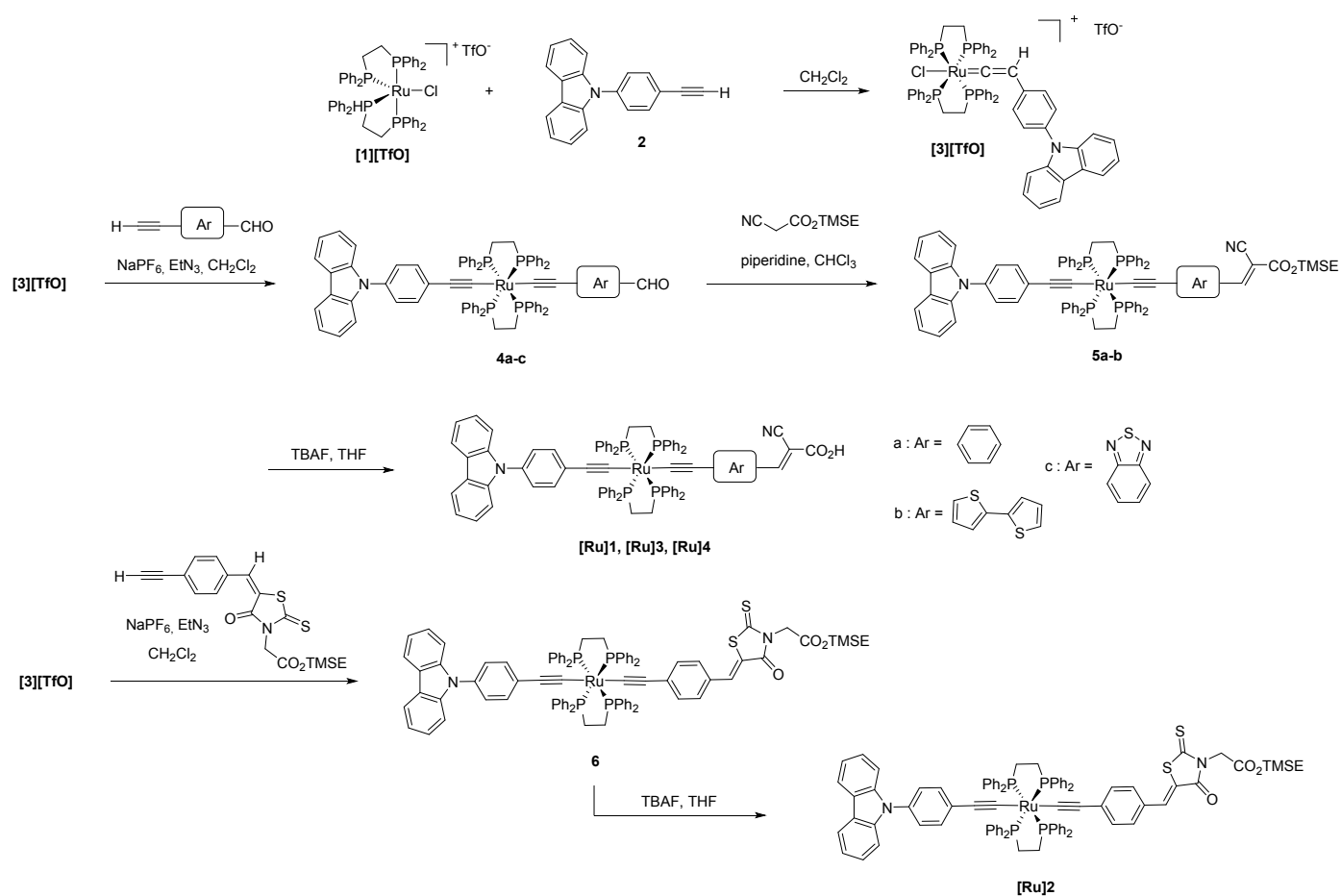
**Scheme S2.** Synthetic route to **VI**: i) rhodanine-3-acetic acid, ammonium acetate, acetic acid; ii) K<sub>2</sub>CO<sub>3</sub>, MeOH; iii) HBTU, DIPEA, 2-trimethylsilylethanol, DMF.

*Synthesis of IV:* In a Schlenk tube under inert atmosphere, 4-(trimethylsilylethynyl)benzaldehyde **III** (1.00 g, 4.94 mmol, 1 equiv.), rhodanine-3-acetic acid (1.04 g, 5.44 mmol, 1.1 equiv.) and ammonium acetate (0.11 g, 1.48 mmol, 0.3 equiv.) were dissolved in acetic acid (20 mL) and the solution was stirred for 3 h at 120°C. The mixture was cooled to room temperature and a precipitate was formed that was collected by filtration. The solid was washed with water and dried under vacuum to afford **IV** as a yellow powder in 92 % yield (1.70 g, 4.53 mmol). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ = 13.47 (br. s, 1H), 7.89 (s, 1H), 7.67 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 8 Hz), 7.61 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 8 Hz), 4.75 (s, 2H), 0.25 (s, 9H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ = 192.9 (C<sub>q</sub>(C=S)), 167.2 (C<sub>q</sub>(COOH)), 166.3 (C<sub>q</sub>(C=O)), 133.1 (C<sub>q</sub>), 132.7 (CH), 132.5 (CH), 130.9 (CH), 124.4 (C<sub>q</sub>), 122.9 (C<sub>q</sub>), 104.4 (C<sub>q</sub>), 97.9 (C<sub>q</sub>), 45.0 (CH<sub>2</sub>), -0.2 (CH<sub>3</sub>(SiMe<sub>3</sub>)). HR-MS ESI- (m/z): 374.0339 [M-H]<sup>-</sup> (calcd. 374.0346 for [C<sub>17</sub>H<sub>16</sub>NO<sub>3</sub>SiS<sub>2</sub>]<sup>-</sup>). FT-IR (KBr): ν<sub>C=C</sub> = 2152 cm<sup>-1</sup>, ν<sub>C=O(acid)</sub> = 1734 cm<sup>-1</sup>, ν<sub>C=O(amide)</sub> = 1716 cm<sup>-1</sup>, ν<sub>Si-C</sub> = 862-844 cm<sup>-1</sup>.

*Synthesis of V:* To a solution of **IV** (1.65 g, 4.39 mmol, 1 equiv.) in dry MeOH (130 mL) and under inert atmosphere, was added K<sub>2</sub>CO<sub>3</sub> (0.91 g, 6.59 mmol, 1.5 equiv.) and the resulting suspension was stirred at room temperature overnight. The reaction mixture was poured into 3N aqueous HCl (300 mL) at 0°C. A precipitate was formed that was collected by filtration, washed with water and dried under vacuum to afford **V** as an orange powder in 81 % yield (1.08 g, 3.56 mmol). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ = 13.47 (br. s, 1H), 7.91 (s, 1H), 7.70 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 8 Hz), 7.65 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 8 Hz), 4.75 (s, 2H), 4.48 (s, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>): δ = 193.0 (C<sub>q</sub>(C=S)), 167.2 (C<sub>q</sub>(COOH)), 166.3 (C<sub>q</sub>(C=O)), 133.1 (C<sub>q</sub>), 132.7 (CH), 132.6 (CH), 130.9 (CH), 124.1 (C<sub>q</sub>), 122.9 (C<sub>q</sub>), 84.0 (CH(=C-H)), 82.9 (C<sub>q</sub>), 45.0 (CH<sub>2</sub>). FT-IR (KBr): ν<sub>C-H</sub> = 3257 cm<sup>-1</sup>, ν<sub>C=C</sub> = 2105 cm<sup>-1</sup>, ν<sub>C=O(acid)</sub> = 1726 cm<sup>-1</sup>, ν<sub>C=O(amide)</sub> = 1711 cm<sup>-1</sup>.

**Synthesis of VI:** To a solution of **V** (0.50 g, 1.65 mmol, 1 equiv.) and HBTU (0.75 g, 1.98 mmol, 1.2 equiv.) in anhydrous DMF (20 mL) and under inert atmosphere, DIPEA (1.44 mL, 8.24 mmol, 5 equiv.) and 2-trimethylsilylethanol (0.35 mL, 2.47 mmol, 1.5 equiv.) were added and the resulting suspension was stirred at room temperature overnight. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with saturated NH<sub>4</sub>Cl aqueous solution and pure water. The organic layers were combined, dried over MgSO<sub>4</sub> and evaporated to dryness. The crude product was purified on silica gel column (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (7:3, v/v) to (1:1, v/v)) to afford **VI** as a yellow powder in 51 % yield (0.34 g, 0.84 mmol). <sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.74 (s, 1H), 7.60 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz), 7.49 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz), 4.82 (s, 2H), 4.27 (m, 2H), 3.34 (s, 1H), 1.03 (m, 2H), 0.05 (s, 9H). <sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 193.3 (C<sub>q</sub>(C=S)), 167.3 (C<sub>q</sub>(CO<sub>2</sub>TMSE)), 166.3 (C<sub>q</sub>(C=O)), 133.9 (C<sub>q</sub>), 133.3 (CH), 132.9 (CH), 130.9 (CH), 124.9 (C<sub>q</sub>), 124.1 (C<sub>q</sub>), 83.1 (CH(=C-H)), 80.7 (C<sub>q</sub>), 64.9 (CH<sub>2</sub>(TMSE)), 45.4 (CH<sub>2</sub>), 17.6 (CH<sub>2</sub>(TMSE)), -1.5 (CH<sub>3</sub>(SiMe<sub>3</sub>)). HR-MS ESI+ (m/z): 426.0641 [M+Na]<sup>+</sup> (calcd. 426.0624 for [C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>NaSiS<sub>2</sub>]<sup>+</sup>). FT-IR (KBr): ν<sub>C-H</sub> = 3258 cm<sup>-1</sup>, ν<sub>C=C</sub> = 2103 cm<sup>-1</sup>, ν<sub>C=O(ester)</sub> = 1736 cm<sup>-1</sup>, ν<sub>C=O(amide)</sub> = 1713 cm<sup>-1</sup>.

### 3. Synthesis of organometallic complexes



**General procedure for the preparation of Ru-diacetylide intermediate complexes 4b-c and 6.** To a solution of [3][TfO] (1 equiv.), ethynyl-aryl-carbaldehyde (1.1 equiv.) and NaPF<sub>6</sub> (2 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> and under inert atmosphere, was added distilled Et<sub>3</sub>N (3 equiv.). The reaction mixture was stirred for 24 h at room temperature. The organics were further washed with degassed water and evaporated to dryness. Precipitation from a CH<sub>2</sub>Cl<sub>2</sub>/pentane mixture afforded pure Ru-diacetylide intermediate complexes.

**Synthesis of 4b:** General procedure was applied using [3][TfO] (0.70 g, 0.52 mmol), 5'-ethynyl-[2,2']bithiophene-5-carbaldehyde (0.13 g, 0.57 mmol), NaPF<sub>6</sub> (0.18 g, 1.04 mmol), CH<sub>2</sub>Cl<sub>2</sub> (75 mL) and Et<sub>3</sub>N (0.21 mL, 1.56 mmol). Pure **4b** was obtained as a red solid in 90 % yield (0.64 g, 0.46 mmol). <sup>31</sup>P NMR (240 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 52.63 (s, P<sub>(dppf)</sub>). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.82 (s, 1H), 8.17 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz), 7.73–7.69 (m, 8H), 7.68 (d, 1H), <sup>3</sup>J<sub>H-H</sub> = 3.9 Hz, 7.49 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz), 7.47–7.44 (m, 2H), 7.36–7.33 (m, 10H), 7.31–7.28 (m, 2H), 7.26 (t, 4H, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz), 7.23 (t, 4H, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz), 7.20 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 3.7 Hz), 7.18 (d, 1H, <sup>3</sup>J<sub>H-H</sub> = 3.9 Hz),

7.08 (t, 8H,  $^3J_{\text{H-H}} = 7.7$  Hz), 7.05–7.02 (m, 10H), 6.21 (d, 1H,  $^3J_{\text{H-H}} = 3.7$  Hz), 2.73–2.64 (m, 8H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 182.5$  ( $\text{CH}_{(\text{CHO})}$ ), 150.1 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 148.8 ( $\text{C}_{\text{q}}$ ), 141.5 ( $\text{C}_{\text{q}}$ ), 140.3 ( $\text{C}_{\text{q}}$ ), 138.3 ( $\text{CH}$ ), 137.3 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 137.0 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 134.8 ( $\text{CH}$ ), 134.5 ( $\text{C}_{\text{q}}$ ), 134.2 ( $\text{CH}$ ), 133.0 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 132.9 ( $\text{C}_{\text{q}}$ ), 131.4 ( $\text{CH}$ ), 130.0 ( $\text{C}_{\text{q}}$ ), 129.4 ( $\text{CH}$ ), 129.3 ( $\text{C}_{\text{q}}$ ), 129.2 ( $\text{CH}$ ), 127.7 ( $\text{CH}$ ), 127.6 ( $\text{CH}$ ), 126.8 ( $\text{CH}$ ), 126.7 ( $\text{CH}$ ), 126.6 ( $\text{CH}$ ), 126.2 ( $\text{CH}$ ), 123.6 ( $\text{C}_{\text{q}}$ ), 122.8 ( $\text{CH}$ ), 120.5 ( $\text{CH}$ ), 120.0 ( $\text{CH}$ ), 117.8 ( $\text{C}_{\text{q}}$ ), 110.3 ( $\text{CH}$ ), 110.0 ( $\text{C}_{\text{q}}$ ), 31.80 (m,  $\text{CH}_2(\text{dppe})$ ). HR-MS ESI+ (m/z): 1404.3 [ $\text{M}+\text{Na}$ ] $^+$  (calcd. 1404.2 for [ $\text{C}_{83}\text{H}_{65}\text{NOP}_4\text{RuS}_2\text{Na}$ ] $^+$ ). FT-IR (KBr):  $\nu_{\text{C}=\text{C}} = 2040$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}} = 1658$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}(\text{Thiophene})} = 1433$   $\text{cm}^{-1}$ ,  $\nu_{\text{P-Ph}} = 1096$   $\text{cm}^{-1}$ .

**Synthesis of 4c:** General procedure was applied using **[3][TfO]** (0.50 g, 0.33 mmol), 7-ethynyl-2,1,3-benzothiadiazole-4-carbaldehyde (**II**) (0.07 g, 0.36 mmol),  $\text{NaPF}_6$  (0.11 g, 0.66 mmol),  $\text{CH}_2\text{Cl}_2$  (35 mL) and  $\text{Et}_3\text{N}$  (0.14 mL, 1 mmol). Pure **4c** was obtained as a dark blue solid in 78 % yield (0.35 g, 0.26 mmol).  $^{31}\text{P}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 52.81$  (s,  $\text{P}_{(\text{dppe})}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 10.57$  (s, 1H), 8.18 (d, 2H,  $^3J_{\text{H-H}} = 8$  Hz), 7.94 (d, 1H,  $^3J_{\text{H-H}} = 8$  Hz), 7.80 (m, 8H), 7.48 (m, 6H), 7.38 (d, 2H,  $^3J_{\text{H-H}} = 8$  Hz), 7.30–7.06 (m, 26H), 6.76 (m, 8H), 6.25 (d, 1H,  $^3J_{\text{H-H}} = 8$  Hz), 3.05 (m, 4H), 2.77 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 188.2$  ( $\text{CH}_{(\text{CHO})}$ ), 171.2 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 156.9 ( $\text{C}_{\text{q}}$ ), 154.1 ( $\text{C}_{\text{q}}$ ), 141.2 ( $\text{CH}$ ), 137.1 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 136.5 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 134.6 ( $\text{CH}$ ), 133.8 ( $\text{CH}$ ), 133.6 ( $\text{C}_{\text{q}}$ ), 132.9 ( $\text{C}_{\text{q}}$ ), 131.8 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 131.1 ( $\text{CH}$ ), 129.9 ( $\text{C}_{\text{q}}$ ), 129.6 ( $\text{C}_{\text{q}}$ ), 129.3 ( $\text{CH}$ ), 128.7 ( $\text{CH}$ ), 127.5 ( $\text{CH}$ ), 127.2 ( $\text{CH}$ ), 126.5 ( $\text{CH}$ ), 126.0 ( $\text{CH}$ ), 123.3 ( $\text{C}_{\text{q}}$ ), 122.2 ( $\text{C}_{\text{q}}$ ), 122.0 ( $\text{C}_{\text{q}}$ ), 120.3 ( $\text{CH}$ ), 119.8 ( $\text{CH}$ ), 119.2 ( $\text{C}_{\text{q}}$ ), 110.1 ( $\text{CH}$ ), 31.66 (m,  $\text{CH}_2(\text{dppe})$ ). HR-MS FD+ (m/z): 1351.2719 [ $\text{M}$ ] $^+$  (calcd. 1351.2686 for [ $\text{C}_{81}\text{H}_{63}\text{N}_3\text{OP}_4\text{RuS}$ ]). FT-IR (KBr):  $\nu_{\text{C}=\text{C}} = 2042$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}} = 1665$   $\text{cm}^{-1}$ ,  $\nu_{\text{P-Ph}} = 1095$   $\text{cm}^{-1}$ .

**Synthesis of 6:** General procedure was applied using **[3][TfO]** (0.15 g, 0.11 mmol), **VI** (0.05 g, 0.12 mmol),  $\text{NaPF}_6$  (0.04 g, 0.22 mmol),  $\text{CH}_2\text{Cl}_2$  (15 mL) and  $\text{Et}_3\text{N}$  (0.05 mL, 0.33 mmol). The crude product was dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and pentane was added under stirring. Pure **6** was obtained as a purple solid in 80% yield (0.14 g, 0.09 mmol).  $^{31}\text{P}$  NMR (120 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 52.91$  (s,  $\text{P}_{(\text{dppe})}$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.17$  (d, 2H,  $^3J_{\text{H-H}} = 7.8$  Hz), 7.76 (s, 1H), 7.66 (m, 8H), 7.51–7.18 (m, 26H), 7.12–6.91 (m, 18H), 6.75 (d, 2H,  $^3J_{\text{H-H}} = 8.3$  Hz), 4.85 (s, 2H), 4.28 (m, 2H), 2.69 (m, 8H), 1.05 (m, 2H), 0.07 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 193.8$  ( $\text{C}_{\text{q}}(\text{C}=\text{S})$ ), 167.6 ( $\text{C}_{\text{q}}(\text{COOTMSE})$ ), 166.6 ( $\text{C}_{\text{q}}(\text{C}=\text{O})$ ), 150.0 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 141.5 ( $\text{C}_{\text{q}}$ ), 137.4 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 137.1 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 135.0 ( $\text{CH}$ ), 134.7 ( $\text{CH}$ ), 134.4 ( $\text{CH}$ ), 133.3 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 132.9 ( $\text{C}_{\text{q}}$ ), 131.4 ( $\text{CH}$ ), 131.2 ( $\text{CH}$ ), 131.2 ( $\text{CH}$ ), 130.0 ( $\text{C}_{\text{q}}$ ), 129.4 ( $\text{CH}$ ), 129.3 ( $\text{C}_{\text{q}}$ ), 129.3 ( $\text{CH}$ ), 127.8 ( $\text{C}_{\text{q}}$ ), 127.6 ( $\text{CH}$ ), 127.6 ( $\text{CH}$ ), 126.6 ( $\text{CH}$ ), 126.2 ( $\text{CH}$ ), 123.6 ( $\text{C}_{\text{q}}$ ), 120.6 ( $\text{CH}$ ), 120.2 ( $\text{C}_{\text{q}}$ ), 120.0 ( $\text{CH}$ ), 118.8 ( $\text{C}_{\text{q}}$ ), 117.8 ( $\text{C}_{\text{q}}$ ), 110.3 ( $\text{CH}$ ), 64.8 ( $\text{CH}_2(\text{TMSE})$ ), 45.4 ( $\text{CH}_2$ ), 31.8 (m,  $\text{CH}_2(\text{dppe})$ ), 17.6 ( $\text{CH}_2(\text{TMSE})$ ), -1.5 ( $\text{CH}_3(\text{SiMe}_3)$ ). HR-MS ESI+ (m/z): 1589.4 [ $\text{M}+\text{Na}$ ] $^+$  (calcd. 1589.3 for [ $\text{C}_{91}\text{H}_{80}\text{N}_2\text{O}_3\text{P}_4\text{RuS}_2\text{SiNa}$ ] $^+$ ). FT-IR (KBr):  $\nu_{\text{C}=\text{C}} = 2046$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}(\text{ester})} = 1750$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}(\text{amide})} = 1709$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}(\text{Ph } \pi\text{-conj.})} = 1568$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}(\text{ester})} = 1173$   $\text{cm}^{-1}$ ,  $\nu_{\text{P-Ph}} = 1098$   $\text{cm}^{-1}$ ,  $\nu_{\text{Si-C}} = 833$   $\text{cm}^{-1}$ .

**General procedure for Knoevenagel condensation.** To a solution of carbaldehyde-functionalized Ru-complex (1 equiv.) and 2-trimethylsilylethylcyano-ethanoate (2 equiv.), in dry  $\text{CHCl}_3$  and under inert atmosphere, was added piperidine (4 equiv.). The reaction mixture was refluxed for 48 h. The organics were further washed with degassed water and evaporated to dryness. Precipitation from a  $\text{CH}_2\text{Cl}_2$ /pentane mixture afforded pure complexes **5b-c**.

**Synthesis of 5b:** General procedure for the Knoevenagel condensation was applied using **4b** (0.25 g, 0.18 mmol), 2-trimethylsilylethylcyano-ethanoate (0.07 g, 0.36 mmol), piperidine (0.07 mL, 0.72 mmol) and  $\text{CHCl}_3$  (30 mL). Pure **5b** was obtained as a dark blue solid in 82 % yield (0.23 g, 0.15 mmol).  $^{31}\text{P}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 52.52$  (s,  $\text{P}_{(\text{dppe})}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.24$  (s, 1H), 8.17 (d, 2H,  $^3J_{\text{H-H}} = 7.8$  Hz), 7.73–7.66 (m, 8H), 7.50–7.43 (m, 5H), 7.36–7.21 (m, 21H), 7.18 (d, 1H,  $^3J_{\text{H-H}} = 4.1$  Hz), 7.10–6.99 (m, 18H), 6.20 (d, 1H,  $^3J_{\text{H-H}} = 3.8$  Hz), 4.43–4.36 (m, 2H), 2.75–2.62 (m, 8H), 1.18–1.12 (m, 2H), 0.10 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 163.8$  ( $\text{C}_{\text{q}}(\text{COOTMSE})$ ), 152.5 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 149.4 ( $\text{C}_{\text{q}}$ ), 146.1 ( $\text{CH}$ ), 141.5 ( $\text{C}_{\text{q}}$ ), 140.2 ( $\text{CH}$ ), 137.3 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 137.0 (m,  $\text{C}_{\text{q}}(\text{dppe})$ ), 135.2 ( $\text{C}_{\text{q}}$ ), 134.8 ( $\text{CH}$ ), 134.2 ( $\text{CH}$ ), 133.0 ( $\text{C}_{\text{q}}$ ), 132.9 ( $\text{C}_{\text{q}}$ ), 132.9 (quint.,  $\text{C}_{\text{q}}(\text{Ru-C}\equiv)$ ), 131.4 ( $\text{CH}$ ), 130.0 ( $\text{C}_{\text{q}}$ ), 129.5 ( $\text{CH}$ ), 129.2 ( $\text{CH}$ ), 129.2 ( $\text{C}_{\text{q}}$ ), 127.7 ( $\text{CH}$ ), 127.7 ( $\text{CH}$ ), 127.5 ( $\text{CH}$ ), 127.1 ( $\text{CH}$ ), 126.6 ( $\text{CH}$ ), 126.2 ( $\text{CH}$ ), 123.6 ( $\text{C}_{\text{q}}$ ), 123.1 ( $\text{CH}$ ), 120.6 ( $\text{CH}$ ), 120.1 ( $\text{CH}$ ), 117.9 ( $\text{C}_{\text{q}}(\text{Ru}=\text{C}_-$ ), 117.1 ( $\text{C}_{\text{q}}(\text{Ru}=\text{C}_-$ ), 110.8 ( $\text{C}_{\text{q}}$ ), 110.3 ( $\text{CH}$ ), 96.3 ( $\text{C}_{\text{q}}(\text{C}=\text{N})$ ), 65.0 ( $\text{CH}_2$ ), 31.8 (m,  $\text{CH}_2(\text{dppe})$ ), 17.8 ( $\text{CH}_2$ ), -1.4 ( $\text{CH}_3(\text{SiMe}_3)$ ). HR-MS FD+ (m/z): 1542.32922 [ $\text{M}$ ] $^+$  (calcd. 1542.33004 for [ $\text{C}_{91}\text{H}_{78}\text{N}_2\text{O}_2\text{P}_4\text{RuS}_2\text{Si}$ ]). FT-IR (KBr):  $\nu_{\text{C}=\text{N}} = 2213$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}} = 2037$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}} = 1713$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}(\text{Thiophene})} = 1420$   $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}} = 1195$   $\text{cm}^{-1}$ ,  $\nu_{\text{P-Ph}} = 1095$   $\text{cm}^{-1}$ ,  $\nu_{\text{Si-C}} = 836$   $\text{cm}^{-1}$ .

**Synthesis of 5c:** General procedure for the Knoevenagel condensation was applied using **4c** (0.17 g, 0.12 mmol), 2-trimethylsilylethylcyano-ethanoate (0.044 g, 0.24 mmol), piperidine (0.05 mL, 0.48 mmol) and  $\text{CHCl}_3$  (20 mL). Pure **5c** was obtained as a dark green solid in 80 % yield (0.14 g, 0.09 mmol).  $^{31}\text{P}$  NMR (240 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 52.75$  (s,  $\text{P}_{(\text{dppe})}$ ).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 9.13$  (s, 1H), 8.62 (d, 1H,  $^3J_{\text{H-H}} = 8$  Hz), 8.17 (d, 2H,  $^3J_{\text{H-H}} = 8$  Hz), 7.77 (m, 8H), 7.47 (m, 6H), 7.39 (d, 2H,  $^3J_{\text{H-H}} = 8$  Hz), 7.38–7.07 (m, 26H), 6.77 (m, 8H), 6.30 (d, 1H,  $^3J_{\text{H-H}}$

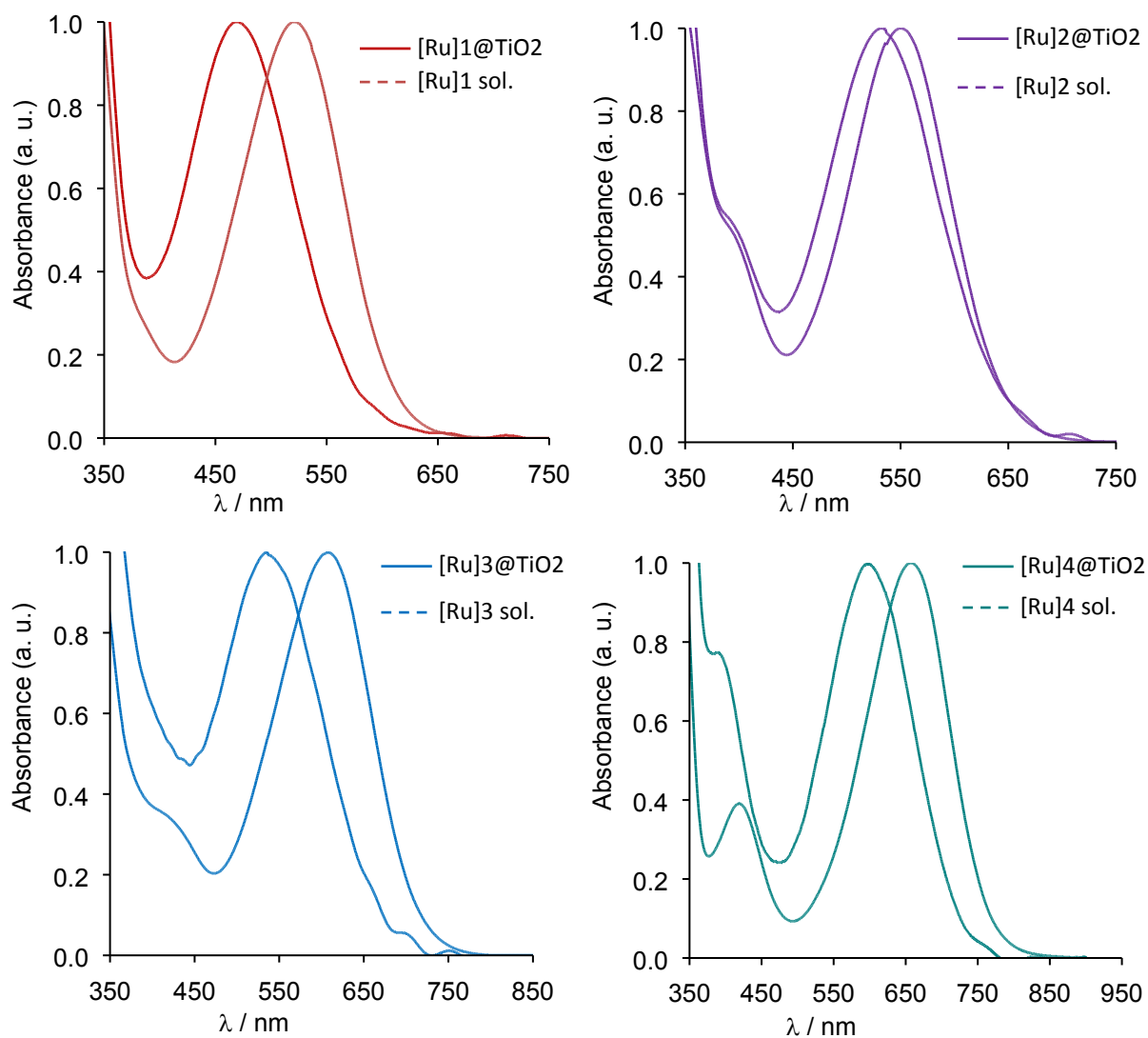
= 8Hz), 4.46 (m, 2H), 3.03 (m, 4H), 2.77 (m, 4H), 1.20 (m, 2H), 0.13 (s, 9H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 176.9 (quint.,  $C_{q(\text{Ru-C}\equiv)}$ ), 163.8 ( $C_{q(\text{COOTMSE})}$ ), 156.0 ( $C_q$ ), 155.7 ( $C_q$ ), 147.6 (CH), 141.2 ( $C_q$ ), 137.0 (m,  $C_{q(\text{dppe})}$ ), 136.3 (m,  $C_{q(\text{dppf})}$ ), 134.6 (CH), 133.8 (CH), 132.9 ( $C_q$ ), 131.2 (quint.,  $C_{q(\text{Ru-C}\equiv)}$ ), 131.1 (CH), 129.3 (CH), 128.8 (CH), 127.4 (CH), 127.2 (CH), 126.4 (CH), 126.0 (CH), 123.3 ( $C_q$ ), 120.3 (CH), 119.8 (CH), 117.9 ( $C_q$ ), 117.4 ( $C_q$ ), 110.1 (CH), 98.5 ( $C_{q(\text{C}\equiv\text{N})}$ ), 64.8 ( $\text{CH}_2$ ), 31.6 (m,  $\text{CH}_2(\text{dppf})$ ), 17.6 ( $\text{CH}_2$ ), -1.5 ( $\text{CH}_3(\text{SiMe}_3)$ ). HR-MS  $\text{FD}^+$  (m/z): 1518.3451 [ $\text{M}$ ] $^+$  (calcd. 1518.3452 for [ $\text{C}_{89}\text{H}_{76}\text{N}_4\text{O}_2\text{P}_4\text{RuSSi}$ ]). FT-IR (KBr):  $\nu_{\text{C}\equiv\text{N}}$  = 2215  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}}$  = 2040  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}}$  = 1718  $\text{cm}^{-1}$ ,  $\nu_{\text{C}-\text{O}}$  = 1180  $\text{cm}^{-1}$ ,  $\nu_{\text{P}-\text{Ph}}$  = 1096  $\text{cm}^{-1}$ ,  $\nu_{\text{Si}-\text{C}}$  = 836  $\text{cm}^{-1}$ .

**General procedure for silyl-ester deprotection.** To a solution of TMSE-protected complex (1 equiv.) in dry THF and under inert atmosphere was added TBAF (1M sol. in THF, 2 equiv.). The reaction mixture was stirred overnight at room temperature. After solvent removal the resulting solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and thoroughly washed with degassed citric acid aqueous solution (10 % m) and pure water. The organics were evaporated to dryness and the solid was further washed with pentane. Slow crystallization from a  $\text{CH}_2\text{Cl}_2$ /pentane mixture afforded pure complexes **[Ru]2-4**.

**Synthesis of [Ru]2:** General procedure for silyl-ester deprotection was applied using **6** (0.1 g, 0.065 mmol), TBAF (1M sol. in THF, 0.13 mL, 0.13 mmol) and THF (10 mL). Pure **[Ru]2** was obtained as a purple powder (0.07 g, 0.05 mmol) in 83 % yield.  $^{31}\text{P}$  NMR (240 MHz, THF-d8):  $\delta$  = 53.36 (s,  $\text{P}(\text{dppf})$ ).  $^1\text{H}$  NMR (600 MHz, THF-d8):  $\delta$  = 8.14 (d, 2H,  $^3J_{\text{H-H}}$  = 7.8 Hz), 7.75–7.67 (m, 9H), 7.48–7.43 (m, 10H), 7.40–7.34 (m, 6H), 7.25–7.16 (m, 10H), 7.09 (d, 2H,  $^3J_{\text{H-H}}$  = 8.1 Hz), 7.04 (t, 8H,  $^3J_{\text{H-H}}$  = 7.5 Hz), 6.97 (t, 8H,  $^3J_{\text{H-H}}$  = 7.5 Hz), 6.80 (d, 2H,  $^3J_{\text{H-H}}$  = 8.1 Hz), 4.82 (s, 2H), 2.78–2.67 (m, 8H).  $^{13}\text{C}$  NMR (150 MHz, THF-d8):  $\delta$  = 193.8 ( $C_{q(\text{C}=\text{S})}$ ), 167.5 ( $C_{q(\text{COOH})}$ ), 167.3 ( $C_{q(\text{C}=\text{O})}$ ), 148.9 (quint.,  $C_{q(\text{Ru-C}\equiv)}$ ), 141.8 ( $C_q$ ), ( $C_q$ ), 131.8 (CH), 131.6 (CH), 131.3 (CH), 130.5 ( $C_q$ ), 129.5 (CH), 129.4 (CH), 128.5 ( $C_q$ ), 127.8 (CH), 127.8 (CH), 126.7 (CH), 126.3 (CH), 124.1 ( $C_q$ ), 123.1 ( $C_q$ ), 120.7 (CH), 120.2 (CH), 119.4 ( $C_q$ ), 118.1 ( $C_q$ ), 110.5 (CH), 45.1 ( $\text{CH}_2$ ), 32.1 (m,  $\text{CH}_2(\text{dppf})$ ). MS MALDI-TOF (m/z): 1431.1 [ $\text{M}-\text{C}_2\text{H}_2\text{O}_2+\text{Na}$ ] $^+$  (calcd. 1431.3 for [ $\text{C}_{84}\text{H}_{66}\text{N}_2\text{NaOP}_4\text{RuS}_2$ ] $^+$ ) (Perfect matching between experimental and theoretical isotopic patterns). FT-IR (KBr):  $\nu_{\text{C}=\text{C}}$  = 2044  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}(\text{acid})}$  &  $\text{C}=\text{O}(\text{amide})$  = 1710  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}(\text{Ph } \pi\text{-conj.})}$  = 1567  $\text{cm}^{-1}$ ,  $\nu_{\text{C}-\text{O}(\text{acid})}$  = 1173  $\text{cm}^{-1}$ ,  $\nu_{\text{P}-\text{Ph}}$  = 1097  $\text{cm}^{-1}$ .

**Synthesis of [Ru]3:** General procedure for silyl-ester deprotection was applied using **5b** (0.20 g, 0.13 mmol), TBAF (1M in THF, 0.26 mL, 0.26 mmol) and THF (20 mL). Pure **[Ru]3** was obtained as a dark blue powder in 80 % yield (0.15 g, 0.10 mmol).  $^{31}\text{P}$  NMR (240 MHz, THF-d8):  $\delta$  = 55.01.  $^1\text{H}$  NMR (600 MHz, THF-d8):  $\delta$  = 8.30 (s, 1H), 8.14 (d, 2H,  $^3J_{\text{H-H}}$  = 7.8 Hz), 7.80–7.73 (m, 9H), 7.45 (d, 2H,  $^3J_{\text{H-H}}$  = 8.2 Hz), 7.41–7.34 (m, 12H), 7.25 (d, 1H,  $^3J_{\text{H-H}}$  = 3.8 Hz), 7.25–7.21 (m, 7H), 7.19 (t, 4H,  $^3J_{\text{H-H}}$  = 7.6 Hz), 7.09 (d, 2H,  $^3J_{\text{H-H}}$  = 8.3 Hz), 7.06 (t, 8H,  $^3J_{\text{H-H}}$  = 7.6 Hz), 7.00 (t, 8H,  $^3J_{\text{H-H}}$  = 7.6 Hz), 6.21 (d, 1H,  $^3J_{\text{H-H}}$  = 3.8 Hz), 2.71 (m, 8H).  $^{13}\text{C}$  NMR (150 MHz, THF-d8):  $\delta$  = 164.2 ( $C_{q(\text{COOH})}$ ), 151.7 (quint.,  $C_{q(\text{Ru-C}\equiv)}$ ), 145.9 (CH), 148.9 ( $C_q$ ), 141.8 ( $C_q$ ), 140.1 (CH), 137.8 (m,  $C_{q(\text{dppf})}$ ), 137.4 (m,  $C_{q(\text{dppf})}$ ), 135.2 (CH), 135.1 ( $C_q$ ), 134.6 (CH), 133.8 ( $C_q$ ), 133.4 ( $C_q$ ), 133.3 (quint.,  $C_{q(\text{Ru-C}\equiv)}$ ), 131.8 (CH), 130.5 ( $C_q$ ), 129.8 ( $C_q$ ), 129.6 (CH), 129.4 (CH), 127.9 (CH), 127.9 (CH), 127.4 (CH), 127.3 (CH), 126.7 (CH), 126.3 (CH), 124.1 ( $C_q$ ), 123.1 (CH), 120.7 (CH), 120.2 (CH), 118.3 ( $C_q$ ), 116.9 ( $C_q$ ), 111.0 ( $C_q$ ), 110.5 (CH), 97.9 ( $C_q$ ), 32.1 (m,  $\text{CH}_2(\text{dppf})$ ). MS MALDI-TOF (m/z): 1447.9 [ $\text{M}$ ] $^+$  (calcd. 1448.3 for [ $\text{C}_{86}\text{H}_{66}\text{N}_2\text{O}_2\text{P}_4\text{RuS}_2$ ] $^+$ ) (Perfect matching between experimental and theoretical isotopic patterns). FT-IR (KBr):  $\nu_{\text{C}\equiv\text{N}}$  = 2215  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}}$  = 2035  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{O}}$  = 1714  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}(\text{Thiophene})}$  = 1420  $\text{cm}^{-1}$ ,  $\nu_{\text{C}-\text{O}}$  = 1217  $\text{cm}^{-1}$ ,  $\nu_{\text{P}-\text{Ph}}$  = 1095  $\text{cm}^{-1}$ . Elem. Anal. Calcd for  $\text{C}_{86}\text{H}_{66}\text{N}_2\text{O}_2\text{N}_2\text{P}_4\text{RuS}_2$ : C, 71.31; H, 4.59; N, 1.93; S, 4.43; Found: C, 70.83; H, 4.59; N, 1.91; S, 4.29.

**Synthesis of [Ru]4:** General procedure for silyl-ester deprotection was applied using **5c** (0.052 g, 0.03 mmol), TBAF (1M in THF, 0.06 mL, 0.06 mmol) and THF (5 mL). Pure **[Ru]4** was obtained as a dark blue powder in 75 % yield (0.036 g, 0.022 mmol).  $^{31}\text{P}$  NMR (240 MHz, THF-d8):  $\delta$  = 52.68 (s,  $\text{P}(\text{dppf})$ ).  $^1\text{H}$  NMR (600 MHz, THF-d8):  $\delta$  = 9.20 (s, 1H), 8.67 (d, 1H,  $^3J_{\text{H-H}}$  = 8 Hz), 8.17 (d, 2H,  $^3J_{\text{H-H}}$  = 8 Hz), 7.79 (m, 8H), 7.48 (m, 6H), 7.31 (d, 2H,  $^3J_{\text{H-H}}$  = 8 Hz), 7.28–7.06 (m, 26H), 6.78 (m, 8H), 6.30 (d, 1H,  $^3J_{\text{H-H}}$  = 8Hz), 4.46 (m, 2H), 3.09 (m, 4H), 2.78 (m, 4H).  $^{13}\text{C}$  NMR (150 MHz, THF-d8):  $\delta$  = 173.3 (quint.,  $C_{q(\text{Ru-C}\equiv)}$ ), 163.6 ( $C_{q(\text{COOH})}$ ), 155.8 ( $C_q$ ), 155.4 ( $C_q$ ), 146.1 ( $C_q$ ), 140.9 (CH), 137.1 (m,  $C_{q(\text{dppf})}$ ), 136.2 (m,  $C_{q(\text{dppf})}$ ), 134.5 (CH), 133.6 (CH), 132.8 ( $C_q$ ), 131.3 ( $C_q$ ), 130.8 (CH), 130.6 (quint.,  $C_{q(\text{Ru-C}\equiv)}$ ), 130.2 ( $C_q$ ), 129.5 ( $C_q$ ), 128.9 (CH), 128.4 (CH), 127.1 (CH), 126.8 (CH), 126.2 ( $C_q$ ), 126.0 (CH), 125.7 ( $C_q$ ), 125.5 (CH), 123.7 ( $C_q$ ), 123.3 (CH), 120.2 ( $C_q$ ), 120.0 ( $C_q$ ), 119.8 (CH), 119.5 (CH), 118.1 ( $C_q$ ), 116.7 ( $C_q$ ), 109.6 (CH), 100.2 ( $C_q$ ), 31.3 (m,  $\text{CH}_2(\text{dppf})$ ). HR-MS  $\text{FD}^+$ : 1418.2883 [ $\text{M}$ ] $^+$  (calcd. 1418.2744 for [ $\text{C}_{84}\text{H}_{64}\text{N}_4\text{O}_2\text{P}_4\text{RuS}$ ]). FT-IR (KBr):  $\nu_{\text{C}\equiv\text{N}}$  = 2217  $\text{cm}^{-1}$ ,  $\nu_{\text{C}=\text{C}}$  = 2043  $\text{cm}^{-1}$ ,  $\nu_{\text{C}-\text{O}}$  = 1715  $\text{cm}^{-1}$ ,  $\nu_{\text{C}-\text{O}}$  = 1185  $\text{cm}^{-1}$ ,  $\nu_{\text{P}-\text{Ph}}$  = 1096  $\text{cm}^{-1}$ .



**Figure S1.** Normalized electronic absorption spectra of [Ru]1-[Ru]4 adsorbed on 3- $\mu\text{m}$  TiO<sub>2</sub> transparent film (plain) and in CH<sub>2</sub>Cl<sub>2</sub> solutions (dashed).

**[Ru]1**

**[Ru]2**

**[Ru]3**

**[Ru]4**

**Figure S2.** TD-DFT simulated absorption spectra of **[Ru]1-[Ru]4**. Absorption bands enlarged using Gaussian functions with full-width at half-height (FWHH) of 5 nm to reproduce the experimental spectra.



## Transition assignment for [Ru]1

NB : numbers in brackets represent the calculated coefficient corresponding to each transitions.

Transition #1:  $\Delta E_{ge} = 2.63$  eV /  $\lambda_{ge} = 470$  nm /  $f_{ge} = 1.044$

$H \rightarrow L$  (0.64);  $H-2 \rightarrow L$  (-0.21)

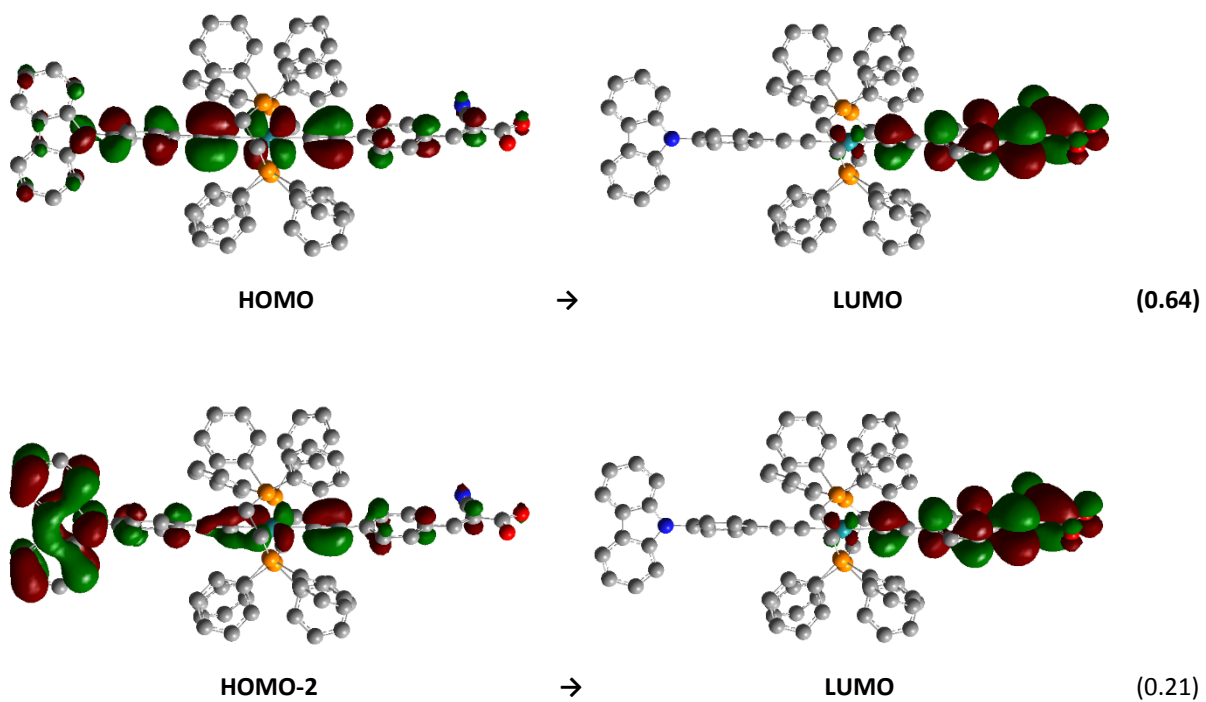


Figure S3a.

Transition #2:  $\Delta E_{ge} = 4.13 \text{ eV} / \lambda_{ge} = 300 \text{ nm} / f_{ge} = 0.911$

$H \times L+1$  (0.15);  $H \times L+3$  (0.38);  $H \times L+4$  (0.43);  $H-2 \times L$  (0.11)

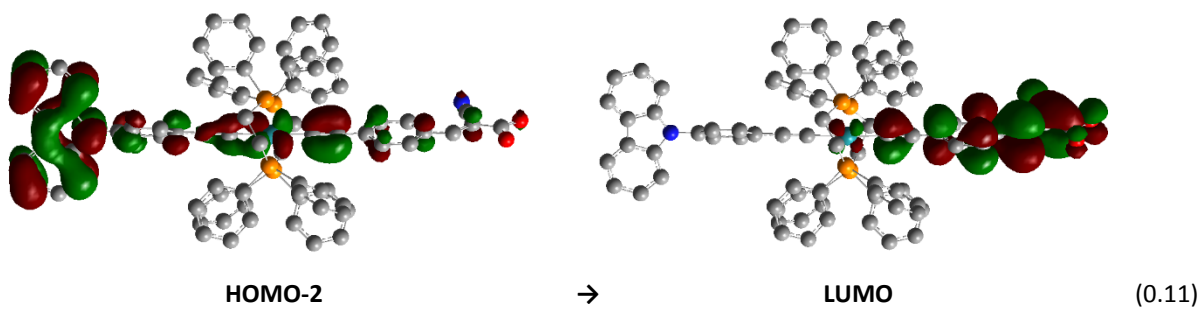
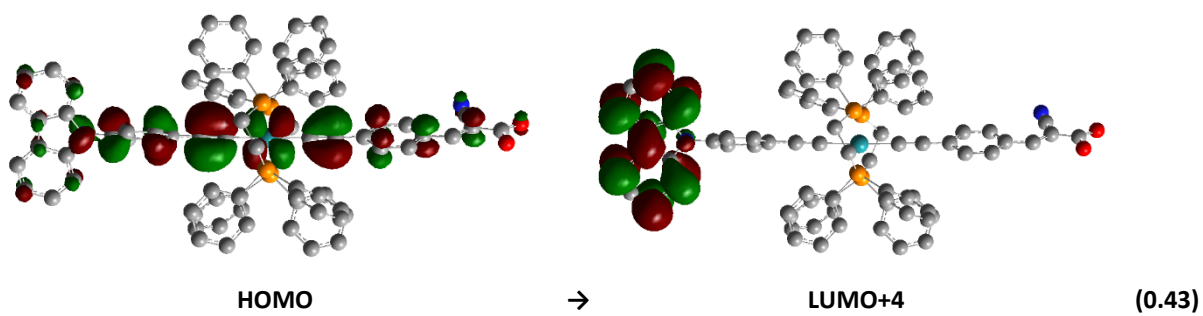
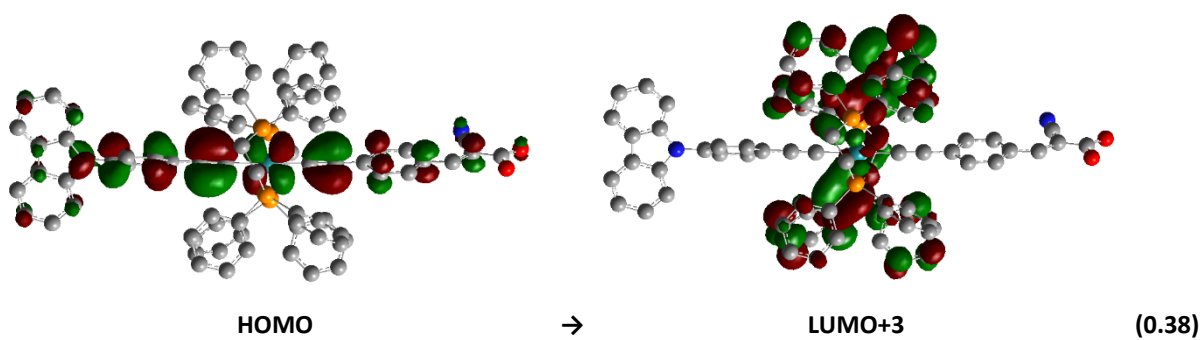
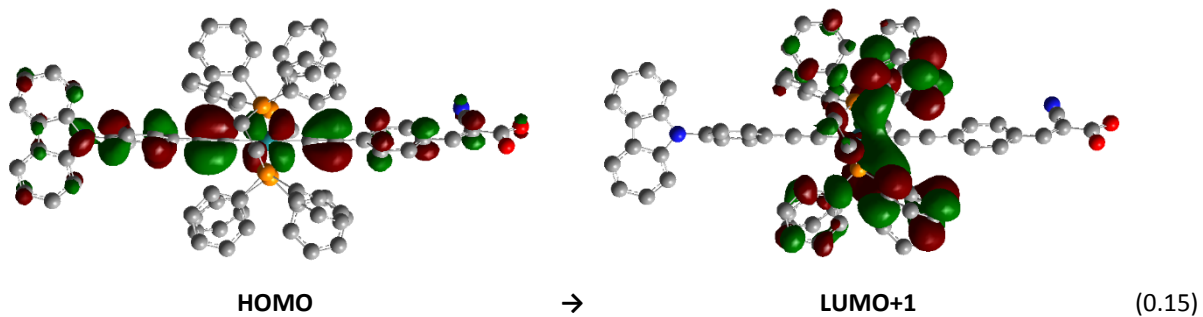


Figure S3b

## Transition assignment for [Ru]2

Transition #1:  $\Delta E_{ge} = 2.50 \text{ eV} / \lambda_{ge} = 496 \text{ nm} / f_{ge} = 1.339$

H $\times$ L (0.63); H-1 $\times$ L (-0.18); H-2 $\times$ L (-0.18)

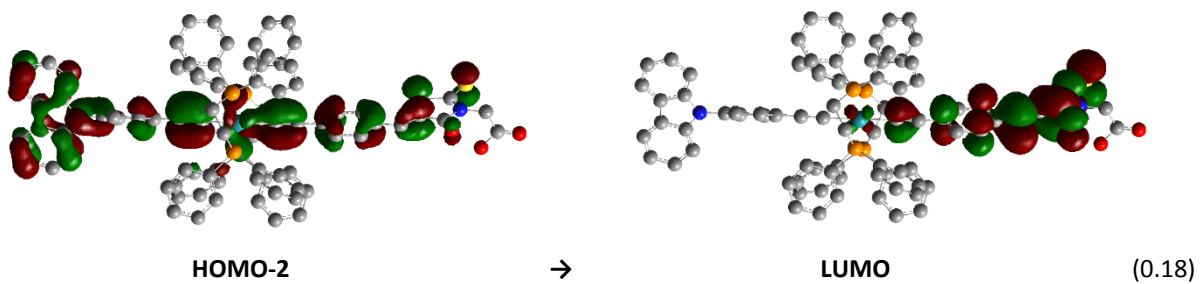
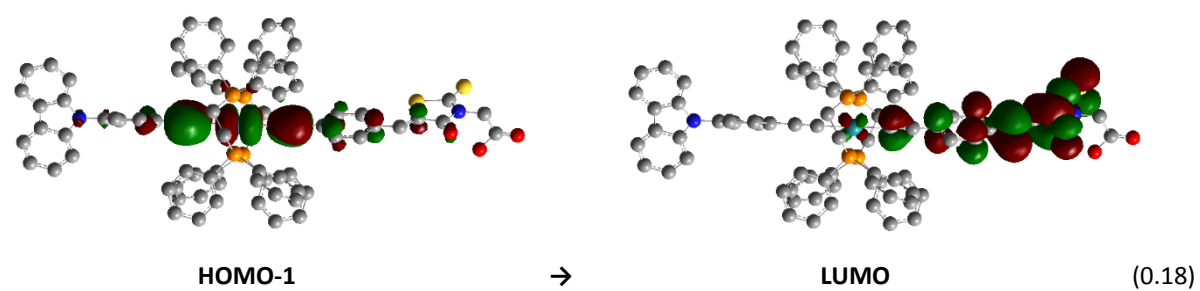
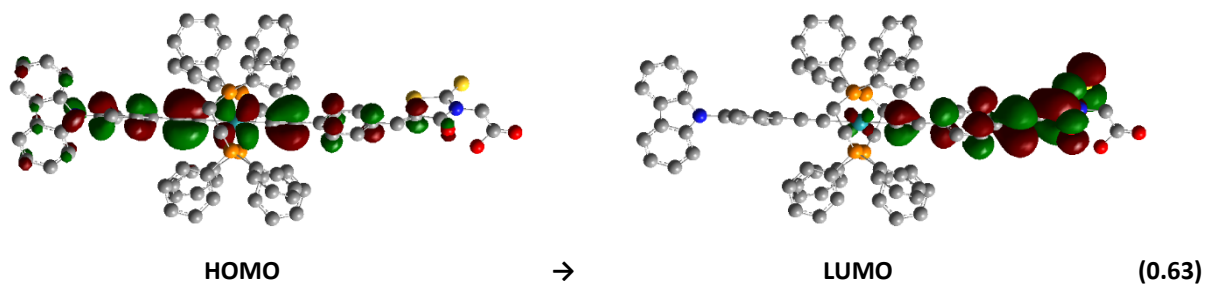


Figure S3c

Transition #2:  $\Delta E_{ge} = 4.02 \text{ eV} / \lambda_{ge} = 308 \text{ nm} / f_{ge} = 0.593$

H-1 $\times$ L+1 (-0.19); H $\times$ L+1 (0.53); H $\times$ L+4 (-0.18); H $\times$ L+5 (-0.19)

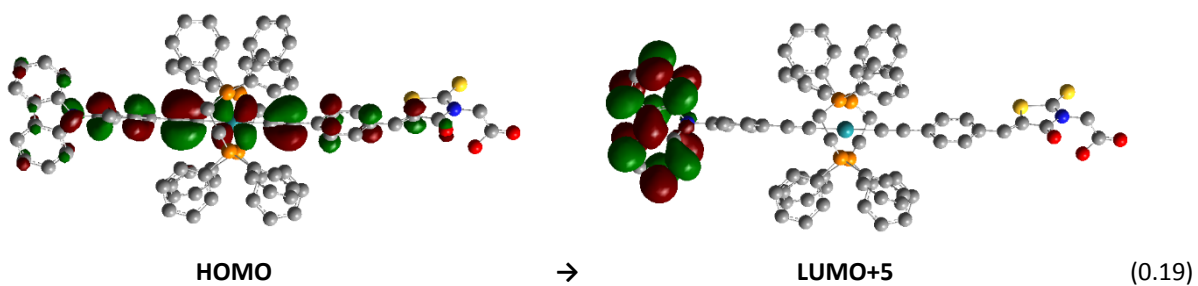
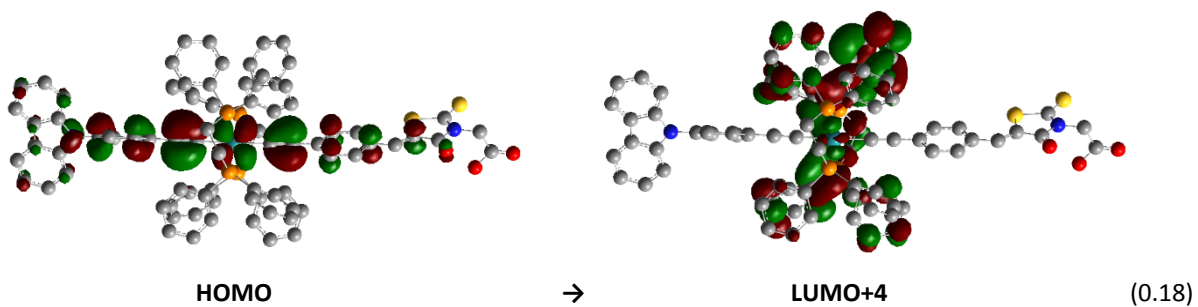
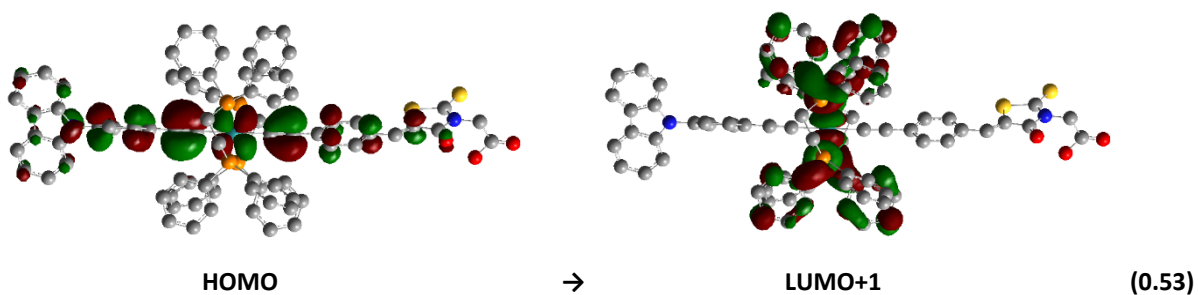
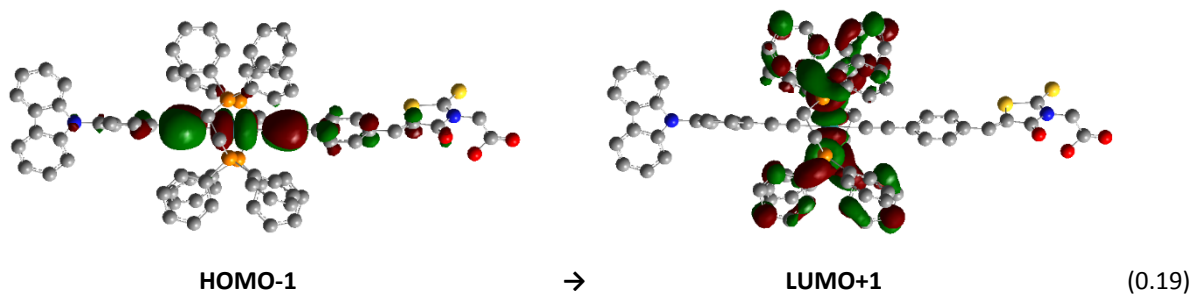


Figure S3d

## Transition assignment for [Ru]3

Transition #1:  $\Delta E_{ge} = 2.13 \text{ eV} / \lambda_{ge} = 580 \text{ nm} / f_{ge} = 1.733$

H $\times$ L (0.64); H-1 $\times$ L (0.23)

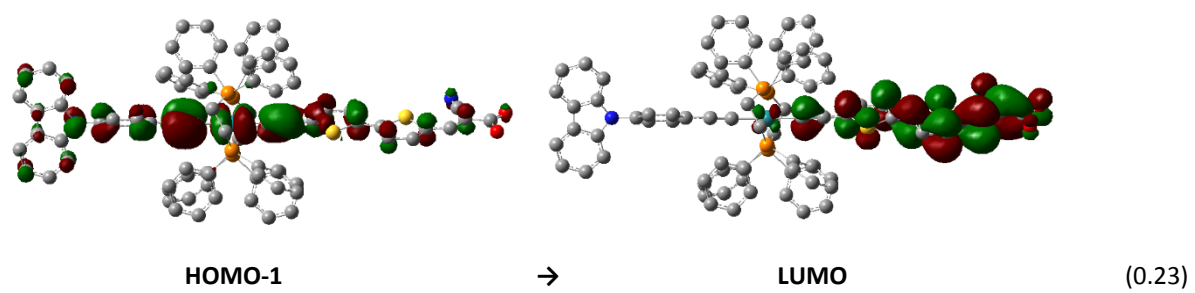
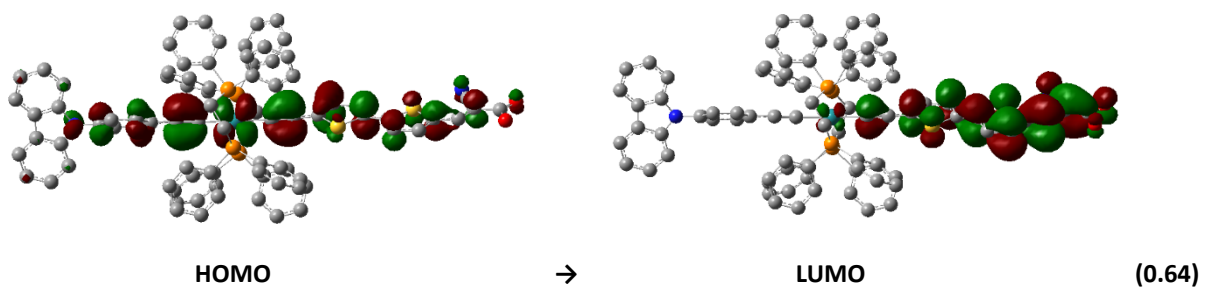


Figure S3e

Transition #2:  $\Delta E_{ge} = 4.14$  eV /  $\lambda_{ge} = 299$  nm /  $f_{ge} = 0.864$

H-1 $\times$ L+1 (-0.21); H-1 $\times$ L+4 (-0.21); H-1 $\times$ L+5 (-0.20); **H $\times$ L+4 (0.37)**; H $\times$ L+5 (0.30)

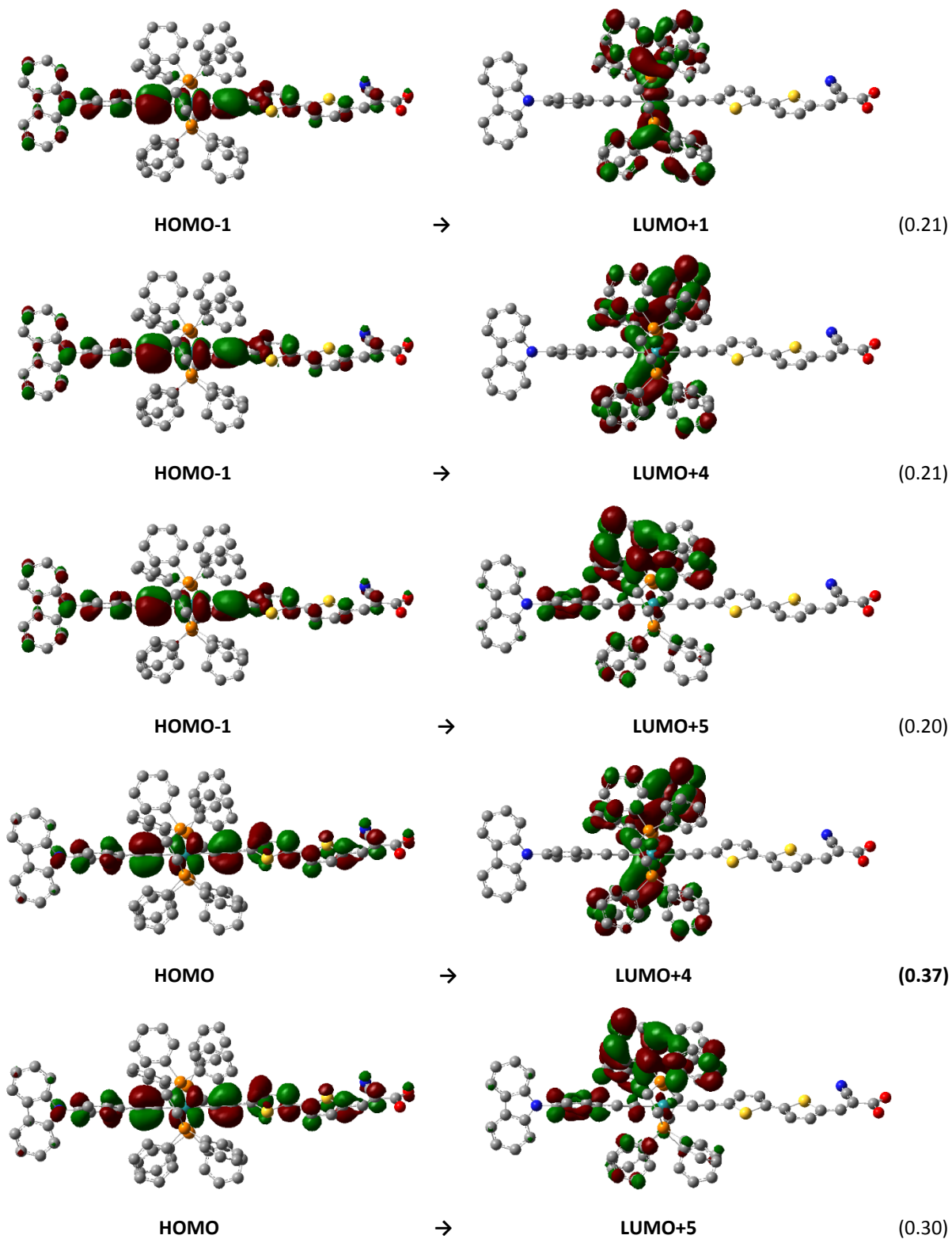


Figure S3f

## Transition assignment for [Ru]4

Transition #1:  $\Delta E_{ge} = 1.93 \text{ eV} / \lambda_{ge} = 643 \text{ nm} / f_{ge} = 0.861$

H $\times$ L (0.64); H-2 $\times$ L (-0.27)

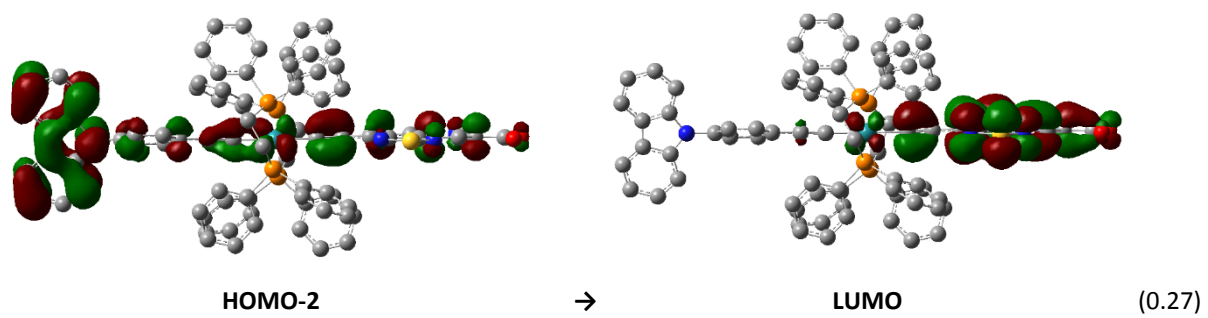
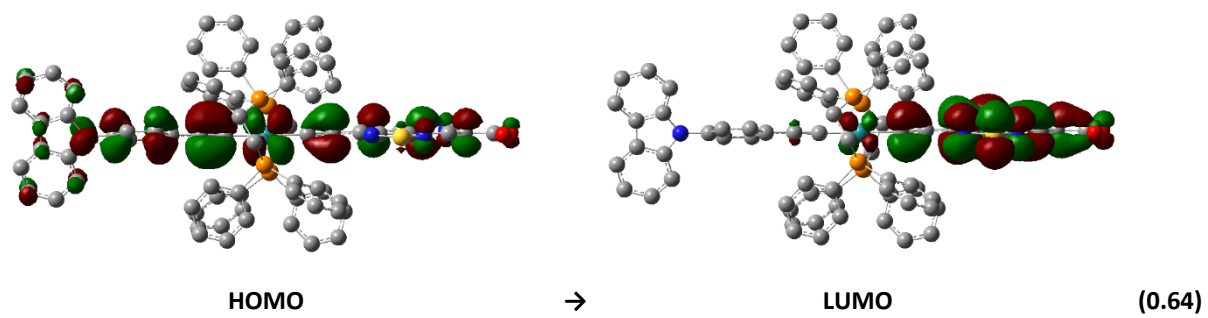


Figure S3g

Transition #2:  $\Delta E_{ge} = 3.16 \text{ eV} / \lambda_{ge} = 391 \text{ nm} / f_{ge} = 0.406$

H $\rightarrow$ L+1 (0.51); H-1 $\rightarrow$ L+1 (0.21); H-2 $\rightarrow$ L+1 (-0.20)

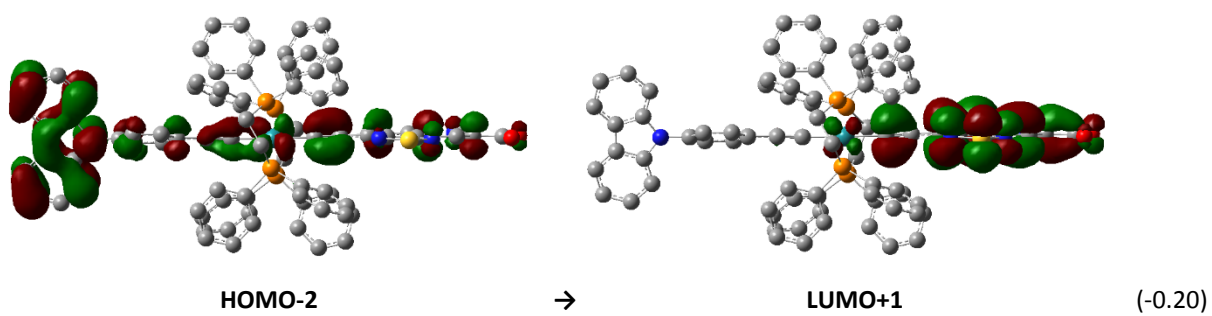
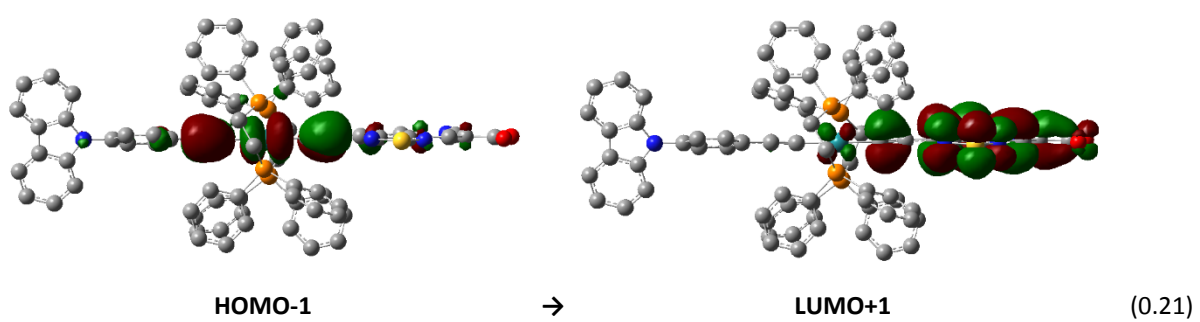
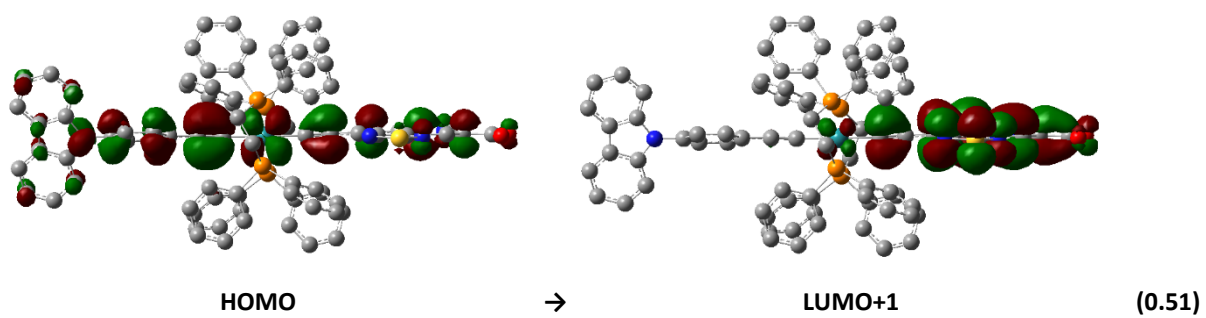


Figure S3h



Transition #3:  $\Delta E_{ge} = 4.18 \text{ eV}$  /  $\lambda_{ge} = 296 \text{ nm}$  /  $f_{ge} = 0.945$

$H \rightarrow L+3$  (-0.17);  $H \rightarrow L+4$  (0.54)

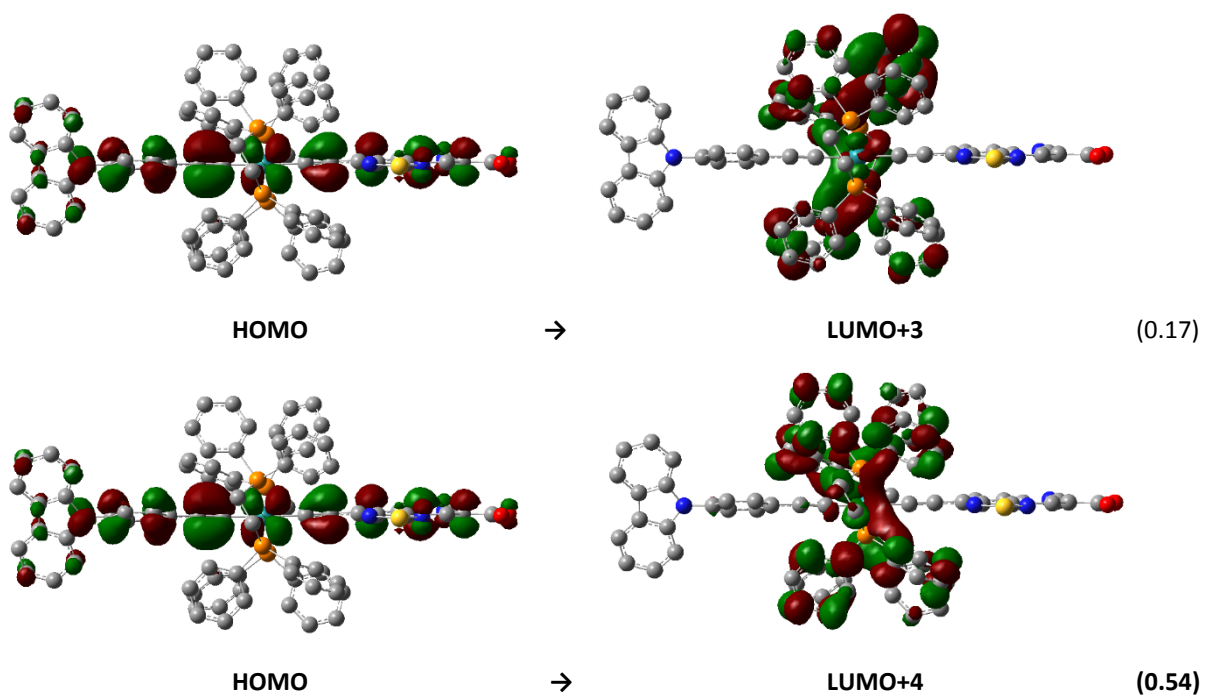
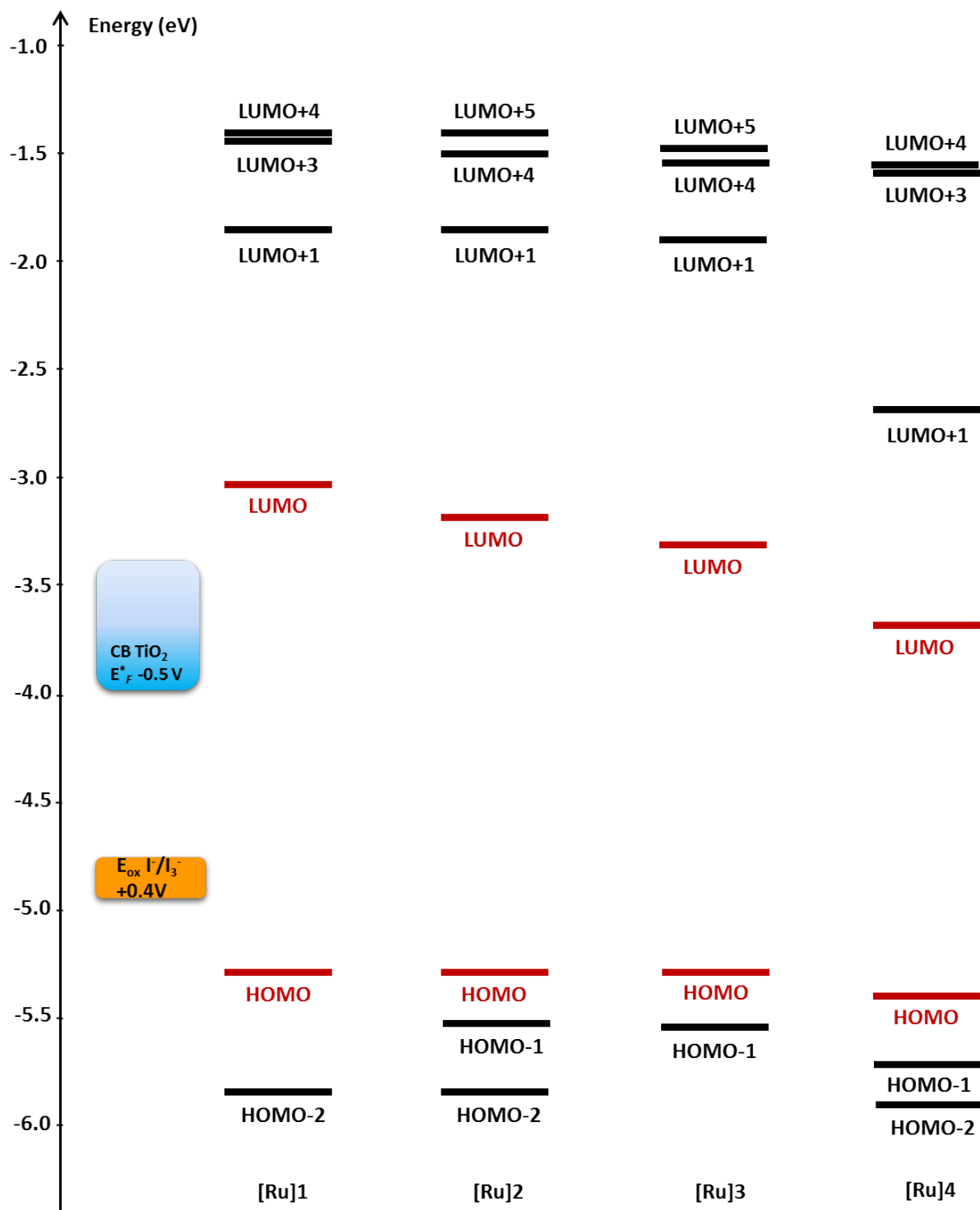


Figure S3i

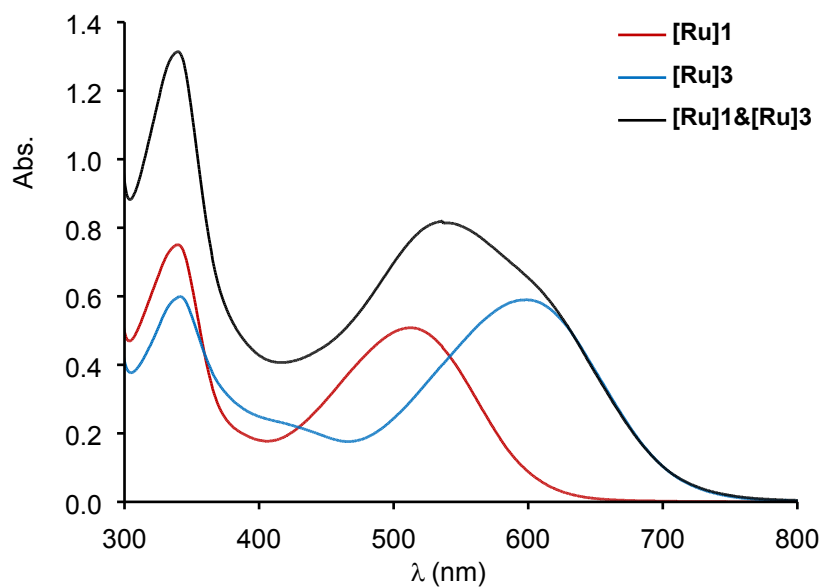


**Figure S4.** Calculated energy diagram of the main transition-involved molecular orbitals of [Ru]1-[Ru]4 (B3LYP).

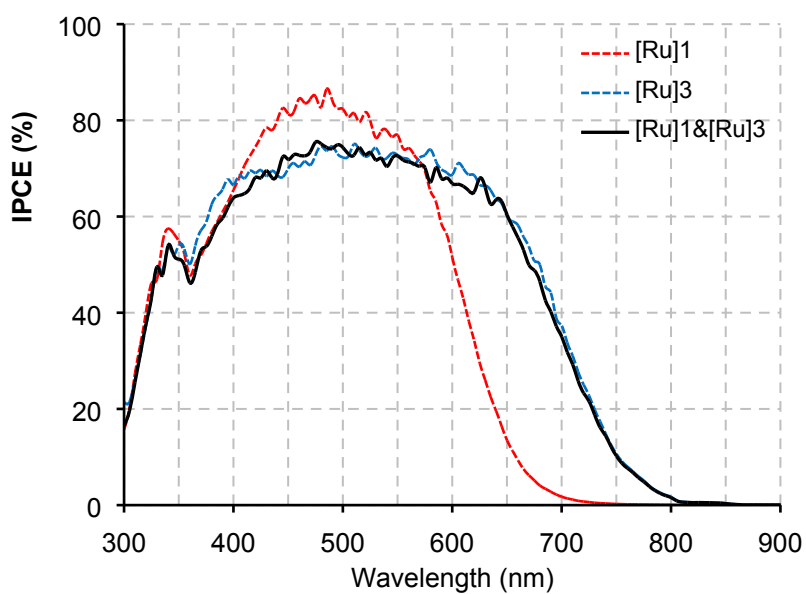
**Table S1.** Calculated energies of the main transition-involved molecular orbitals of **[Ru]1-[Ru]4**.

	<b>[Ru]1</b>	<b>[Ru]2</b>	<b>[Ru]3</b>	<b>[Ru]4</b>
LUMO+5	-1.278	-1.456	-1.489	-1.511
LUMO+4	-1.452	-1.503	-1.542	-1.553
LUMO+3	-1.485	-1.540	-1.559	-1.575
LUMO+1	-1.858	-1.861	-1.920	-2.647
<b>LUMO</b>	<b>-3.032</b>	<b>-3.185</b>	<b>-3.322</b>	<b>-3.672</b>
<b>HOMO</b>	<b>-5.265</b>	<b>-5.248</b>	<b>-5.246</b>	<b>-5.407</b>
HOMO-1	-5.541	-5.530	-5.567	-5.746
HOMO-2	-5.855	-5.840	-5.861	-5.908

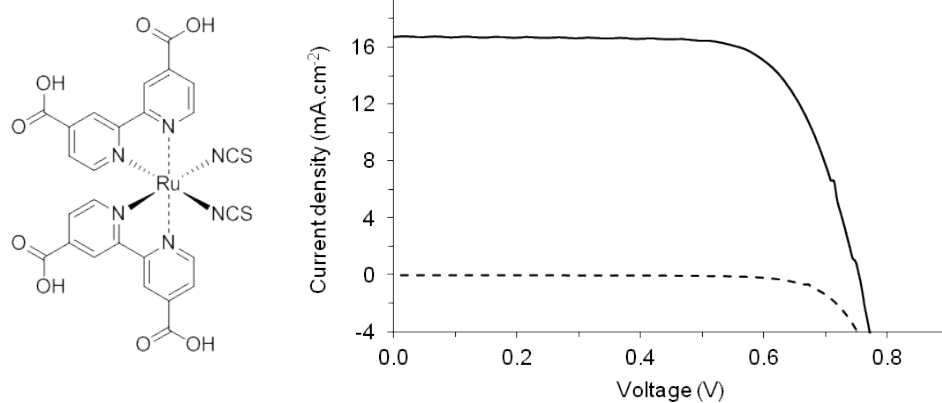
Note : the LUMO+1 of **[Ru]4** presents a much lower energy than in the three other dyes because the orbital is located on the benzothiadiazole acceptor group, which is low in energy, while in **[Ru]1-[Ru]3** this MO is located on the [Ru(dppe)<sub>2</sub>] central motif.



**Figure S5.** Electronic absorption spectra of **[Ru]1** ( $C = 1.7 \times 10^{-5} \text{ M}^{-1}$ ), **[Ru]3** ( $C = 1.7 \times 10^{-5} \text{ M}^{-1}$ ) and the mixture **[Ru]1&[Ru]3** in a 1:1 molar ratio ( $C_{\text{dye}} = 1.7 \times 10^{-5} \text{ M}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$ .



**Figure S6.** IPCE action spectra of a co-sensitized DSSC device including **[Ru]1&[Ru]3** in a [4:1] molar ratio (black plain line), and single-dye devices including **[Ru]1** (red dotted line) or **[Ru]3** (blue dotted line).



**Figure S7.** Molecular structure of the commercial dye N3 and  $J(V)$  curves (plain: light; dashed: dark) of DSSC based on this benchmark-dye. The corresponding data are as follows:  $J_{SC} = 16.71 \text{ mA cm}^{-2}$ ,  $V_{OC} = 755 \text{ mV}$ ,  $ff = 71.9 \%$  and  $\eta = 9.07 \%$ .