

# **Distinguishable photovoltaic performance on dye-sensitized solar cells by using ruthenium sensitizers with a pair of isomeric ancillary ligands**

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## **Electronic Supporting Information**

### **Experimental Section**

#### **Materials and measurements**

All reagents were purchased from commercial suppliers and used as received. Compounds **1** and **OM1** were prepared according to a literature method.<sup>1</sup> Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. UV-vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm. <sup>1</sup>H NMR spectra were obtained on a Bruker AM-500 NMR spectrometer, using TMS (SiMe<sub>4</sub>) as an internal reference at room temperature. Coupling constants are given in hertz. Electrospray ionization mass spectra (ESI-MS) were recorded by a ThermoFisher Scientific LCQ Fleet mass spectrometer in a scan range of 100-2000 amu. Photovoltaic measurements were recorded with a Newport Oriel solar simulator (Model 91160) equipped with a class a xenon light source powered by a Newport power supply. The power output of the lamp was measured to 1 Sun (100 mW·cm<sup>-2</sup>) using a certified Si reference cell. The current-voltage (*I*-*V*) characteristic of each cell was obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley digital source meter (Model 2400). IPCE measurements were performed on a Newport QE measurement system (Model 70104).

#### **Syntheses**

**Compound 2.** Compound 2 was synthesized using a similar procedure to that of compound 1. A degassed three-necked flask containing 4-bromothiophene-2-carbaldehyde (0.19 g, 1.00 mmol), 9-phenyl-9*H*-carbazol-3-ylboronic acid (0.35 g, 1.20 mmol), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.12 g, 0.10 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (1.30 g, 4.00 mmol) was added a degassed mixture of dioxane (50 mL) and water (5 mL). The mixture was stirred and heated to reflux for 4 h under argon atmosphere. The mixture was then allowed to cool to room temperature and extracted with chloroform. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by column chromatography over silica gel using hexane/CH<sub>2</sub>Cl<sub>2</sub> (*v/v* = 1:1) as the eluent to give 0.22 g (62 %) of compound 2 as light yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm) δ: 10.05 (s, 1H), 8.37 (d, 1H, *J* = 1.3 Hz), 8.21 (d, 1H, *J* = 7.8 Hz), 8.19 (d, 1H, *J* = 1.3 Hz), 7.92 (s, 1H), 7.66 (m, 3H), 7.65 (d, 2H, *J* = 2.3 Hz), 7.61 (t, 1H), 7.48 (m, 3H), 7.46 (t, 1H). EI-TOF-MS (*m/z*): 353.1 [M]<sup>+</sup>. *Anal. Calcd.* for C<sub>23</sub>H<sub>15</sub>NOS: C, 78.16; H, 4.28; N, 3.96 %. Found: C, 77.96; H, 4.54; N, 3.86 %.

**Compound 3.** A mixture of 1,10-phenanthroline-5,6-dione (0.25 g, 1.20 mmol), compound 1 (0.35 g, 1.00 mmol), ammoniumacetate (1.55 g, 20.2 mmol) and glacial acetic acid (30 mL) was refluxed for 2 h. After that, the mixture was poured into 200 mL cold water, and the resulting precipitate was isolated by filtration. The crude products were washed with water and purified by chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (*v/v* = 5:2) as the eluent to afford compound 3 as yellow solid in a yield of 0.43 g (80 %). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm) δ: 9.07 (s, 2H), 8.88 (d, *J* = 8.1 Hz, 2H), 8.76 (s, 1H), 8.43 (d, *J* = 7.5 Hz, 1H), 8.29 (s, 1H), 7.96 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 3H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.54-7.46 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40-7.35 (m, 1H). Negative ESI-MS in methanol (*m/z*): 542.4 [M]<sup>-</sup>. *Anal. Calcd.* for C<sub>33</sub>H<sub>21</sub>N<sub>5</sub>S: C, 77.33; H, 3.89; N, 12.88 %. Found: C, 77.16; H, 3.94; N, 12.86 %.

**Compound 4.** A mixture of 1,10-phenanthroline-5,6-dione (0.25 g, 1.20 mmol), compound **2** (0.35 g, 1.00 mmol), ammoniumacetate (1.55 g, 20.2 mmol) and glacial acetic acid (30 mL) was refluxed for 2 h. After the reaction, the mixture was poured into 200 mL cold water, and the resulting precipitate was isolated by filtration. The crude products were washed with water and purified by chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (v/v = 5:2) as the eluent to afford compound **4** as brown solid in a yield of 0.41 g (75 %). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm)  $\delta$ : 9.06 (d, *J* = 2.9 Hz, 2H), 8.92 (s, 2H), 8.70 (s, 1H), 8.43 (s, 1H), 8.36-8.32 (m, 1H), 8.08 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 3H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.52-7.46 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H). Negative ESI-MS in methanol (*m/z*): 542.5 [M]<sup>-</sup>. *Anal. Calcd.* for C<sub>35</sub>H<sub>21</sub>N<sub>5</sub>S: C, 77.33; H, 3.89; N, 12.88 %. Found: C, 77.09; H, 4.04; N, 12.81 %.

**Compound 5.** [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (0.12 g, 0.20 mmol) and ligand **3** (0.22 g, 0.40 mmol) were added to dry methanol (20 mL). The reaction mixture was heated at 80 °C under N<sub>2</sub> for 4 h. The filtrate was evaporated to dryness under reduced pressure and loaded on a silica column. The separation was achieved using CH<sub>2</sub>Cl<sub>2</sub>/MeOH eluent (v/v = 30:1). A bright yellow fraction was collected and evaporated to dryness, affording yellow solid **5** in a yield of 0.31 g (90 %). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm)  $\delta$ : 9.87 (d, *J* = 4.6 Hz, 2H), 9.31 (s, 2H), 8.93 (s, 1H), 8.73 (s, 1H), 8.32 (d, *J* = 7.5 Hz, 1H), 8.19 (s, 2H), 8.11 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.79-7.65 (m, 4H), 7.58 (d, *J* = 6.7 Hz, 1H), 7.46 (t, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 6.9 Hz, 1H), 6.35 (d, *J* = 5.8 Hz, 2H), 6.13 (d, *J* = 5.7 Hz, 2H), 2.21 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 6H). Positive ESI-MS in methanol (*m/z*): 814.6 [M-Cl]<sup>+</sup>. *Anal. Calcd* for C<sub>45</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>5</sub>RuS: C, 63.60; H, 4.15; N, 8.24 %. Found: C, 63.11; H, 4.32; N, 8.13 %.

**Compound 6.** [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (0.12 g, 0.20 mmol) and ligand **4** (0.22 g, 0.40 mmol) were added to dry methanol (20 mL). The reaction mixture was heated at 80 °C under N<sub>2</sub> for 4 h. The filtrate was evaporated to dryness under reduced pressure and loaded on a silica column. The separation was achieved using CH<sub>2</sub>Cl<sub>2</sub>/MeOH eluent (v/v = 30:1). A bright yellow fraction was collected and evaporated to dryness,

affording yellow solid **6** in a yield of 0.32 g (92 %). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm)  $\delta$ : 9.85 (d, *J* = 5.0 Hz, 2H), 9.37 (s, 2H), 8.72 (s, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 8.31 (s, 1H), 8.18 (s, 2H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.75-7.66 (m, 5H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 6.3 Hz, 2H), 6.12 (d, *J* = 6.3 Hz, 2H), 2.22 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 6H). Positive ESI-MS in methanol (*m/z*): 814.7 [M-Cl]<sup>+</sup>. *Anal. Calcd* for C<sub>45</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>5</sub>RuS: C, 63.60; H, 4.15; N, 8.24 %. Found: C, 63.32; H, 4.42; N, 8.09 %.

**Compound BM1.** Compound **5** (0.26 g, 0.30 mmol) and dcby (0.74 g, 0.30 mmol) were added to dry DMF (20 mL). The reaction mixture was heated at 160 °C for 4 h in the dark. Excess NH<sub>4</sub>NCS was added to the reaction mixture and heated at 130 °C for 4h. After the reaction, the solvent was removed by a rotary evaporator. Then the solid was dissolved in a basic methanol (tetrabutylammonium hydroxide) solution and purified by Sephadex LH-20 column with methanol as the eluent. The main red band was collected, and the solvent was evaporated. The resultant solid was dissolved in water, and a few drops of 0.02 M HNO<sub>3</sub> were added to precipitate the product. The mixture was left to stand in a refrigerator overnight. The resulting precipitate was filtered and washed thoroughly with distilled water and dried in vacuo, affording the target product in a 30 % yield. Mp >300 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm)  $\delta$ : 9.57 (s, 2H), 9.18 (s, 1H), 9.00 (s, 1H), 8.63 (s, 2H), 8.35 (s, 4H), 8.00 (s, 1H), 7.66 (d, *J* = 26.5 Hz, 7H), 7.55 (s, 3H), 7.42 (s, 2H), 7.32 (d, *J* = 15.3 Hz, 3H), 3.11 (d, *J* = 7.1 Hz, 10H), 1.51 (s, 10H), 1.25 (dd, *J* = 14.3, 7.2 Hz, 10H), 0.87 (t, *J* = 7.3 Hz, 15H). Negative ESI-MS in methanol (*m/z*): 1004.7 [M]<sup>-</sup>. *Anal. Calcd.* for C<sub>49</sub>H<sub>29</sub>N<sub>9</sub>O<sub>4</sub>RuS<sub>3</sub>: C, 58.56; H, 2.91; N, 12.54 %. Found: C, 58.45; H, 3.08; N, 12.41 %.

**Compound BM2.** The synthetic procedure of **BM2** was similar to that described of **BM1**. Compound **6** (0.26 g, 0.30 mmol), dcby (0.74 g, 0.30 mmol) and excess NH<sub>4</sub>NCS were used in the reaction. After purification, 0.08 g (25 %) product was obtained. Mp >300°C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm)  $\delta$ : 9.62 (d, *J* = 4.7 Hz, 1H), 9.55 (s, 1H), 9.18 (s, 1H), 8.99 (s, 1H), 8.68 (s, 1H), 8.45 (s, 1H), 8.36 (d, *J* = 21.0 Hz, 3H), 8.03 (s, 1H), 7.82 (s, 3H), 7.69 (d, *J* = 21.7 Hz, 5H), 7.55 (d, *J* = 28.6 Hz, 3H), 7.48-7.36 (m, 4H), 7.32 (s, 1H), 3.21-3.10 (m, 10H), 1.57 (s, 10H), 1.30 (dd,

$J = 14.0, 7.0$  Hz, 10H), 0.93 (t,  $J = 7.1$  Hz, 15H). Negative ESI-MS in methanol ( $m/z$ ): 1004.7 [M]<sup>-</sup>. *Anal. Calcd* for C<sub>49</sub>H<sub>29</sub>N<sub>9</sub>O<sub>4</sub>RuS<sub>3</sub>: C, 58.56; H, 2.91; N, 12.54 %. Found: C, 58.34; H, 3.13; N, 12.34 %.

**Compound OM2.** A mixture of compound **2** (0.07 g, 0.20 mmol) and cyanoacetic acid (0.04g, 0.50 mmol) was added MeCN (15 mL) and several drops of piperidine as a catalyst. The mixture was refluxed for 15 h, and the solvent was removed by a rotary evaporator. The residue washed thoroughly with distilled MeCN and dried in vacuo, and finally 0.08 g (90 %) yellow product was obtained. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, ppm)  $\delta$ : 9.33 (s, 1H), 8.66 (s, 1H), 8.30 (s, 3H), 8.25 (s, 1H), 7.80 (d,  $J = 8.3$  Hz, 1H), 7.69 (d,  $J = 6.9$  Hz, 2H), 7.64 (d,  $J = 6.8$  Hz, 2H), 7.57 (d,  $J = 6.6$  Hz, 1H), 7.45 (d,  $J = 7.3$  Hz, 1H), 7.41 (t,  $J = 9.3$  Hz, 2H), 7.34 (t,  $J = 6.8$  Hz, 1H). Negative ESI-MS in methanol ( $m/z$ ): 419.4 [M]<sup>-</sup>. *Anal. Calcd.* for C<sub>26</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S: C, 74.27; H, 3.84; N, 6.66 %. Found: C, 74.11; H, 4.06; N, 6.42 %.

**Fabrication of dye-sensitized solar cells.** Photo-anodes composed of transparent TiO<sub>2</sub> (20 nm) layer and FTO glass were obtained according to an already reported procedure.<sup>4</sup> The TiO<sub>2</sub> electrodes were immersed into the dye solution (0.50 mM in acetonitrile and *tert*-butanol (1:1, v/v)). The dye-adsorbed TiO<sub>2</sub> electrode and Pt counter electrode were assembled into a sealed sandwich-type cell. A drop of electrolyte was then introduced into the cell, which was composed of 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide, 0.05M iodine, 0.5 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile. The drilled holes were sealed with a microscope cover slide and Surlyn to avoid leakage of the electrolyte solution.

#### **X-ray data collection and solution**

Single-crystal samples of **1**, **2** and **OM1** were covered in glue and mounted on glass fibers for data collection on a Bruker SMART 1K CCD area detector at 291(2) K, respectively, using graphite mono-chromated Mo *K* $\alpha$  radiation ( $\lambda = 0.71073$  Å). The collected data were reduced by using the program SAINT<sup>2</sup> and empirical absorption corrections were done by SADABS<sup>3</sup> program. The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic

absences by using XPREP. The structures were solved by direct method and refined by least-squares method. All non-hydrogen atoms were refined on  $F^2$  by full-matrix least-squares procedure using anisotropic displacement parameters. All the other hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters at 1.2 times of the equivalent isotropic U of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. All calculations were carried out with the SHELXTL PC program package.<sup>4</sup> The summary of the crystal data, experimental details and refinement results for compounds **1** and **2** is listed in Table 1. Selected bond distances and bond angles of compounds **1** and **2** are given in Table 2, while intermolecular hydrogen bonding interactions are listed in Table 3.

### DFT calculations

All calculations were performed with the Gaussian 09 program package,<sup>5</sup> employing the DFT method with Becke's three parameter hybrid function and Lee-Yang-Parr's gradient corrected correlation function (B3LYP). The LanL2DZ effective core potential was used for the Ru atom, and the 6-31G\*\* basis set was applied for all other atoms.

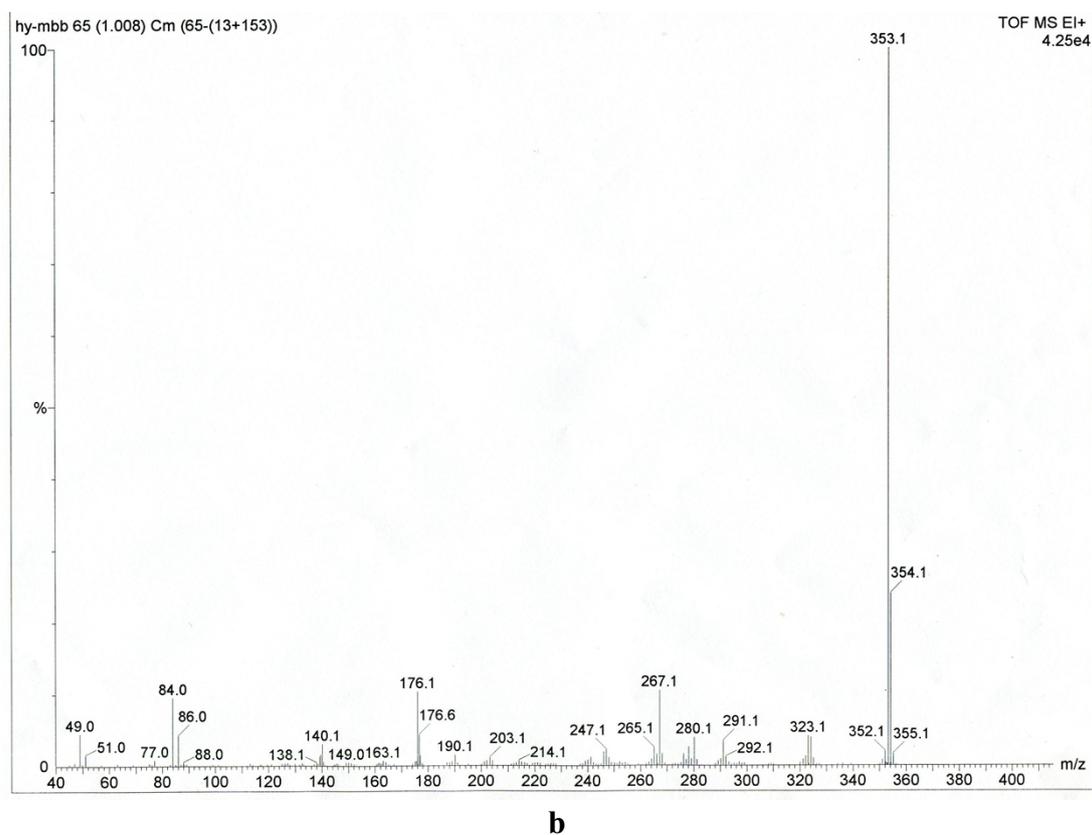
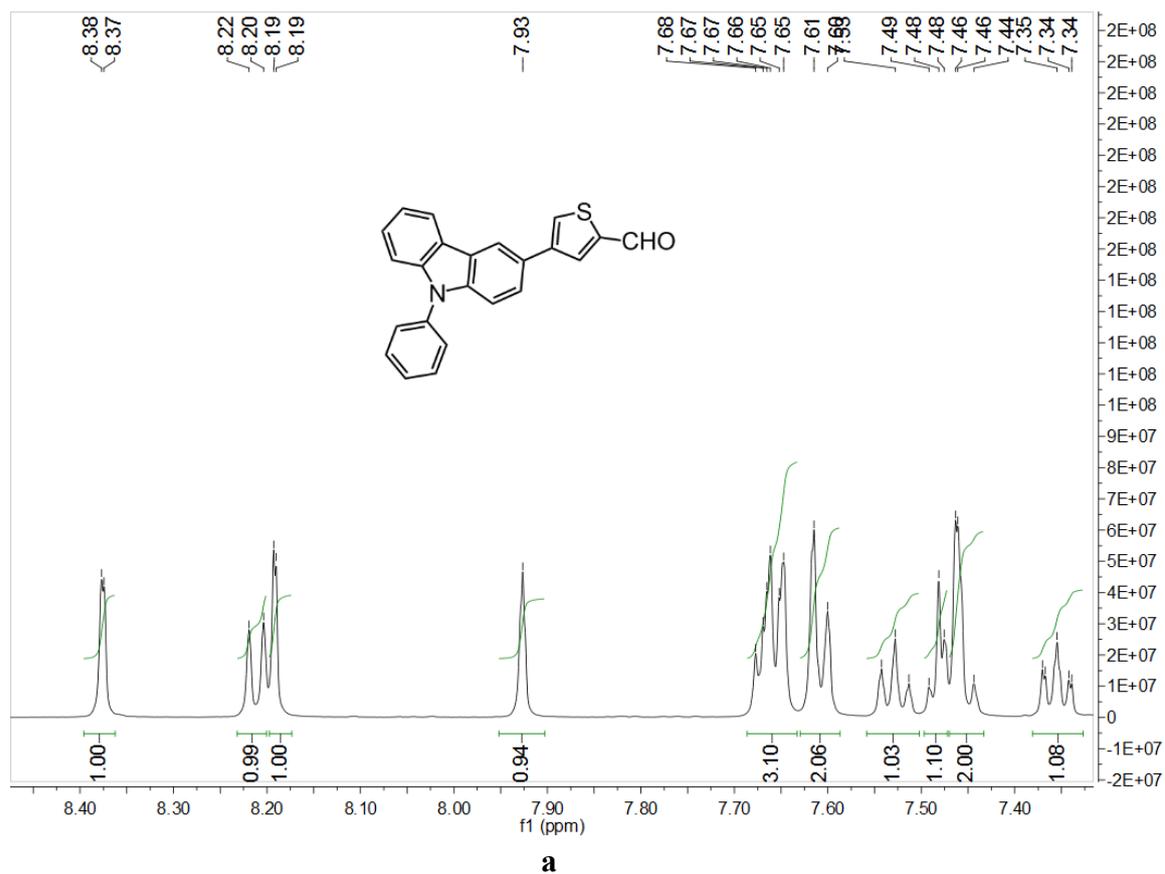
### References

- S1 E. Lee, N. Jung, J. Kim, C. Im, Y. Seo, H. Hwang, and Y. Kang, *Bull. Korean Chem. Soc.*, 2012, **33**, 293.
- S2 Siemens. SAINT v4 software reference manual. Madison, Wisconsin, USA: Siemens Analytical X-Ray Systems, Inc.; 2000.
- S3 Sheldrick GM. SADABS, program for empirical absorption correction of area detector data. Germany: Univ. of Gottingen; 2000.
- S4 Siemens. SHELXTL, Version 6.10 reference manual. Madison, Wisconsin, USA: Siemens Analytical X-Ray Systems, Inc.; 2000.
- S5 P. Wang; S. M. Zakeeruddin; P. Comte; R. Charvet; R. Humphry-Baker; M. Grätzel. *J. Phys. Chem. B.* 2003, **107**, 14336.

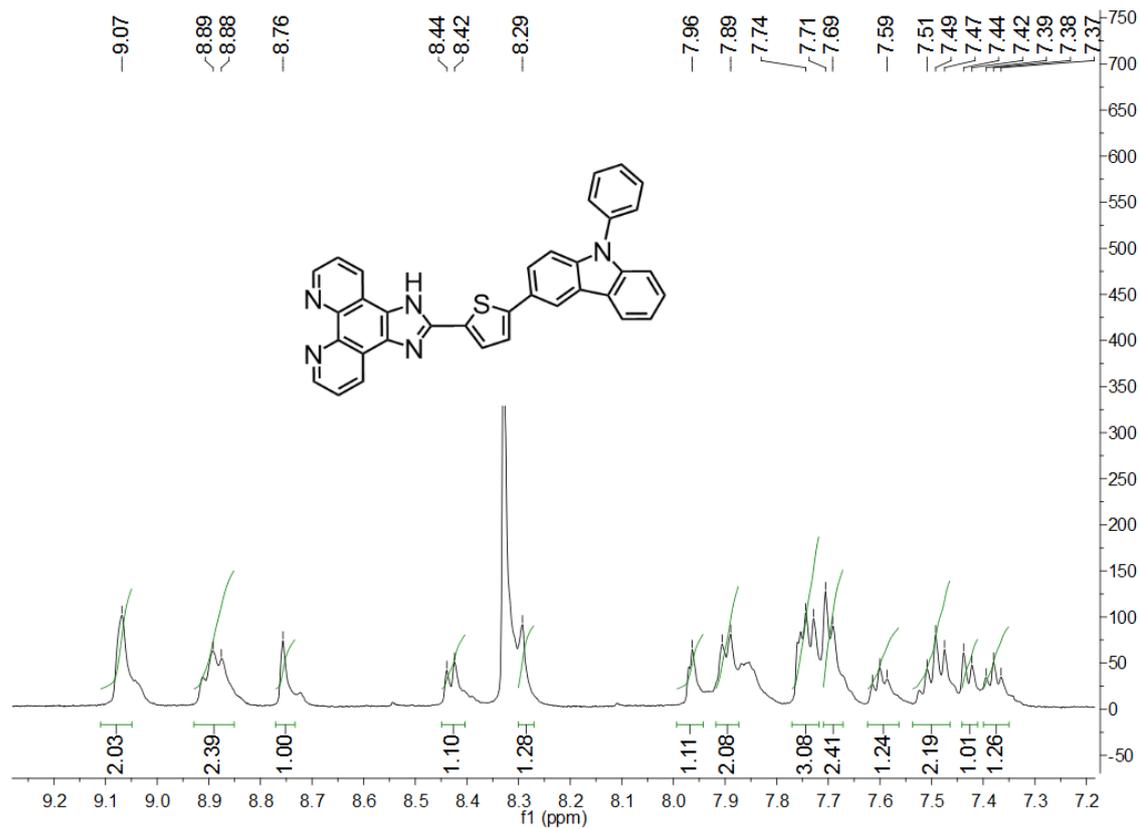
**Table S11.** Crystallographic data of compounds **1**, **2** and **OM1**.

Compound	<b>1</b>	<b>2</b>	<b>OM1</b>
Formula	C <sub>23</sub> H <sub>15</sub> NOS	C <sub>23</sub> H <sub>15</sub> NOS	C <sub>29</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub> S
<i>MW</i>	353.42	353.42	493.56
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P2</i> <sub>1</sub> / <i>c</i>	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	13.297(6)	7.5420(6)	9.090(5)
<i>b</i> /Å	14.286(7)	16.0923(14)	9.383(5)
<i>c</i> /Å	10.070(5)	14.6720(13)	15.108(8)
$\alpha$ /°	90.00	90.00	79.476(9)
$\beta$ /°	103.840(7)	102.015(2)	81.970(8)
$\gamma$ /°	90.00	90.00	81.163(9)
<i>V</i> /Å <sup>3</sup>	1857.3(15)	1741.7(3)	1243.6(12)
<i>Z</i>	4	4	2
<i>T</i> /K	291(2)	291(2)	291(2)
Radiation, $\lambda$ /Å	0.71073	0.71073	0.71073
<i>D</i> <sub>calcd</sub> , g/cm <sup>3</sup>	1.264	1.348	1.318
$\mu$ /mm <sup>-1</sup>	0.185	0.210	0.167
<i>F</i> (000)	736	736	516
Crystal size/mm <sup>3</sup>	0.14 × 0.14 × 0.12	0.11 × 0.10 × 0.10	0.12 × 0.10 × 0.08
$\theta$ range/°	1.58-28.37	1.90-27.53	1.38-27.55
Reflections measured	12416	11702	8356
Unique reflections	4590	4001	5657
<i>R</i> <sub>int</sub>	0.0843	0.0249	0.0229
Reflections with <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )	2300	2920	3278
Number of parameters	235	452	452
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.006	1.042	328
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0669, 0.1558	0.0435, 0.1129	0.0526, 0.1118
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1308, 0.1853	0.0616, 0.1251	0.1098, 0.1334
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ /e·Å <sup>-3</sup>	0.335, -0.455	0.264, -0.308	0.217, -0.276

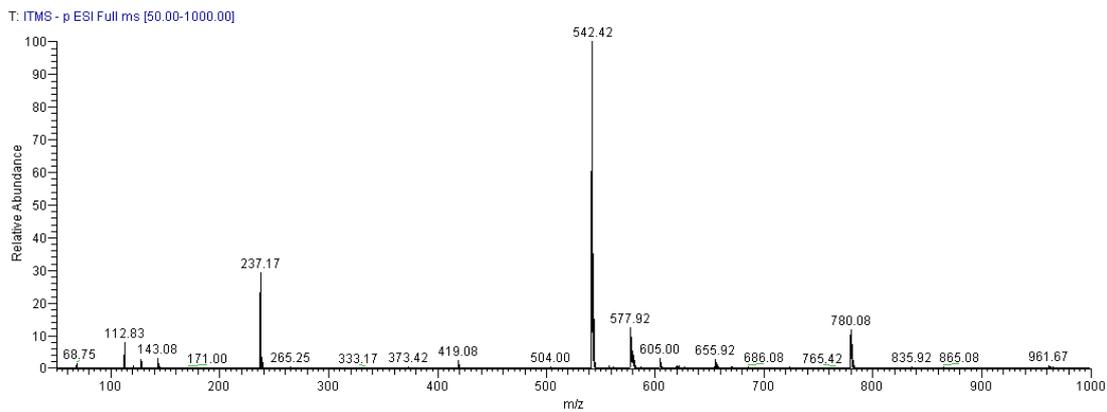
$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left[ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right]^{1/2}$$



**Figure S11.** <sup>1</sup>H NMR (a) and EI-TOF-MS (b) spectra of compound 2.

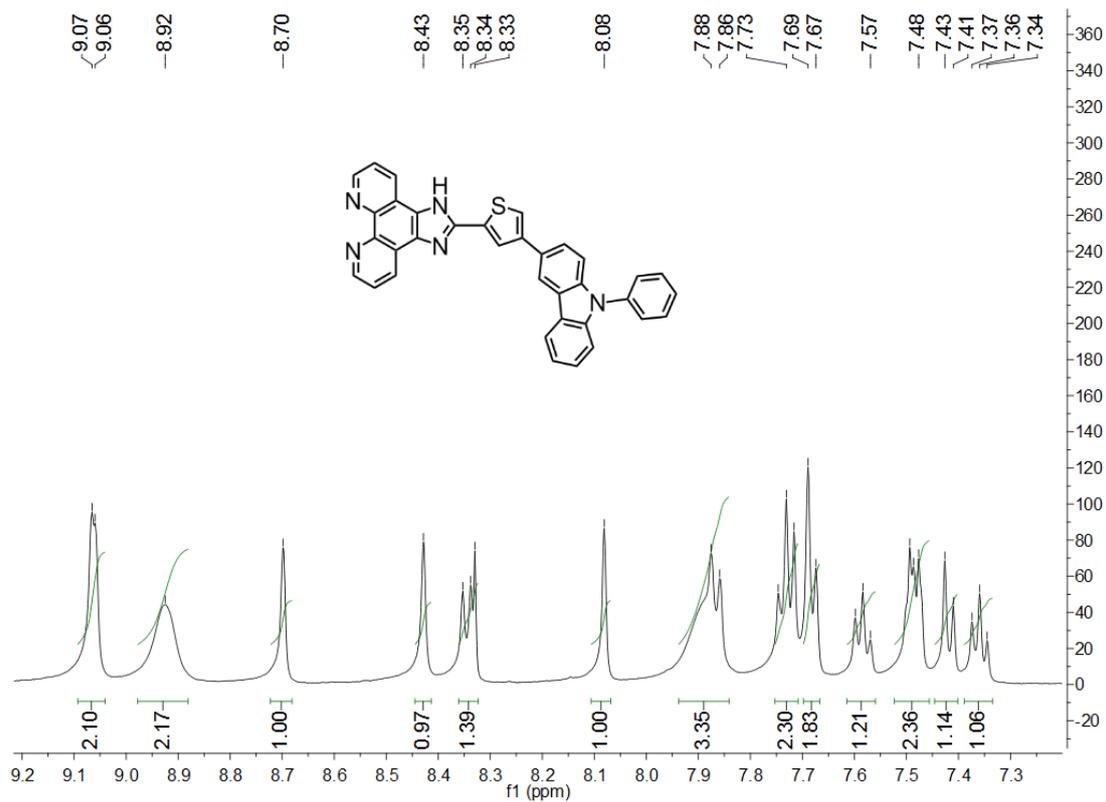


**a**

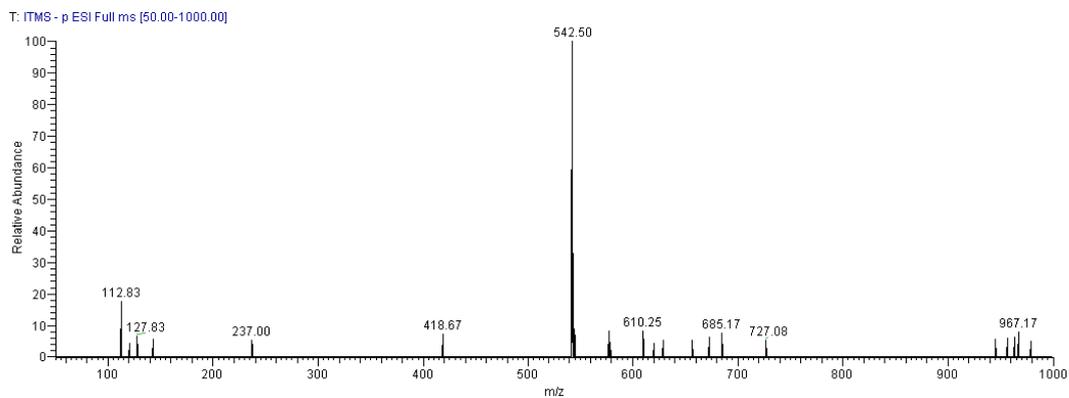


**b**

**Figure S12.**  $^1\text{H}$  NMR (**a**) and ESI-MS (**b**) spectra of compound **3**.

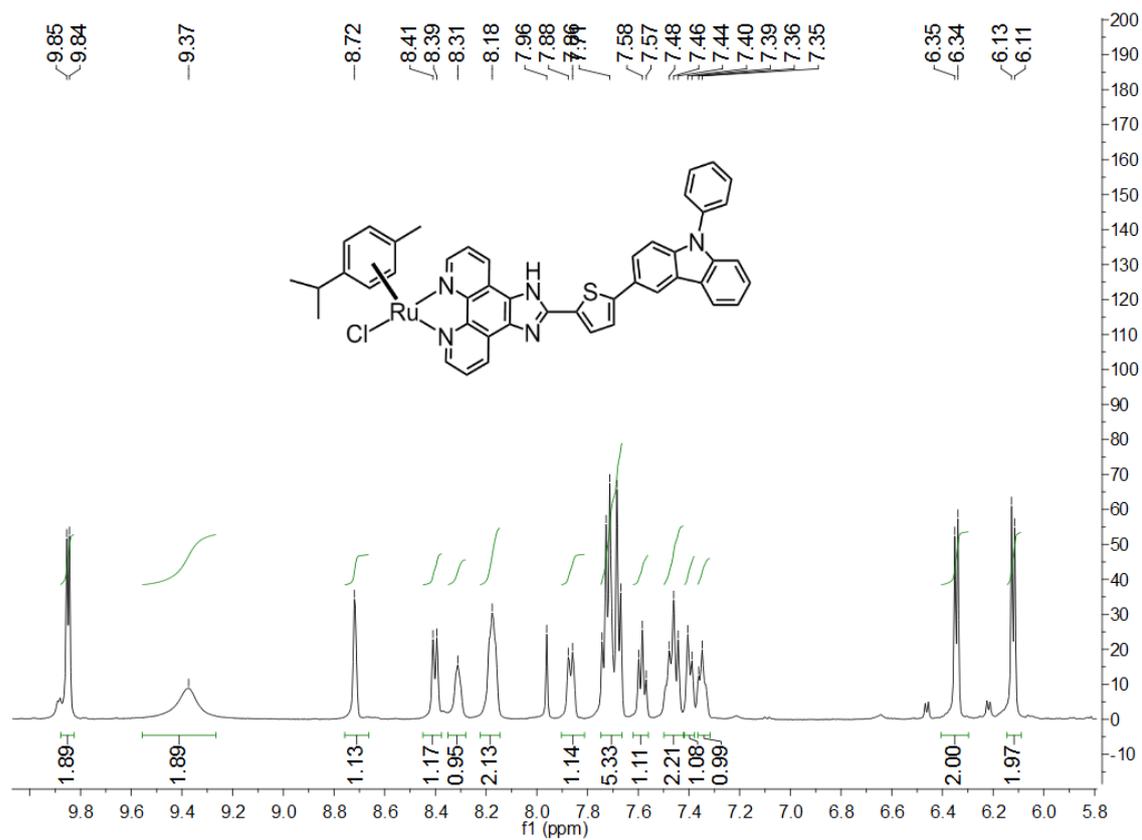


**a**

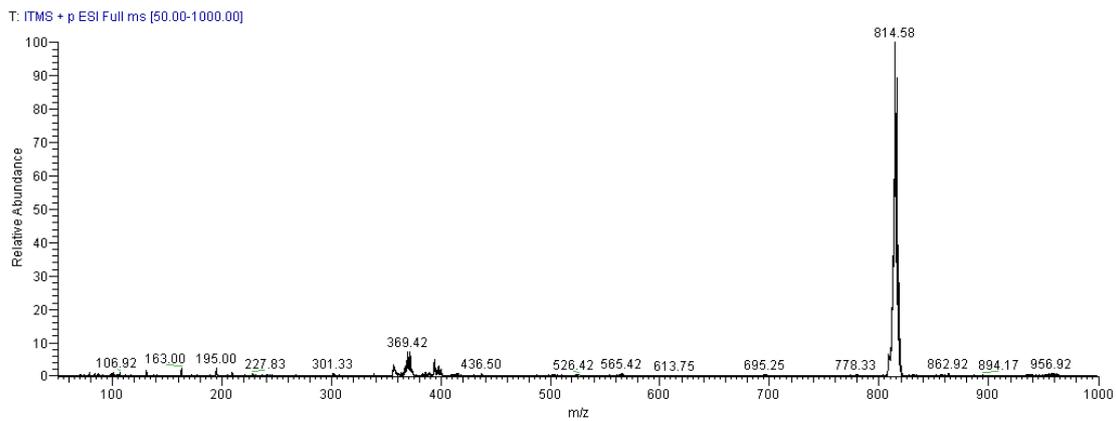


**b**

**Figure SI3.**  $^1\text{H}$  NMR (a) and ESI-MS (b) spectra of compound 4.

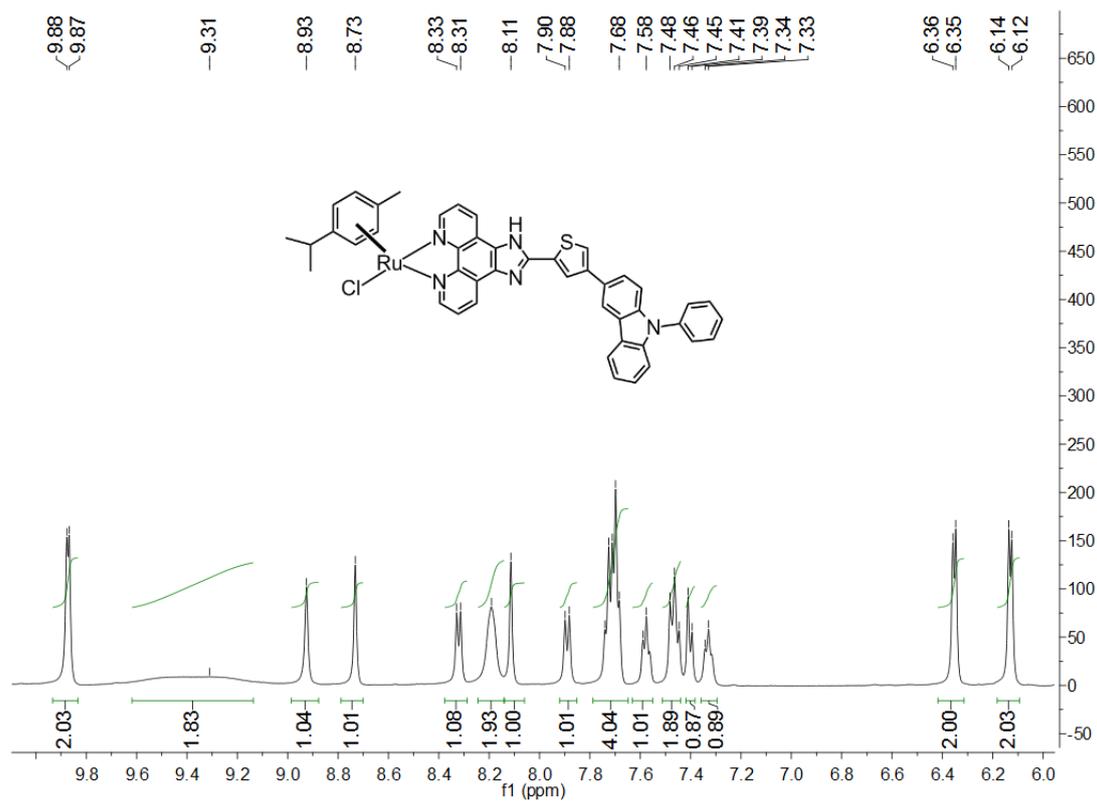


**a**

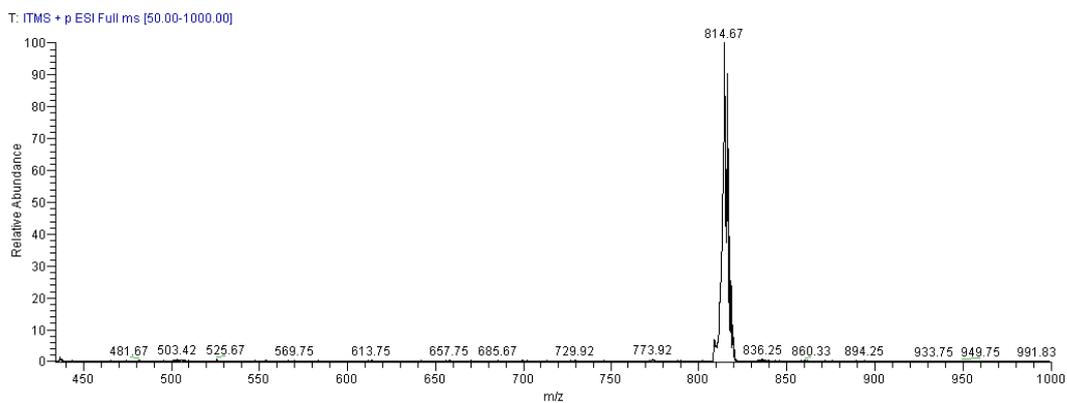


**b**

**Figure S14.**  $^1\text{H}$  NMR (**a**) and ESI-MS (**b**) spectra of compound **5**.

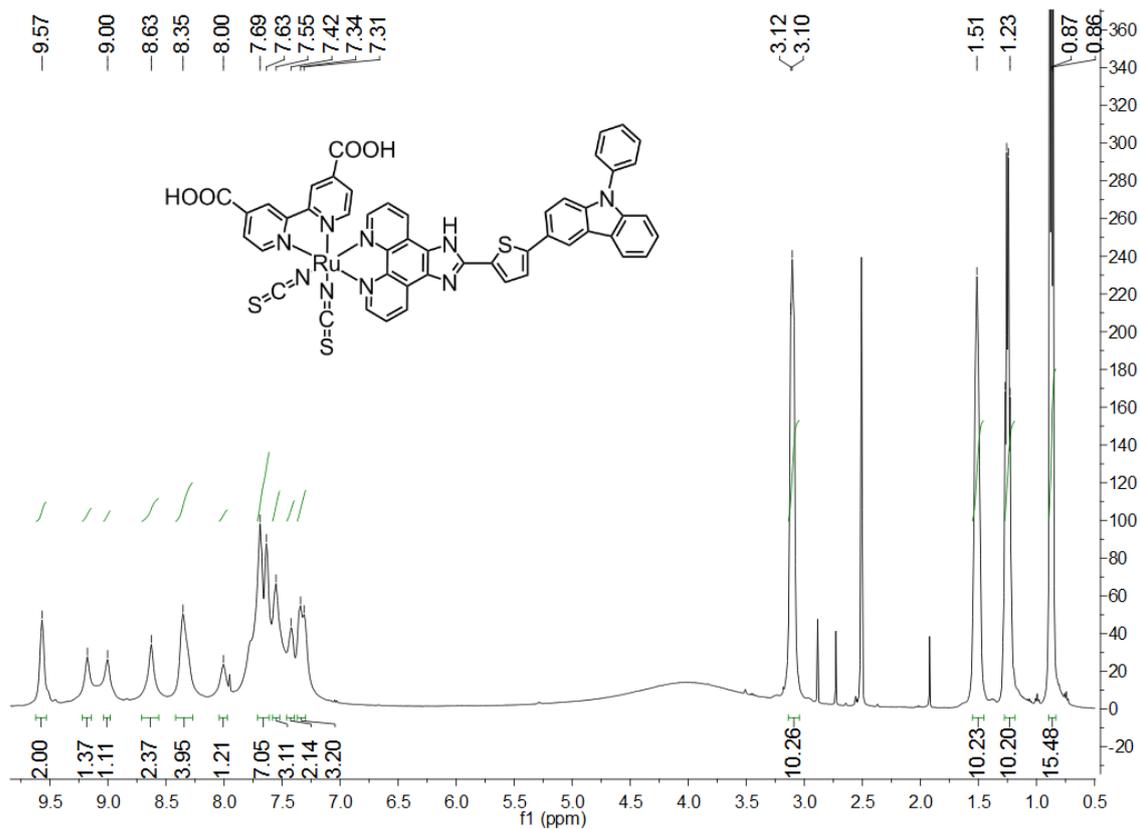


**a**

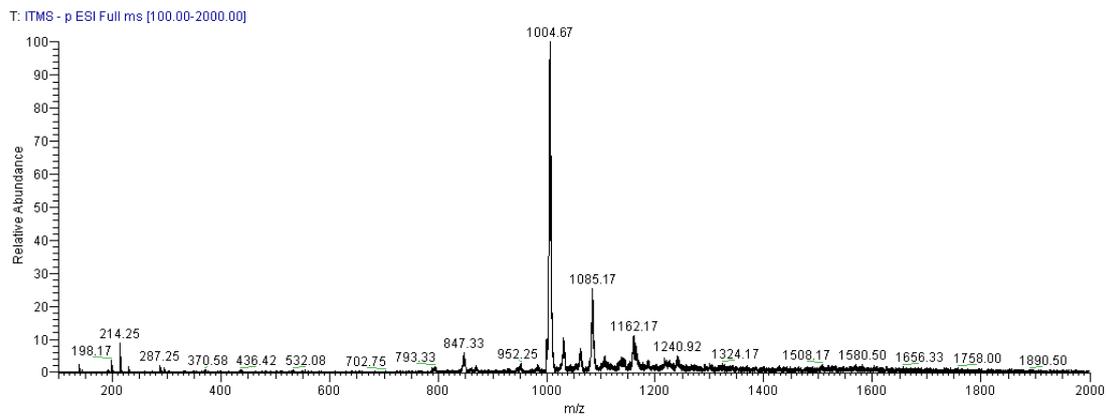


**b**

**Figure S15.**  $^1\text{H}$  NMR (a) and ESI-MS (b) spectra of compound 6.

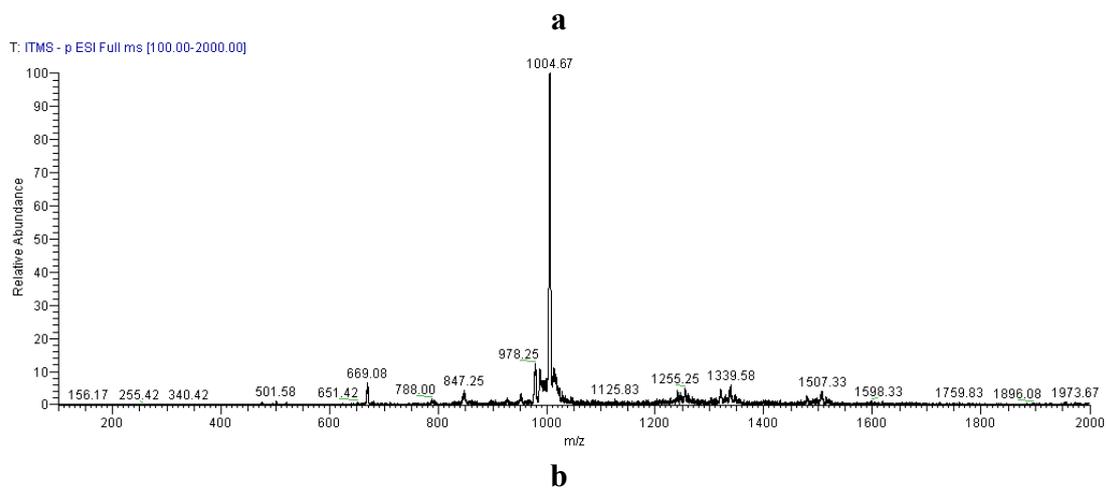
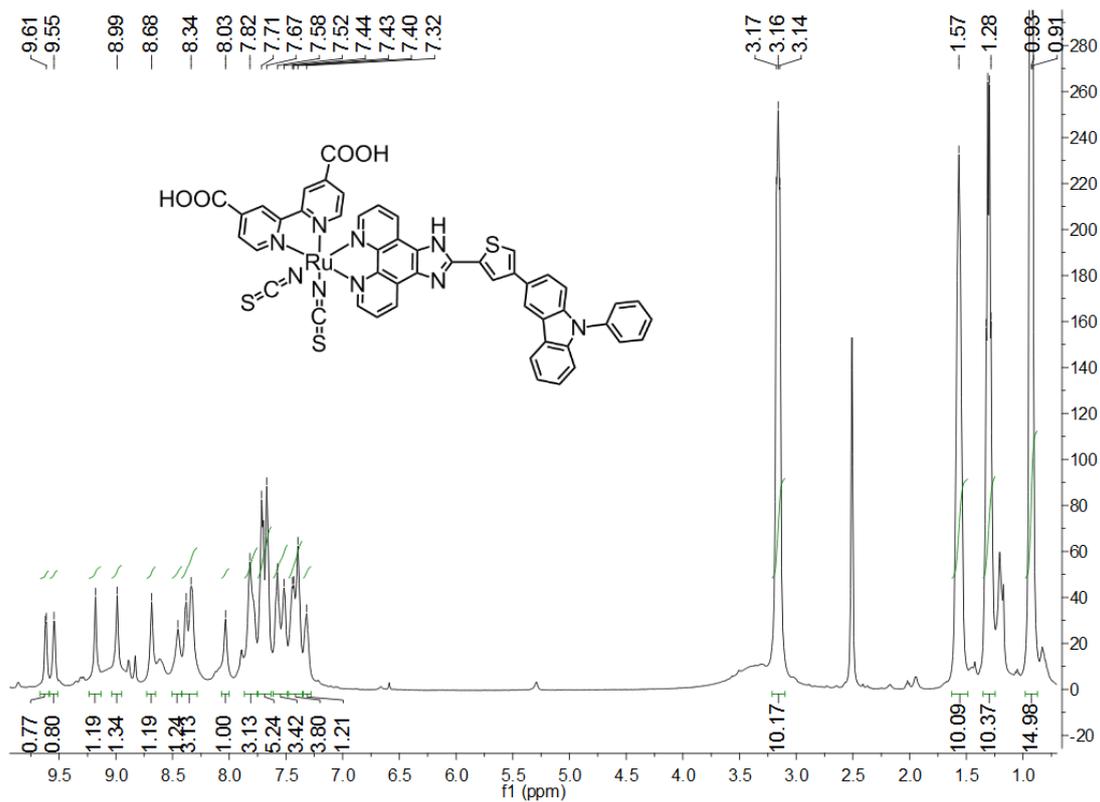


**a**

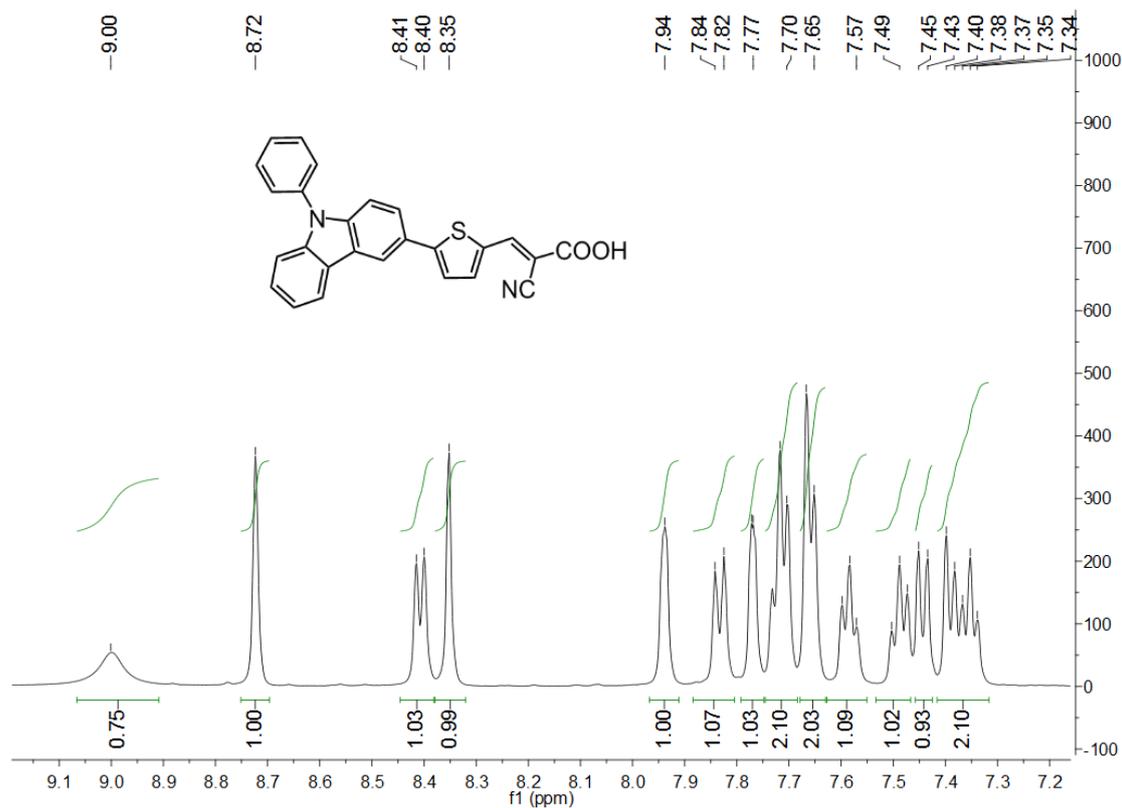


**b**

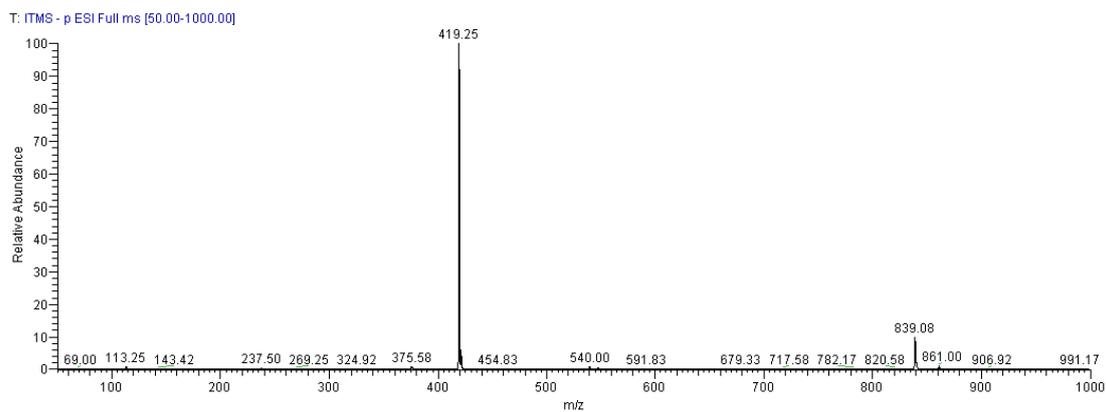
**Figure SI6.** <sup>1</sup>H NMR (a) and ESI-MS (b) spectra of compound **BM1**.



**Figure S17.** <sup>1</sup>H NMR (a) and ESI-MS (b) spectra of compound **BM2**.

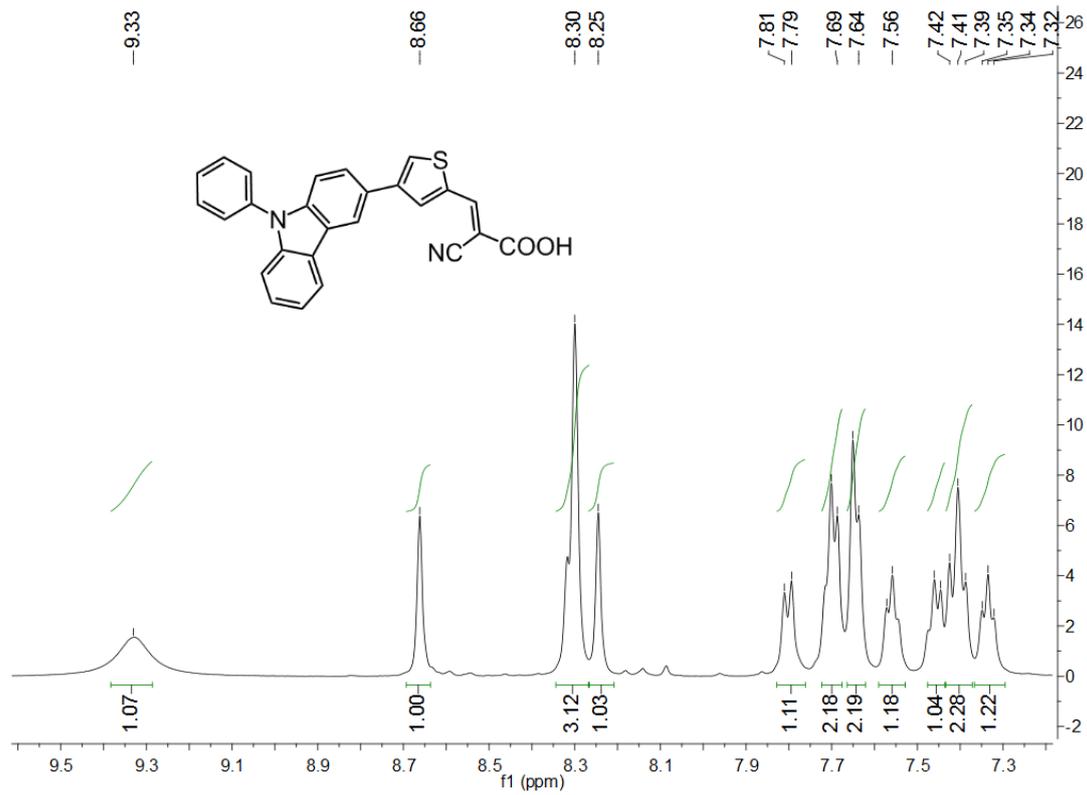


**a**

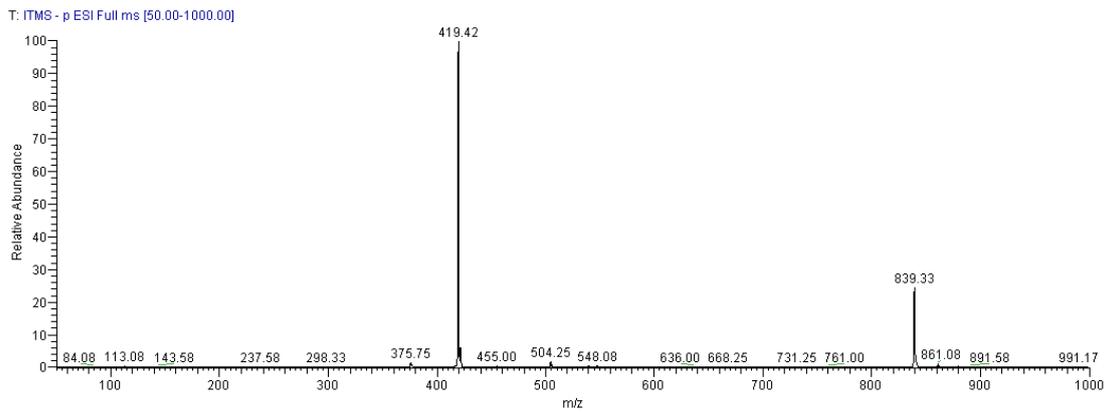


**b**

**Figure S18.** <sup>1</sup>H NMR (a) and ESI-MS (b) spectra of compound **OM1**.

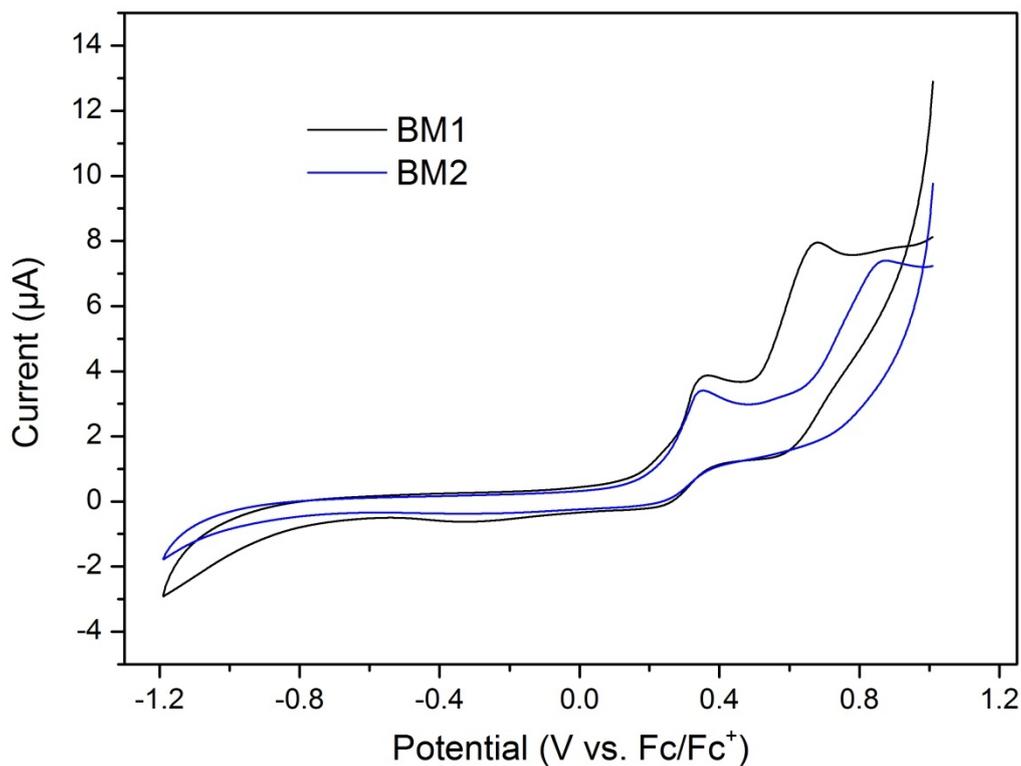


**a**

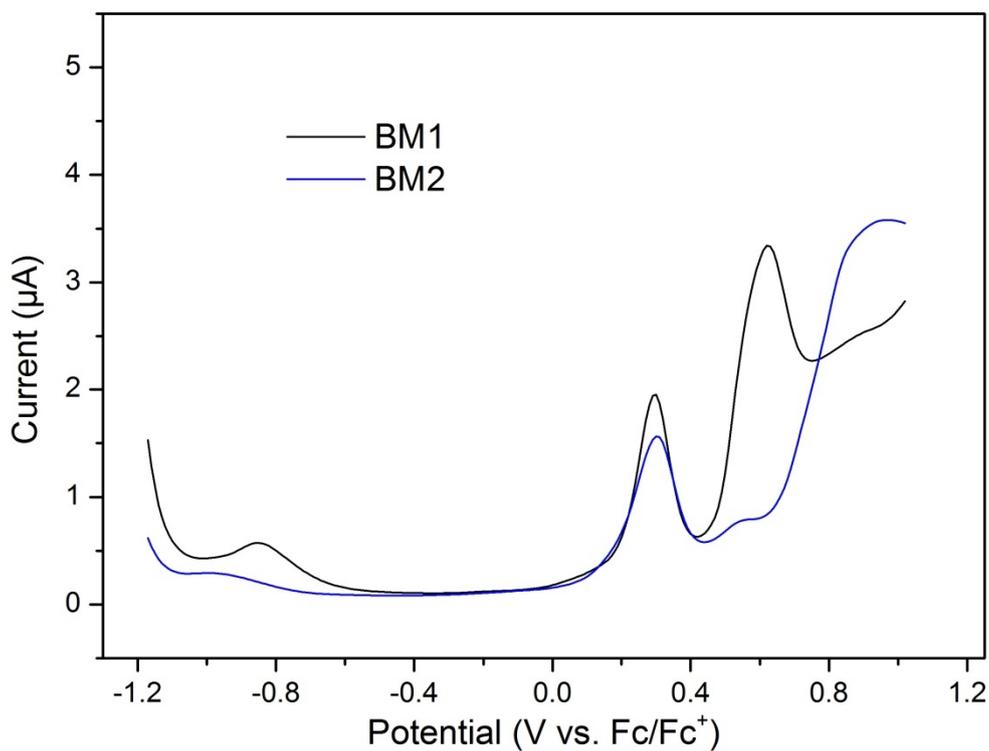


**b**

**Figure S19.** <sup>1</sup>H NMR (a) and ESI-MS (b) spectra of compound **OM2**.

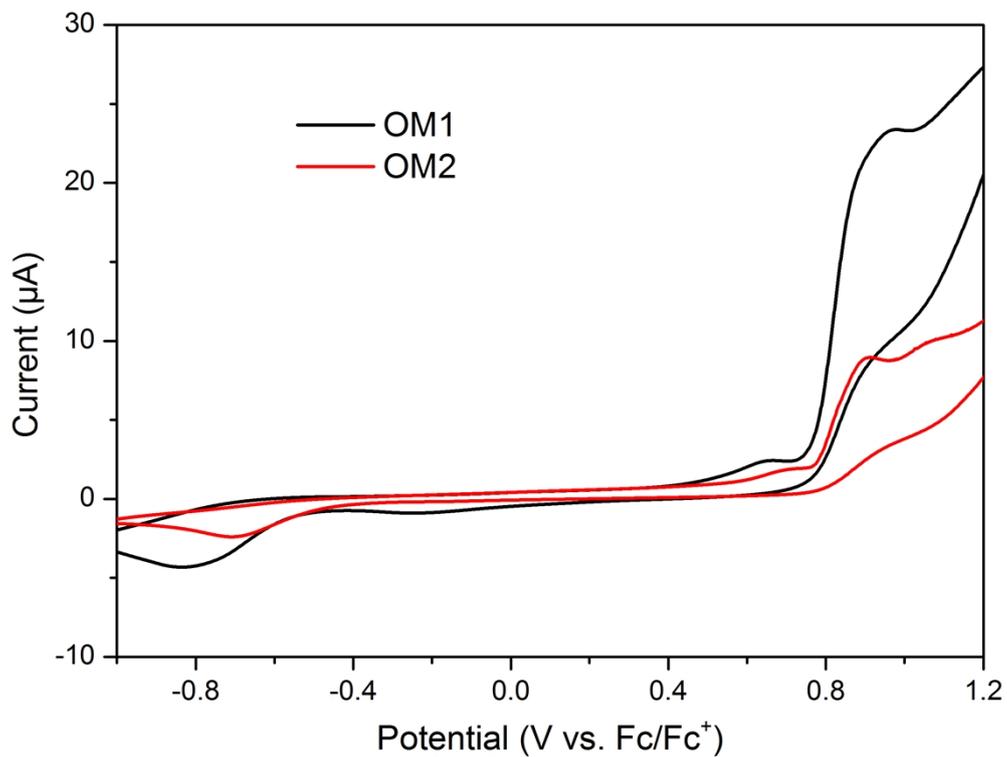


**a**

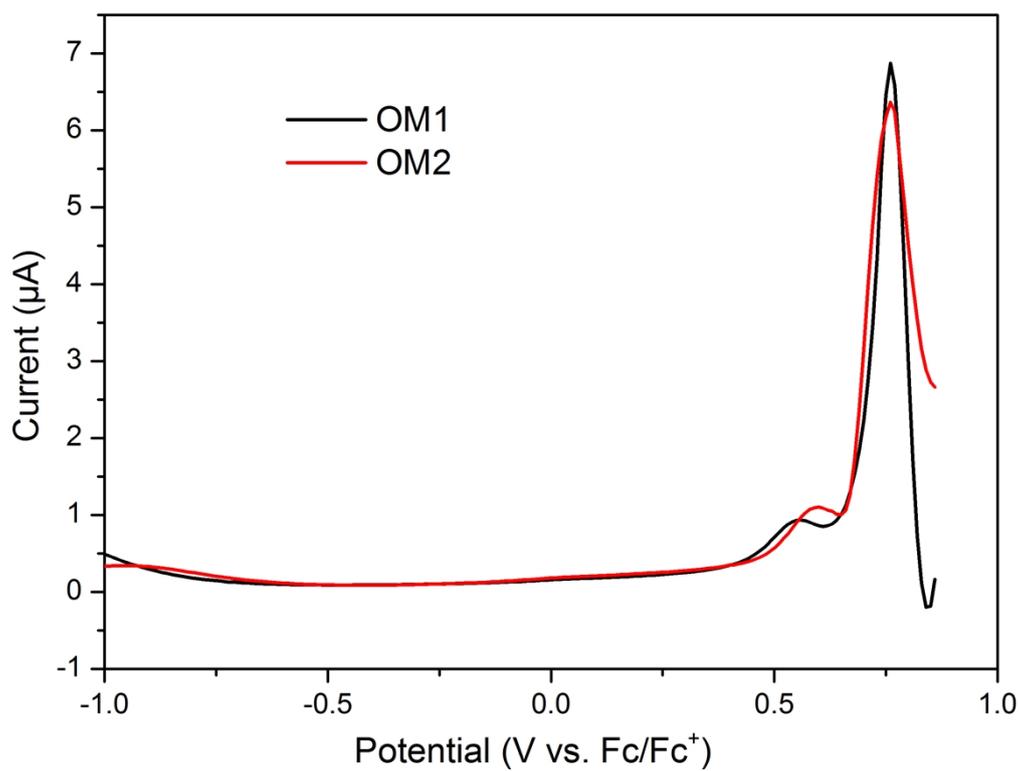


**b**

**Figure S110.** Cyclic (a) and differential-pulse (b) voltammetry curves of ruthenium sensitizers **BM1** and **BM2** recorded in  $1.00 \times 10^{-3}$  M solutions of tetrabutylammonium perchlorate in DMF.

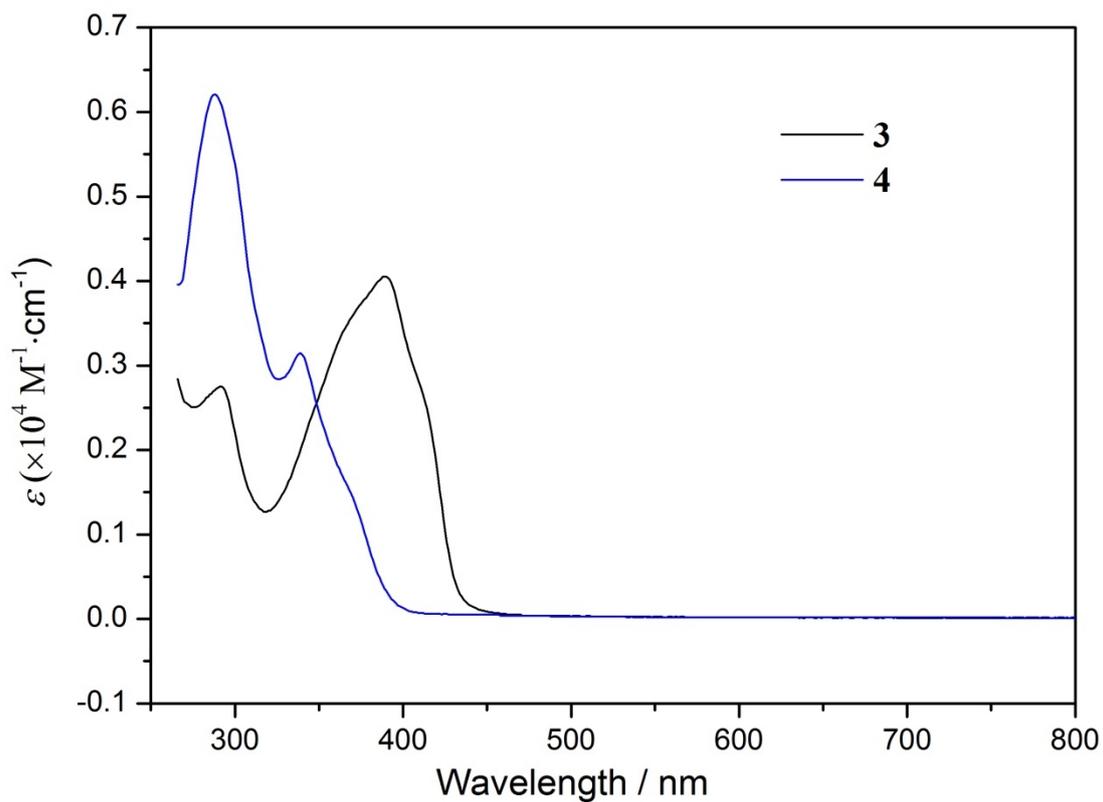


a

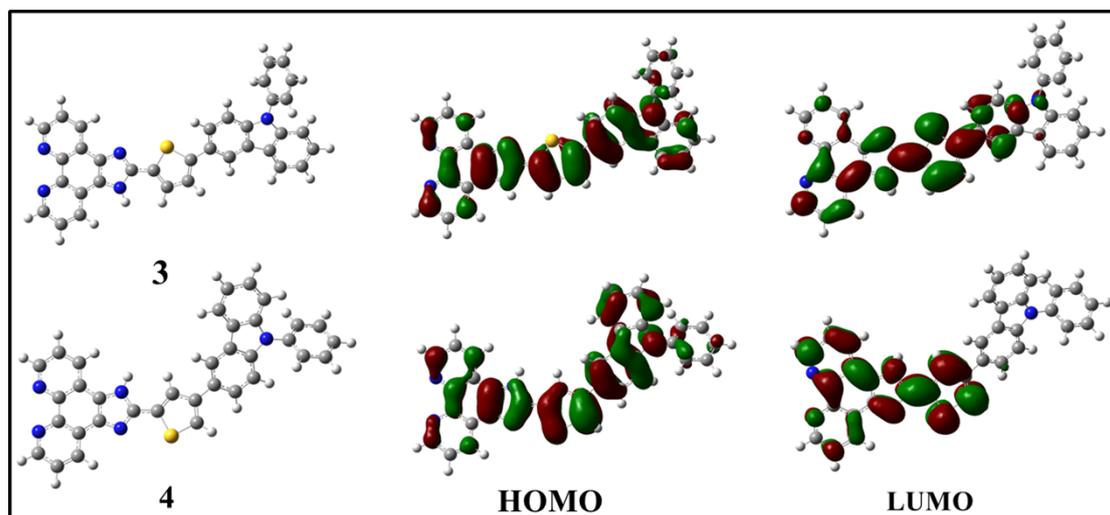


b

**Figure SI11.** Cyclic (a) and differential-pulse (b) voltammetry curves of **OM1** and **OM2** recorded in  $1.00 \times 10^{-3}$  M solutions of tetrabutylammonium perchlorate in DMF.



**Figure SI12.** UV-vis absorption spectra of two ancillary ligands **3** and **4** in their DMF solutions with the same concentration of  $1.00 \times 10^{-5}$  M.



**Figure SI13.** Frontier orbitals of ancillary ligands **3** and **4**.