

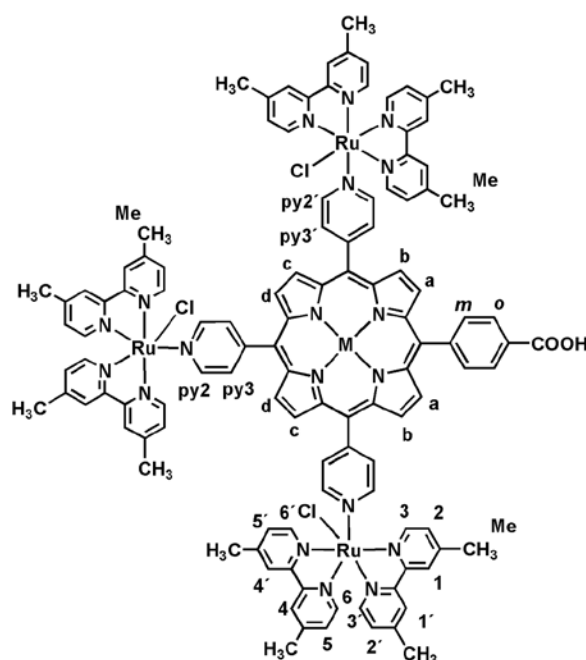
## Supporting Information

### Sevenfold Enhancement on Porphyrin Dye Efficiency by Coordination of Ruthenium Polypyridine Complexes

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*Porphyrin Dyes · Solar Cells · TiO<sub>2</sub> Devices · Supramolecular Photosensitizers · Antenna Effect*



**Figure 1.** Schematic structure of the supramolecular porphyrin dye, where  $M = 2H^+$  or  $Zn^{2+}$ . The numbers and letters are the labels for the different protons used for analysis of the NMR spectra.

### Experimental Section

The elemental analyses (CHN) were performed in a Perkin-Elmer CHN 2400 apparatus. The mass spectra were obtained in a Bruker Daltonics Esquire 3000 Coupled Plus, typically setting the capillary potential to 3 kV and the sample injection flux to 180  $\mu\text{L h}^{-1}$ . UV-vis spectra were recorded on a HP-8453A diode-array spectrophotometer, in the 190 to 1100 nm range.  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX500 spectrophotometer using  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$ ,  $\text{DMSO}-d_6$  or  $\text{CD}_3\text{CN}$  as solvent.

$[\text{Ru}(\text{dmbipy})_2\text{Cl}_2]$  were synthesized according to a previously reported method.<sup>1</sup>

### 5-(4-carboxyphenyl)-10,15,20-tri(4-pyridyl)porphyrin, MCTPyP<sup>1</sup>:

The free-base porphyrin was prepared by refluxing 4-formylbenzaldehyde (1.27 g, 8.46 mmol), 4-pyridylcarboxaldehyde (2.0 mL, 20.9 mmol) and nitrobenzene (150 mL) in glacial acetic acid (300 mL). The resultant black crude solid was filtered off in a silica gel plug and purified by silica gel column chromatography using chloroform/methanol (85:15, v/v) as eluent. The dark purple solid was then purified by recrystallization from a chloroform/methanol/acetone mixture (Yield: 0.257 g, 6%). Analysis Calcd for C<sub>42</sub>H<sub>27</sub>N<sub>7</sub>O<sub>2</sub>·2H<sub>2</sub>O: C, 72.30; H, 4.48; N, 14.05; Found: C, 71.98; H, 4.49; N, 13.67. ESI-MS *m/z*: calcd for C<sub>42</sub>H<sub>28</sub>N<sub>7</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 662.2; Found 662.2. <sup>1</sup>H NMR (CDCl<sub>3</sub>/CD<sub>3</sub>OD, 500 MHz, δ/ppm): 8.23 (m, 6 H, β-H-Py), 8.30 (d, 2 H, *J* = 8.3 Hz, *o*-H-PhCOOH), 8.49 (d, 2 H, *J* = 8.3 Hz, *m*-H-PhCOOH), 8.89 (broad s, 8 H, β-H), 9.00 (m, 6 H, α-H-Py). <sup>13</sup>C NMR (CDCl<sub>3</sub>/CD<sub>3</sub>OD, 125 MHz, δ/ppm): 116.9, 117.2, 120.4, 128.1, 129.5, 130.7, 134.3, 145.7, 147.6, 150.4, 169.2 (COOH).

**{5-(4-carboxyphenyl)-10,15,20-tri(4-pyridyl)porphyrinate}zinc(II), Zn-MCTPyP:** The zinc(II) porphyrin was prepared by refluxing MCTPyP (0.025 g, 0.037 mmol) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.0245 g, 0.113 mmol) in DMF (10 mL) for 2h. The solvent was removed in a flash-evaporator and 20 mL of distilled water was added to the reaction mixture. The dark-brown precipitate was centrifuged, washed four times with distilled water and dried overnight under vacuum. The solid was purified by silica gel column chromatography using chloroform as eluent and recrystallized from a chloroform/methanol mixture (Yield: 0.040 g, 67%). Analysis Calcd for C<sub>42</sub>H<sub>25</sub>N<sub>7</sub>O<sub>2</sub>Zn·3H<sub>2</sub>O: C, 64.75; H, 4.01; N, 12.58; Found: C, 63.51; H, 3.83; N, 12.14. ESI-MS *m/z*: calcd for C<sub>42</sub>H<sub>26</sub>N<sub>7</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 724.1; Found 724.1. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz, δ/ppm): 8.29 (m, 6 H, β-H-Py), 8.33 (d, 2 H, *J* = 8.3 Hz, *o*-H-PhCOOH), 8.51 (d, 2 H, *J* = 8.3 Hz, *m*-H-PhCOOH), 8.91 (m, 8 H, β-H), 9.04 (m, 6 H, α-H-Py). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz, δ/ppm): 116.3, 118.1, 122.2, 129.2, 130.5, 131.9, 137.8, 146.7, 149.1, 152.6, 171.1 (COOH).

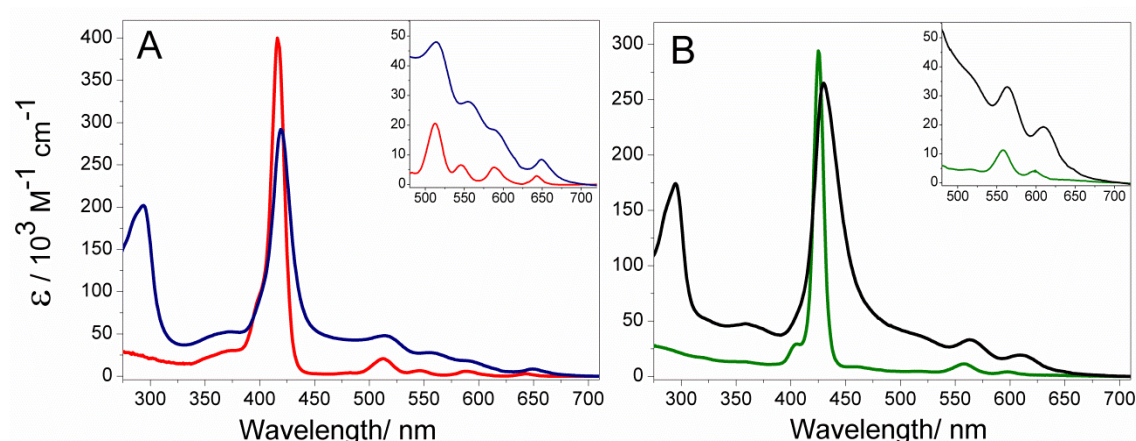
### 5-(4-carboxyphenyl)-Hexakis(4,4'-dimethyl-2,2'-bipyridyl-1κ<sup>2</sup>N, 1κ<sup>2</sup>N', 2κ<sup>2</sup>N, 2κ<sup>2</sup>N', 3κ<sup>2</sup>N, 3κ<sup>2</sup>N')trichloro-1κCl, 2κCl, 3κCl-(μ<sub>3</sub>-10,15,20-tri(4-pyridyl-1κN, 2κN', 3κN''-porphyrin))-triruthenium trifluoromethanesulfonate, MCTPyPRu<sub>3</sub><sup>2</sup>:

The ruthenated free-base porphyrin was obtained by refluxing MCTPyP (0.031 g, 0.046 mmol) with an excess of *cis*-[Ru(dmbpy)<sub>2</sub>Cl<sub>2</sub>] (0.081 g, 0.149 mmol) in DMF/glacial acetic acid mixture (6:4, v/v, 10 mL) for an hour. The solvent was removed in a flash evaporator and the ruthenated porphyrin precipitated out with a saturated aqueous solution of lithium trifluoromethanesulfonate. The crude red-brown solid was purified using a neutral alumina plug and methanol as eluent. The dark-brown solid was centrifuged, washed with distilled water and dried overnight under vacuum (Yield: 0.056 g, 54%) Analysis Calcd for C<sub>117</sub>H<sub>90</sub>Cl<sub>3</sub>F<sub>9</sub>N<sub>19</sub>O<sub>11</sub>Ru<sub>3</sub>S<sub>3</sub>·5H<sub>2</sub>O: C, 51.78; H, 4.05; N, 9.81; Found: C, 51.24; H, 4.18; N, 10.38. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz, δ/ppm): -3.12 (s, 2 H, inner NH), 2.50 (m, 18 H, *trans*-CH<sub>3</sub>-bpy, **Me**), 2.73 (m, 18 H, *cis*-CH<sub>3</sub>-bpy, **Me**), 7.55 (m, 6 H, H-bpy, **4,4'**), 7.63 (m, 6 H, H-bpy, **2,2'**), 7.73 (m, 3 H, H-bpy, **5'**), 7.86 (d, 2 H, *J* = 6.5 Hz, *o*-H-PhCOOH, **o**), 8.02 (m, 6 H, H-bpy, **6,1,1'**), 8.28 (d, 8 H, *J* = 8.0 Hz, β-H-Py and *m*-H-PhCOOH, **py<sub>3</sub>, m**), 8.43 (m, 9 H, H-bpy, **5**), 8.50 (dd, 2 H, *J* = 8.5 Hz, H-bpy, **3,3'**), 8.89 (m, 14 H, β-H and α-H-Py, **a,b,c,d,py<sub>2</sub>**), 9.96 (dd, 2 H, *J* = 6.5 Hz, H-bpy, **6'**). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz, δ/ppm): 25.1 (*trans*-CH<sub>3</sub>), 32.2 (*cis*-CH<sub>3</sub>), 116.8, 117.9, 121.0, 125.9 (bpy), 128.3, 129.6, 131.9, 134.9, 146.8, 147.5, 148.3 (bpy), 150.2, 150.9 (bpy), 158.0 (bpy), 168.4 (COOH).

### 5-(4-carboxyphenyl)-{Hexakis(4,4'-dimethyl-2,2'-bipyridyl-1κ<sup>2</sup>N, 1κ<sup>2</sup>N', 2κ<sup>2</sup>N, 2κ<sup>2</sup>N', 3κ<sup>2</sup>N, 3κ<sup>2</sup>N')trichloro-1κCl, 2κCl, 3κCl-(μ<sub>3</sub>-10,15,20-tri(4-pyridyl-1κN, 2κN', 3κN''-porphyrinate)zinc(II))-triruthenium trifluoromethanesulfonate, Zn-MCTPyPRu<sub>3</sub><sup>2</sup>:

The ruthenated zinc(II) porphyrin was obtained by refluxing Zn-MCTPyP (0.025 g, 0.034 mmol) with an excess of *cis*-[Ru(dmbpy)<sub>2</sub>Cl<sub>2</sub>] (0.057 g, 0.106 mmol) in DMF/glacial acetic acid mixture (6:4, v/v, 10 mL) for an hour. The solvent was removed in a flash evaporator and the ruthenated porphyrin precipitated out with a saturated lithium trifluoromethanesulfonate aqueous solution. The crude red-brown solid was purified using a neutral alumina plug and methanol as eluent. The dark-brown solid was centrifuged, washed with distilled water and dried overnight under vacuum (Yield: 0.081 g, 79%). Analysis Calcd for C<sub>117</sub>H<sub>97</sub>Cl<sub>3</sub>F<sub>9</sub>N<sub>19</sub>O<sub>11</sub>Ru<sub>3</sub>S<sub>3</sub>Zn·3H<sub>2</sub>O: C, 50.93; H, 3.84; N, 9.64; Found: C, 50.48; H, 3.62; N, 9.72. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz, δ/ppm): 2.52 (m, 18 H, *trans*-CH<sub>3</sub>-bpy, **Me**), 2.72 (m, 18 H, *cis*-CH<sub>3</sub>-bpy, **Me**), 7.54 (m, 6 H, H-bpy), 7.63 (m, 6 H, H-bpy, **4,4'**), 7.78 (m, 3 H, H-bpy, **2,2',5'**), 7.86 (d, 2 H, *J* = 6.5 Hz, *o*-H-PhCOOH, **o**), 8.00 (m, 6 H, H-bpy, **6,1,1'**), 8.20 (d, 8 H, *J* = 8.0 Hz, β-H-Py and *m*-H-PhCOOH, **py<sub>3</sub>, m**), 8.43 (m, 9 H, H-bpy, **5**), 8.52 (dd, 2 H, *J* = 8.5 Hz, H-bpy, **3,3'**), 8.87 (m, 14 H, β-H and α-H-Py, **a,b,c,d,py<sub>2</sub>**), 9.96 (dd, 2 H, *J* = 6.5 Hz, H-bpy, **6'**). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 125 MHz, δ/ppm): 26.0 (*trans*-CH<sub>3</sub>), 32.8 (*cis*-CH<sub>3</sub>), 116.3, 118.1, 122.2, 126.1 (bpy), 128.8, 129.9, 132.9, 135.3, 146.9, 148.5, 149.0 (bpy), 150.8, 151.1 (bpy), 158.4 (bpy), 168.9 (COOH).

### Absorption spectra in DMF solution



**Figure 2.** UV-vis spectra of MCTPyP (red, A), MCTPyPRu<sub>3</sub> (blue, A), Zn-MCTPyP (green, B) and Zn-MCTPyPRu<sub>3</sub> (black, B), in DMF solution.

### Preparation of Nanoporous TiO<sub>2</sub> Electrodes

The nanoporous TiO<sub>2</sub> film was deposited on F-doped SnO<sub>2</sub> (FTO) TEC15 conducting glass (sheet resistance ~15 Ω cm<sup>-2</sup>). A colloidal TiO<sub>2</sub> paste<sup>3</sup> was obtained by gently grinding 6.0 g of TiO<sub>2</sub> powder (Degussa P25) in 2.0 mL of distilled H<sub>2</sub>O and 0.2 mL of acetylacetone (Aldrich), in a mortar with a pestle, for about 40 min. Then, 8.0 mL of distilled water and 0.1 mL of Triton X-100 (Aldrich) were slowly added with continuous mixing for 10 min. The deposition area was delimited with a plastic adhesive tape on previously cleaned conductive glass sheets, and several drops of the TiO<sub>2</sub> paste were spread as evenly as possible onto the surface using a glass rod. The electrodes were then dried in air and fired in a furnace, at 450 °C, for 30 min. The thickness of the TiO<sub>2</sub> film (~10 μm) was determined by the adhesive tape.

### Adsorption of the Porphyrin Dyes

The nanoporous TiO<sub>2</sub> electrodes were immersed for 48 h in 1.0 × 10<sup>-4</sup> M solutions of MCTPyP and Zn-MCTPyP in DMF, or MCTPyPRu<sub>3</sub> and Zn-MCTPyPRu<sub>3</sub> solutions in 9:1 v/v acetone/ethanol mixture, washed with the respective solvents and dried in air. The surface coverage was estimated using two methods: a) from the direct measurement of the optical density of the electrodes using a clean TiO<sub>2</sub> electrode as reference; and b) from the absorbance difference (at the Soret band), before and after the adsorption process, in the porphyrin dye solution.

### Preparation of the Counter electrode

A drop of 0.05 mol L<sup>-1</sup> solution of H<sub>2</sub>PtCl<sub>6</sub> in isopropanol was spread on the surface of FTO glass pieces, dried and fired at 400 °C in air for 20 min.

### Assembly of solar cells

The nanoporous TiO<sub>2</sub> and Pt counter electrodes were assembled using a 40 μm thick hot melt spacer/sealing Surllyn frame to get the cells. The electrolyte solution (0.5 M *tert*-butylpyridine, 0.6 M tetrabutylammonium iodide, 0.1M LiI, 0.1M I<sub>2</sub> in methoxypropionitrile) was introduced through a drilled hole and then sealed with epoxy resin.

### Measurement of the photoelectrochemical properties

An Oriel Spectral Luminator was used as light source for the IPCE measurements, controlling the power delivered at cell position (1 and 2 mW cm<sup>-2</sup>) with a standard Si photodiode (1830-C Newport Optical Power Meter). The I-V curves were registered in an ABB class Oriel solar simulator (AM 1.5, IEC, JIS, ASTM) calibrated with a Si cell (VLSI standards, Oriel P/N 91150V) and interfaced to a computer-controlled Keithley 2400 instrument.

### Excited-state redox potentials in solution

Cyclic voltammetry experiments were performed with 1 × 10<sup>-3</sup> M porphyrin dye solutions in dry *N,N'*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (TBAClO<sub>4</sub>). A typical three electrodes cell consisting of a platinum disk working electrode, a platinum wire auxiliary electrode and an Ag/Ag<sup>+</sup> (0.010 M, in acetonitrile) reference electrode was used in all experiments. The zero-zero spectroscopic energies of supramolecular MCTPyPRu<sub>3</sub> and Zn-MCTPyPRu<sub>3</sub> dyes were estimated considering the average of the lowest energy UV-vis absorption band and the fluorescence band energy of the parent porphyrins and the [Ru(dmbpy)<sub>2</sub>Cl(py)]<sup>+</sup> complex.<sup>4</sup>

**Table 1. Ground and excited state redox potentials and zero-zero spectroscopic energies of the porphyrin dyes**

Porphyrin	E (S <sup>+</sup> /S)/ eV	E <sup>00</sup>	E( <sup>1</sup> Dye*/Dye <sup>+</sup> )/ eV
MCTPyP	1.27	1.91	-0.64
Zn-MCTPyP	1.04	1.98	-0.94
MCTPyPRu <sub>3</sub> <sup>a</sup>	1.25	1.91	-0.66
MCTPyPRu <sub>3</sub> <sup>b</sup>	0.84	2.13	-1.29
Zn-MCTPyPRu <sub>3</sub> <sup>a</sup>	1.01	1.98	-0.97
Zn-MCTPyPRu <sub>3</sub> <sup>b</sup>	0.81	2.13	-1.32

\*All potentials are given *versus* NHE. Values estimated for the <sup>a</sup>porphyrin and <sup>b</sup>ruthenium complex moiety.

### Summary of the solar cell parameters

**Table 2: DSSC parameters under Air Mass 1.5 calibrated white light source (100 mW cm<sup>-2</sup>).**

Porphyrin	Jsc (mA cm <sup>-2</sup> )	Voc (mV)	Fill Factor (%)	η (%)
MCTPyP	0.49	392	58	0.11
ZnMCTPyP	0.81	380	55	0.17
MCTPyPRu <sub>3</sub>	3.1	410	61	0.77
Zn-MCTPyPRu <sub>3</sub>	4.6	500	52	1.2

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