Electronic Supplementary Information

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

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Table of Content

1. Materials and methods
2. Synthesis of organic precursors
3. Synthesis of organometallic complexes

Figure S1. Normalized electronic absorption spectra of [Ru]1-[Ru]4 adsorbed on 3-µm TiO₂ transparent film (plain) and in CH₂Cl₂ solutions (dashed).

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.

Figure S3a. Transition assignment for [Ru]1 (transition #1).

Figure S3b. Transition assignment for [Ru]1 (transition #2).

Figure S3c. Transition assignment for [Ru]2 (transition #1).

Figure S3d. Transition assignment for [Ru]2 (transition #2).

Figure S3e. Transition assignment for [Ru]3 (transition #1).

Figure S3f. Transition assignment for [Ru]3 (transition #2).

Figure S3g. Transition assignment for [Ru]4 (transition #1).

Figure S3h. Transition assignment for [Ru]4 (transition #2).

Figure S3i. Transition assignment for [Ru]4 (transition #3).

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.

Figure S5. Electronic absorption spectra of [Ru]1 (C = 1.7 x 10⁻⁵ M⁻¹) , [Ru]3 (C = 1.7 x 10⁻⁵ M⁻¹) and the mixture [Ru]1&[Ru]3 in a 1:1 molar ratio (C_dye = 1.7 x 10⁻⁵ M⁻¹) in CH₂Cl₂.

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)$_2$][TfO] ([I][TfO]),[1] 4-trimethylsilylethylenebenzaldehyde (III)[2] and 5'-ethynyl-[2,2']bithiophene-5-carbaldehyde[3] were synthesized according to literature procedures. 9-(4-Ethynylphenyl)carbazole (2), 2-trimethylsilyllylethynylcarboxylenoate, [3][TfO] and [Ru]1 were prepared as previously reported.[4]

$^1$H NMR, $^{13}$C NMR and $^{31}$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$_4$NPF$_6$ as salt support at a scan rate of 100 mV.s$^{-1}$.

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$_2$ thin-film (thickness = 9 μm ; surface area = 1 cm$^{-2}$) 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$_2$ was deduced from the difference between the two sets of data.


2. Synthesis of organic precursors

Scheme S1. Synthetic route to 7-ethynyl-2,1,3-benzothiadiazole-4-carbaldehyde (II): i) TMSA, PdCl₂(PPh₃)₂, Cul, Et₃N, THF; ii) K₂CO₃, MeOH.

Synthesis of 7-trimethylsilylthelynly-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.), PdCl₂(PPh₃)₂ (140 mg, 0.20 mmol, 5%) and Cul (19 mg, 0.10 mmol, 2.5%) in dry THF (15 mL) under inert atmosphere, were added distilled Et₃N (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 CH₂Cl₂ 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). ¹H NMR (300 MHz, CDCl₃): δ = 10.75 (s, 1H), 8.17 (d, 1H, 3J_H-H = 12 Hz), 7.90 (d, 1H, 3J_H-H = 12 Hz), 0.35 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ = 191.9 (C_q(C=O)), 155.3 (C_q(C=N)), 152.8 (C_q(C=O)), 142.8 (C_q), 133.6 (CH), 128.3 (CH), 117.1 (C_q), 103.0 (C_q), 100.2 (C_q), 0.08 (CH₃(SiMe₃)).

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 K₂CO₃ (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 Et₂O. The organics were washed with brine, dried over MgSO₄ 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). ¹H NMR (300 MHz, CDCl₃): δ = 10.78 (s, 1H), 8.20 (d, 1H, 3J_H-H = 12 Hz), 7.96 (d, 1H, 3J_H-H = 12 Hz), 3.92 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 192.1 (C_q(C=O)), 155.1 (C_q(C=N)), 151.6 (C_q(C=O)), 142.9 (C_q), 134.2 (CH), 128.5 (CH), 123.6 (C_q), 84.4 (CH), 79.6 (C_q).

Scheme S2. Synthetic route to VI: i) rhodanine-3-acetic acid, ammonium acetate, acetic acid; ii) K₂CO₃, MeOH; iii) HBTU, DIPEA, 2-trimethylsilylethanol, DMF.

Synthesis of IV: In a Schlenk tube under inert atmosphere, 4-trimethylsilylthelynlybenzaldehyde 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). ¹H NMR (300 MHz, DMSO-d₆): δ = 13.47 (br. s, 1H), 7.89 (s, 1H), 7.67 (d, 2H, 3J_H-H = 8 Hz), 7.61 (d, 2H, 3J_H-H = 8 Hz), 4.75 (s, 2H), 0.25 (s, 9H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 192.9 (C_q(C=O)), 167.2 (C_q(COOH)), 166.3 (C_q(C=O)), 133.1 (C_q), 132.7 (CH), 132.5 (CH), 130.9 (CH), 124.4 (C_q), 122.9 (C_q), 104.4 (C_q), 97.9 (C_q), 45.0 (CH₂), -0.2 (CH₃(SiMe₃)). HR-MS ESI- (m/z): 374.0339 [M-H]⁻ (calcd. 374.0346 for [C₆H₄NO₂Si₂]). FT-IR (KBr): ν_C=O = 1734 cm⁻¹, ν_C=O(amide) = 1734 cm⁻¹, ν_C=O(amide) = 1716 cm⁻¹, ν_C=O(amide) = 862-844 cm⁻¹.

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 K₂CO₃ (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). ¹H NMR (300 MHz, DMSO-d₆): δ = 13.47 (br. s, 1H), 7.91 (s, 1H), 7.70 (d, 2H, 3J_H-H = 8 Hz), 7.65 (d, 2H, 3J_H-H = 8 Hz), 4.75 (s, 2H), 4.48 (s, 1H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 193.0 (C_q(C=O)), 167.2 (C_q(COOH)), 166.3 (C_q(C=O)), 133.1 (C_q), 132.7 (CH), 132.6 (CH), 130.9 (CH), 124.1 (C_q), 122.9 (C_q), 84.0 (CH₃(SiMe₃)), 82.9 (C_q), 45.0 (CH₂). FT-IR (KBr): ν_C=H = 3257 cm⁻¹, ν_C=O = 2105 cm⁻¹, ν_C=O(amide) = 1726 cm⁻¹, ν_C=O(amide) = 1711 cm⁻¹.
**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 CH₂Cl₂, washed with saturated NH₄Cl aqueous solution and pure water. The organic layers were combined, dried over MgSO₄ and evaporated to dryness. The crude product was purified on silica gel column (petroleum ether/CH₂Cl₂ (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). ¹H NMR (200 MHz, CD₂Cl₂): δ = 7.74 (s, 1H), 7.60 (d, 2H, J₁H-H = 8.4 Hz), 7.49 (d, 2H, J₁H-H = 8.4 Hz), 4.82 (s, 2H), 4.27 (m, 2H), 3.34 (s, 1H), 1.03 (m, 2H), 0.05 (s, 9H). ¹³C NMR (50 MHz, CD₂Cl₂): δ = 193.3 (C=O(C=S)), 167.3 (C=S(C=O)), 166.3 (C=O(C=S)), 133.9 (C₁₅), 133.3 (C₁₆), 132.9 (CH₂), 130.9 (CH₂), 124.9 (C₁₂), 124.1 (C₁₁), 83.1 (CH₂(C=O)), 80.7 (C₉), 64.9 (CH₂(TMSE)), 45.4 (CH₂), 17.6 (CH₂(TMSE)), -1.5 (CH₃(SAMe₂)), HR-MS ESI⁺ (m/z): 426.0641 [M+Na]⁺ (calcd. 426.0624 for [C₁₀H₁₃NO₃NaSiS₂]⁺). FT-IR (KBr): ν(C=H) = 3258 cm⁻¹, ν(C=O) = 2103 cm⁻¹, ν(C=O(ester)) = 1736 cm⁻¹, ν(C=O(amide)) = 1713 cm⁻¹.

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 NaPF₆ (2 equiv.) in dry CH₂Cl₂ and under inert atmosphere, was added distilled Et₃N (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 CH₂Cl₂/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), NaPF₆ (0.18 g, 1.04 mmol), CH₂Cl₂ (75 mL) and Et₃N (0.21 mL, 1.56 mmol). Pure 4b was obtained as a red solid in 90% yield (0.64 g, 0.46 mmol). ³¹P NMR (240 MHz, CD₂Cl₂): δ = 52.63 (s, P(dppe)). ¹H NMR (600 MHz, CD₂Cl₂): δ = 9.82 (s, 1H), 8.17 (d, 2H, J₁H-H = 7.7 Hz), 7.73–7.69 (m, 8H), 7.68 (d, 1H), J₁H-H = 3.9 Hz, 7.49 (d, 2H, J₁H-H = 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, J₁H-H = 7.4 Hz), 7.23 (t, 4H, J₁H-H = 7.4 Hz), 7.20 (d, 1H, J₁H-H = 3.7 Hz), 7.18 (d, 1H, J₁H-H = 3.9 Hz).
7.08 (t, 8H, \( \delta_{\text{H}} = 7.7 \) Hz), 7.05–7.02 (m, 10H), 6.21 (d, 1H, \( \delta_{\text{H}} = 3.7 \) Hz), 2.73–2.64 (m, 8H). \(^{13}\)C NMR (150 MHz, CD\(_2\)Cl\(_2\)): \( \delta = 182.5 (\text{CH} \_\text{CO}), 150.1 (\text{quint.}, \text{C}_{(\text{q} \_\text{Ru-C≡)}}, 148.8 (\text{C}_p), 141.5 (\text{C}_p), 140.3 (\text{C}_p), 138.3 (\text{CH}), 137.3 (\text{m}, \text{C}_{(\text{q} \_\text{dppe)}}, 137.0 (\text{m}, \text{C}_{(\text{q} \_\text{dppe)}}, 134.8 (\text{CH}), 134.5 (\text{C}_p), 134.2 (\text{CH}), 133.0 (\text{quint.}, \text{C}_{(\text{q} \_\text{Ru-C≡)}}, 132.9 (\text{C}_p), 131.4 (\text{CH}), 130.0 (\text{C}_p), 129.4 (\text{CH}), 129.3 (\text{C}_p), 129.2 (\text{CH}), 127.7 (\text{CH}), 126.7 (\text{CH}), 126.6 (\text{CH}), 126.2 (\text{CH}), 126.1 (\text{CH}), 120.5 (\text{CH}), 120.0 (\text{CH}), 117.8 (\text{C}_p), 110.5 (\text{CH}), 110.0 (\text{C}_p), 31.80 (m, CH\(_{2\text{dppe}}\)). HR-MS ESI\(^{+}\) (m/z): 1404.3 [M+Na\(^{+}\)] (calcd. 1404.2 for \([\text{C}_8\text{H}_8\text{SiOP}_{2}\text{RuS}_2\text{Na}]^+\)).

**Synthesis of 4c:** General procedure was applied using \([3][\text{TO}]\) (0.50 g, 0.33 mmol), 7-ethyl-2,1,3-benzothiadiazole-4-carbaldheyde (II) (0.07 g, 0.36 mmol), NaPF\(_6\) (0.11 g, 0.66 mmol), CH\(_3\)Cl\(_2\) (35 mL) and Et\(_3\)N (0.14 mL, 1 mmol). Pure 4c was obtained as a dark green solid in 78 % yield (0.35 g, 0.26 mmol).

**Synthesis of 6:** General procedure was applied using \([3][\text{TO}]\) (0.15 g, 0.11 mmol), VI (0.05 g, 0.12 mmol), NaPF\(_6\) (0.04 g, 0.22 mmol), CH\(_3\)Cl\(_2\) (15 mL) and Et\(_3\)N (0.05 mL, 0.33 mmol). The crude product was dissolved in a minimum amount of CH\(_3\)Cl\(_2\) and pentane was added under stirring. Pure 6 was obtained as a purple solid in 80 % yield (0.10 g, 0.09 mmol).

**Synthesis of 5b:** General procedure for the Knoevenagel condensation was applied using 4b (0.25 g, 0.18 mmol), 2-trimethylsilylethylene-ethanoate (0.07 g, 0.36 mmol), piperdine (0.07 mL, 0.72 mmol) and CHCl\(_3\) (30 mL).

**Synthesis of 5c:** General procedure for the Knoevenagel condensation was applied using 4c (0.17 g, 0.12 mmol), 2-trimethylsilylethylene-ethanoate (0.044 g, 0.24 mmol), piperdine (0.05 mL, 0.48 mmol) and CHCl\(_3\) (20 mL).

5
Synthesis of [Ru2]: 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 [Ru2] was obtained as a purple powder (0.07 g, 0.05 mmol) in 83 % yield. 31P NMR (240 MHz, THF-d8): δ = 53.36 (s, P(dppe)). 1H NMR (600 MHz, THF-d8): δ = 8.14 (d, 2H, 3J_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_H-H = 8.1 Hz), 7.04 (t, 8H, 3J_H-H = 7.5 Hz), 6.97 (t, 8H, 3J_H-H = 7.5 Hz), 6.80 (d, 2H, 3J_H-H = 8.1 Hz), 4.82 (s, 2H), 2.78–2.67 (m, 8H). 13C NMR (150 MHz, THF-d8): δ = 193.8 (C(q=Si)), 167.5 (C(q=CO)), 167.3 (C(q=O)), 148.9 (quint., C(q=Ru-CO)), 141.8 (C(q)), 131.1 (CH), 131.2 (CH), 130.5 (CH), 129.4 (CH), 128.5 (CH), 127.8 (CH), 127.8 (CH), 126.7 (CH), 126.3 (CH), 124.1 (C(q)), 124.1 (C(q)), 120.7 (CH), 119.4 (C(q)), 118.1 (C(q)), 110.5 (CH), 45.1 (CH), 32.1 (m, CH2(dppe)). MS MALDI-TOF (m/z): 1431.1 [M-C6H4O2+Na]+ (calcd. 1431.3 for [C6H4H2N2O2P2RuS3]+) (Perfect matching between experimental and theoretical isotopic patterns). FT-IR (KBr): ν_Rυ= 1510 cm⁻¹, ν_υ(O=O) = 1673 cm⁻¹, ν_υ(C=O) = 1517 cm⁻¹, ν_υ(P=O) = 1097 cm⁻¹.

Synthesis of [Ru3]: General procedure for silyl-ester deprotection was applied using 5b (0.2 g, 0.13 mmol), TBAF (1M in THF, 0.26 mL, 0.26 mmol) and THF (20 mL). Pure [Ru3] was obtained as a dark blue powder in 80 % yield (0.15 g, 0.10 mmol). 31P NMR (240 MHz, THF-d8): δ = 55.01. 1H NMR (600 MHz, THF-d8): δ = 8.30 (s, 1H), 8.14 (d, 2H, 3J_H-H = 7.8 Hz), 7.80–7.73 (m, 9H), 7.45 (d, 2H, 3J_H-H = 8.2 Hz), 7.41–7.34 (m, 12H), 7.25 (d, 1H, 3J_H-H = 3.8 Hz), 7.25–7.21 (m, 7H), 7.19 (t, 4H, 3J_H-H = 7.6 Hz), 7.09 (d, 2H, 3J_H-H = 8.3 Hz), 7.06 (t, 8H, 3J_H-H = 7.6 Hz), 7.00 (t, 8H, 3J_H-H = 7.6 Hz), 6.21 (d, 1H, 3J_H-H = 3.8 Hz), 2.71 (m, 8H). 13C NMR (150 MHz, THF-d8): δ = 164.2 (C(q=COOH)), 151.7 (quint., C(q=Ru-CO)), 145.9 (CH), 148.9 (C(q)), 141.8 (C(q)), 140.1 (CH), 137.8 (m, C(q=dppe)), 137.4 (m, C(q=dppe)), 135.2 (CH), 135.1 (C(q)), 134.6 (CH), 133.8 (C(q)), 133.4 (C(q)), 133.3 (quint., C(q=dppe)), 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), 126.7 (CH), 126.3 (CH), 124.1 (C(q)), 124.1 (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, CH2(dppe)). MS MALDI-TOF (m/z): 1447.9 [M]+ (calcd. 1448.3 for [C6H4H2N2O2P2RuS3]+) (Perfect matching between experimental and theoretical isotopic patterns). FT-IR (KBr): ν_Rυ = 2215 cm⁻¹, ν_υ(C=O) = 1420 cm⁻¹, ν_υ(C=O(amide)) = 1271 cm⁻¹, ν_υ(P=O) = 1005 cm⁻¹. Elem. Anal. Calcd for C6H4N2O2P2RuS3: 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 [Ru4]: 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 [Ru4] was obtained as a dark blue powder in 75 % yield (0.036 g, 0.022 mmol). 31P NMR (240 MHz, THF-d8): δ = 52.68 (s, P(dppe)). 1H NMR (600 MHz, THF-d8): δ = 9.20 (s, 1H), 8.67 (d, 2H, J_H-H = 8 Hz), 8.17 (d, 2H, J_H-H = 8 Hz), 7.79 (m, 8H), 7.48 (m, 6H), 7.31 (d, 2H, J_H-H = 8 Hz), 7.28–7.06 (m, 26H), 6.78 (m, 8H), 6.30 (d, 1H, J_H-H = 8 Hz), 4.46 (m, 2H), 4.26 (m, 2H), 2.78 (m, 4H). 13C NMR (150 MHz, THF-d8): δ = 173.3 (quint., C(q=Ru-CO)), 163.6 (C(q=COOH)), 155.8 (C(q)), 155.4 (C(q)), 146.1 (C(q)), 146.7 (CH), 146.1 (C(q)), 140.9 (CH), 137.1 (m, C(q=dppe)), 136.2 (m, C(q=dppe)), 134.5 (CH), 133.6 (CH), 132.8 (C(q)), 131.3 (C(q)), 130.8 (CH), 130.6 (quint., C(q=Ru-CO)), 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 (C(q)), 118.1 (C(q)), 116.7 (C(q)), 109.6 (CH), 100.2 (C(q)), 31.3 (m, CH2(dppe)). HR-MS FD+: 1418.2883 [M]+ (calcd. 1418.2744 for [C6H4H2N2O2P2RuS3]+). FT-IR (KBr): ν_Rυ = 2217 cm⁻¹, ν_υ(C=O) = 2043 cm⁻¹, ν_υ(C=O) = 1715 cm⁻¹, ν_υ(C=O) = 1185 cm⁻¹, ν_υ(P=O) = 1096 cm⁻¹.
Figure S1. Normalized electronic absorption spectra of [Ru]1-[Ru]4 adsorbed on 3-µm TiO₂ transparent film (plain) and in CH₂Cl₂ solutions (dashed).
**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 transition.

**Transition #1**: \( \Delta E_{ge} = 2.63 \text{ eV} / \lambda_{ge} = 470 \text{ nm} / f_{ge} = 1.044 \)

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

![HOMO](image1) \( \rightarrow \) ![LUMO](image2) (0.64)

![HOMO-2](image3) \( \rightarrow \) ![LUMO](image4) (0.21)

Figure S3a.
Transition #2: $\Delta E_{ge} = 4.13$ eV / $\lambda_{ge} = 300$ nm / $f_{ge} = 0.911$

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

HOMO $\rightarrow$ LUMO+1 (0.15)
HOMO $\rightarrow$ LUMO+3 (0.38)
HOMO $\rightarrow$ LUMO+4 (0.43)
HOMO-2 $\rightarrow$ LUMO (0.11)

Figure S3b
Transition assignment for [Ru]2

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

\( H \rightarrow L \, (0.63); \, H^{-1} \rightarrow L \, (-0.18); \, H^{-2} \rightarrow L \, (-0.18) \)

Figure S3c
Transition #2: $\Delta E_{ge} = 4.02$ eV / $\lambda_{ge} = 308$ nm / $f_{ge} = 0.593$

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

Figure S3d
Transition assignment for [Ru]3

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

HOMO \rightarrow LUMO (0.64); HOMO-1 \rightarrow LUMO (0.23)

Figure S3e
Transition #2: $\Delta E_{\text{ge}} = 4.14$ eV / $\lambda_{\text{ge}} = 299$ nm / $f_{\text{ge}} = 0.864$

$\text{H-1} \rightarrow \text{L+1} (-0.21); \text{H-1} \rightarrow \text{L+4} (-0.21); \text{H-1} \rightarrow \text{L+5} (-0.20); \text{H} \rightarrow \text{L+4 (0.37); H} \rightarrow \text{L+5 (0.30)}$

Figure S3f
Transition assignment for [Ru]4

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

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

![Diagram of HOMO to LUMO transition](image)

HOMO $\rightarrow$ LUMO (0.64)

![Diagram of HOMO-2 to LUMO transition](image)

HOMO-2 $\rightarrow$ LUMO (0.27)

Figure S3g
Transition #2: $\Delta E_{ge} = 3.16$ eV / $\lambda_{ge} = 391$ 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: $\Delta E_{ge} = 4.18 \text{ eV} / \lambda_{ge} = 296 \text{ nm} / f_{ge} = 0.945$

HOMO $\rightarrow$ LUMO+3 (-0.17); HOMO $\rightarrow$ LUMO+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.

<table>
<thead>
<tr>
<th></th>
<th>[Ru]1</th>
<th>[Ru]2</th>
<th>[Ru]3</th>
<th>[Ru]4</th>
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<tr>
<td>LUMO+5</td>
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<td>HOMO-2</td>
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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)₂] central motif.
Figure S5. Electronic absorption spectra of [Ru]1 (C = 1.7 x 10^{-5} M^{-1}), [Ru]3 (C = 1.7 x 10^{-5} M^{-1}) and the mixture [Ru]1&[Ru]3 in a 1:1 molar ratio (C_{dye} = 1.7 x 10^{-5} M^{-1}) in CH2Cl2.

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 $\eta = 9.07\%$. 