Supporting Information

Zhao et al. 10.1073/pnas.1118339109

SI Materials and Methods.

All chemicals were purchased from Aldrich, Alfa Aesar and Acros, and they were used without further purification. Solvents were obtained from EM Science, and they were used as received unless otherwise noted. Thin layer chromatography (TLC) was performed with silica gel coated glass plates from Analtech. Column chromatography, and it was carried out using Silicycle silica gel 60 with 230–400 mesh.

Spectroscopic Measurements. ^{1}H NMR spectra were recorded on a Varian spectrometer at 400 MHz or 500 MHz. NMR samples were prepared in deuterated solvents with tetramethylsilane as an internal reference using a Wilmad 528-PP 5 mm NMR tube. Mass spectra were obtained with a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF) using cyano-4-hydroxycinnamic acid (CCA) as a matrix. The reported mass is of the most abundant isotopic ratio observed.

Synthesis of the 3P-Ru Dye. This compound was synthesized in six steps as shown in Scheme S1.

Compound 1. 2-Acetylpyridine (12.1 g, 0.1 mol) was added to 150 mL MeOH with stirring followed by addition of 40 mL of 1 M NaOH. 4-bromobenzaldehyde (18.5 g, 0.1 mol) was added to the solution with stirring. After 1 h, the precipitate was collected and crystallized with MeOH. The yield was 38%.

Compound 2. α,β-unsaturated ketone 1 (15.89 g, 55.2 mmol) was added to a 500 mL round-bottom flask with stirring. Then, 15.89 g of 4 Å molecular sieves was added followed by 1.0 g of ytterbium (III) hexafluoroacetylacetonate and 223 mL of CH_2Cl_2. Finally, 10 g of ethyl vinyl ether (52.9 mL) was added to the solution. The mixture was allowed to react for 36 h, and the product was separated by extraction with ethyl acetate/H_2O. The yield was 91%.

Compound 3. Compound 2 (20.36 g, 58.8 mmol) and hydroxylamine hydrochloride (5.94 g, 58.8 mmol) were dissolved in CH_3CN with a final volume of 294 mL and refluxed overnight. The yield was 53%.

Compound 4. Compound 3 (3.11 g, 10 mmol), 579 mg of $Pd(PPh_3)_4$, 2.762 g diethyl phosphate, and 2.024 g of triethylamine (TEA) were added to a two-neck round-bottom flask with stirring. The solution was heated at 80 °C overnight under N_2. The solution was purified by chromatography (SiO_2, hexane/ethylacetate with 5% TEA). The yield was 97%.

Compound 5. Compound 4 (2.525 g, 2.2 mmol) and $RuCl_2$.4DMS complex (1.06 g, 2.2 mmol) were dissolved in 40 mL of 2-methoxyethanol. The mixture was refluxed overnight, and then it diluted with ether to precipitate the solid. The solid was washed with ether, and then it was separated by chromatography (SiO_2, CH_3CN/H_2O/saturated $KNO_3 = 3:6:1$). The first band was collected.

3P-Ru dye. Compound 5 was hydrolyzed by refluxing in 6 M HCl overnight. Upon cooling, the deeply colored precipitate was filtered and dried. The resulting chloride salt of the 3P-Ru dye was dissolved and refluxed in DI H_2O for 1 hr. Finally, the 3P-Ru dye was reprecipitated as the PF_6^- salt by treatment with NH_4PF_6 then filtered and dried. The yield was 90%.

Synthesis of the BIP Mediator. This synthesis was carried out in five steps.

1. *Synthesis of 3,5-di-tert-butyl-2-hydroxybenzaldehyde*. Commercially available 2,4-di-*tert*-butylphenol (10.0 g, 48.5 mmol, 1 equiv.) and hexamethylenetetramine (13.6 g, 97.0 mmol, 2 equiv.) were dissolved in trifluoroacetic acid (40 mL), and the mixture was heated at reflux for 6 h. The reaction was quenched while hot with a 33% (vol/vol) aqueous H_2SO_4 solution (40 mL). The resulting mixture was allowed to cool to room temperature while stirring. The crude product was extracted with diethyl ether (3 × 50 mL), and the extract was neutralized with a saturated aqueous solution of sodium bicarbonate (2 × 100 mL), then washed with water (3 × 100 mL). The organic phase was dried over sodium sulfate, filtered through paper, and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using hexanes/EtOAc (9:1, v/v) as the eluent to afford the title compound as a colorless solid in a 35% yield (4.0 g,). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 11.65 (s, 1H, OH); 9.86 (s, 1H, CHO); 7.60 (d, $J = 1.7$ Hz, 1H, H_6); 7.36 (d, $J = 1.7$ Hz, 1H, H_4); 1.46 (s, 9H, Bu_t); 1.36 (s, 9H, Bu_t). ^{13}C NMR (400 MHz, $CDCl_3$, δ ppm): 191.5; 154.8; 138.4; 138.1; 131.2; 128.3; 123.9; 34.5; 31.2; 31.0. MALDI-TOF (positive mode, cyano-4-hydroxycinnamic acid as matrix): m/z 235.04 $(M + H)^+$ (100 %), calculated 234.20 for $C_{15}H_{22}O_2$.
2. *Synthesis of 2-(3′,5′-di-tert-butyl-2′hydroxyphenyl)-5-carbomethoxybenzimidazole*. Phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate (1.5 g, 6.41 mmol) in nitrobenzene (10 mL) was added dropwise to a suspension of methyl 3,4-diaminobenzoate (1.06 g, 6.41 mmol) in nitrobenzene (10 mL). The mixture was heated at reflux (210 °C) in a sand bath for 12 h under an inert atmosphere. After cooling, and without any workup, the crude mixture was applied to a chromatography column (SiO_2, in hexanes) and nitrobenzene was eluted with a mixture of hexanes/ethyl acetate (95:15, v/v). The target compound was then eluted with a hexanes/ethyl acetate (85:15, vol/vol) mixture as a light orange solid (2.18 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), two tautomers: 13.42 (br, 1H, OH); 11.03 (s, 0.5 H, NH); 10.86 (s, 0.5 H, NH); 8.41 (s, 0.5 H, H_4); 8.13 (s, 0.5 H, H_4); 7.97 (d, $J = 8.0$ Hz, 0.5 H, H_6); 7.92 (d, $J = 8.0$ Hz, 0.5 H, H_6); 7.68 (d, $J = 8.0$ Hz, 0.5 H, H_7); 7.64 (s, 0.5 H, $H_{6'}$); 7.59 (s, 0.5 H, $H_{6'}$); 7.48 (s, 1 H, $H_{4'}$); 7.29 (d, $J = 8.0$ Hz, 0.5 H, H_7); 3.96 and 3.89 (s, 3H, $COOCH_3$); 1.54 (s, 9H, Bu_t); 1.34 and 1.27 (s, 9H, Bu_t). MALDI-TOF (positive mode, cyano-4-hydroxycinnamic acid as matrix): m/z 381.21 $(M + H)^+$ (100 %), calculated 380.20 for $C_{23}H_{28}N_2O_3$.
3. *Synthesis of 2-(3′,5′-di-tert-butyl-2′-hydroxyphenyl)-5-methylhydroxybenzimidazole*. *Note*: For this reaction, tetrahydrofuran was freshly distilled from sodium/benzophenone. Sodium and lithium aluminum hydride are highly flammable and react violently with water. The authors strongly recommend the use of appropriate protective equipment while performing the protocol described in the following.
A solution of 5-carboxymethoxy-2-(3′,5′-di-*tert*-butyl-2′-hydroxyphenyl)benzimidazole (2.00 g, 5.26 mmol) in tetrahydrofuran (25 mL) was added dropwise over a period of ten min to a cooled suspension (ethanol/liquid nitrogen bath, −78 °C) of lithium aluminum hydride (4.00 g, 10.52 mmol) in tetrahydrofuran (25 mL). Upon completion of the addition, the mixture was allowed to warm to room temperature and stirred for 3 h. The reaction flask was then cooled back to −78 °C and

quenched with the dropwise addition of ethanol (25 mL) followed by dropwise addition of water (5 mL). The mixture was allowed to warm to ambient temperature and then filtered through paper, and the solvents were evaporated under reduced pressure. The crude product was dissolved in ether (100 mL) and washed with water (3 × 50 mL). The organic layer was dried over sodium sulfate, filtered through paper, and concentrated under reduced pressure. The residue was recrystallized from dichloromethane/hexanes to yield the target compound as a white solid in 97 % yield (1.8 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), two tautomers: 13.41 (brs, 1H, OH); 9.61 (brs, 0.5 H, NH); 9.45 (brs, 0.5 H, NH); 7.71 (brs, 0.5 H, H_4); 7.68 (s, 0.5 H, H_4); 7.52 (d, $J = 8.6$ Hz, 0.5 H, H_6); 7.48-7.44 (m, 1.5 H, $H_{4'}$ and H_6); 7.43 (brd, $J = 2.0$ Hz, 0.5 H, $H_{6'}$); 7.40 (brd, $J = 2.0$ Hz, 0.5 H, $H_{6'}$); 7.31 (brd, $J = 8.6$ Hz, 0.5 H, H_7); 7.28 (brd, $J = 8.6$ Hz, 0.5 H, H_7); 4.21 (s, 2H, CH_2OH); 1.51 (s, 9H, Bu_t); 1.38 and 1.30 (s, 9H, Bu_t). MALDI-TOF (positive mode, cyano-4-hydroxycinnamic acid as the matrix): m/z 353.22 $(M + H)^+$ (100%), calculated 352.20 for $C_{22}H_{28}N_2O_2$.

4. *Synthesis of 2-(3′,5′-di-tert-butyl-2′-hydroxyphenyl)-5-formylbenzimidazole*. Activated manganese dioxide (3.58 g, 41.25 mmol) was added to a solution of 2-(3′,5′-di-*tert*-butyl-2′-hydroxyphenyl)-5-methylhydroxybenzimidazole (1.45 g, 4.12 mmol) in dichloromethane (150 mL). The mixture was stirred for 5 h at room temperature. The crude suspension was filtered through paper, and then it was concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using a mixture of hexanes/ethyl acetate (90:10, vol/vol) as eluent to afford the title compound as a light yellow solid in 85% yield (1.22 g). NMR (400 MHz, $CDCl_3$, δ ppm): 13.30 (brs, 0.5 H, OH); 13.19 (brs, 0.5 H, OH); 11.00 (brs, 0.5 H, NH); 10.80 (brs, 0.5 H, NH); 10.06 (s, 1 H CHO); 8.21 (d, $J = 8.4$ Hz, 1 H, H_6); 7.81 (s, 2H, H_4 and $H_{6'}$); 7.66 (d, $J = 8.4$ Hz, 1 H, H_7); 7.50 (s, 1 H, $H_{4'}$); 1.51 (s, 9H, Bu_t); 1.36 (s, 9H, Bu_t). MALDI-TOF (positive mode, cyano-4-hydroxycinnamic acid as matrix): m/z 351.32 $(M + H)^+$ (100%), calculated 350.20 for $C_{22}H_{26}N_2O_2$.

5. *Synthesis of diethyl 2-((2-(3,5-di-tert-butyl-2-hydroxyphenyl)-1H-benzo[d]imidazol-5-yl)methylene)malonate*. To a solution of 2-(3′,5′-di-*tert*-butyl-2′-hydroxyphenyl)-5-formylbenzimidazole (1.02 g, 2.92 mmol) in toluene (250 mL) was added diethyl malonate (1.168 g, 1.17 mL, 7.30 mmol), piperidine (0.297 g, 0.35 mL, 3.50 mmol), and acetic acid (0.183 g, 0.175 mL, 3.50 mmol). The reaction mixture was heated at reflux with a Dean-Stark distilling trap for 24 h. The reaction mixture was concentrated under reduced pressure, and the final purification was achieved by column chromatography (SiO_2) using a mixture of hexanes/ethyl acetate (90:10, v/v) as eluent to afford the title compound as a yellow solid in 72% yield (1.09 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm), two tautomers: 13.28 (s, 1H, OH); 10.32 (s, 0.5 H, NH); 10.27 (s, 0.5 H, NH); 7.74 (s, 0.5 H, ArH); 7.70 (s, 0.5 H, ArH); 7.65 (s, 0.5H, ArH); 7.49 (d, $J = 8.0$ Hz, 0.5 H, ArH); 7.43 (m, 1 H, ArH); 7.38 (m, 1 H, ArH); 7.31 (s, 0.5 H, ArH); 7.17 (m, 1 H, ArH); 7.12 (d, 0.5 H, ArH) 4.31 (m, 2H, CH_2); 4.21 (m, 2H, CH_2); 1.54 (s, 9H, Bu_t); 1.29 (s, 9H, Bu_t); 1.20 (m, 6H, CH_2). MALDI-TOF (positive mode, cyano-4-hydroxycinnamic acid as matrix): m/z 493.19 $(M + H)^+$ (100%), calculated 492.3 for $C_{29}H_{36}N_2O_5$.

1. Lee S-HA, et al. (2012) Electron transfer kinetics in water splitting dye-sensitized solar cells based on core-shell oxide electrodes. *Faraday Discuss* 155:165–176.

Synthesis of 2-((2-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-5-yl-methylene)malonic Acid. Starting material diethyl 2-((2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-5-yl) methylene)malonate (0.150 g, 0.32 mmol) was dissolved in 30 mL of tetrahydrofuran, and 15 mL of a 10% NaOH aqueous solution (w/w) was added. The reaction mixture was heated at reflux for 12 h. After cooling, the crude mixture was neutralized with concentrated HCl, and the remaining THF was evaporated under reduced pressure. The resulting yellow precipitate was extracted with ethyl acetate (3 × 15 mL), and the organic layer was washed with water (3 × 150 mL), dried over magnesium sulfate, filtered through paper, and concentrated under reduced pressure. Recrystallization from ethyl acetate/hexanes afforded the title compound as a yellow solid in 98% yield (0.145 g). ^{1}H NMR (400 MHz, CD_3OD δ ppm): 7.91 (s, 1 H, CH = C); 7.81 (s, 1 H, H_4); 7.79 (d, $J = 2.6$ Hz, 1 H, $H_{6'}$); 7.62 (d, $J = 8.6$ Hz, 1 H, H_6); 7.51 (d, $J = 8.6$ Hz, 1 H, H_7); 7.45 (d, $J = 2.6$ Hz, 1 H, $H_{4'}$); 4.92 (brs, residual water from the deuterated solvent); 3.31 (s, residual MeOH from the deuterated solvent); 1.48 (s, 9H, Bu_t); 1.1.37 (s, 9H, Bu_t); MALDI-TOF (positive mode, cyano-4-hydroxycinnamic acid as matrix): m/z 437.49 $(M + H)^+$ (100%), calculated 436.2 for $C_{25}H_{28}N_2O_5$.

Electrochemical Characterization of the BIP Mediator. Electrochemical characterization of the ester form of the benzimidazole-phenol mediator was carried out using a CH Instruments 760D potentiostat with corresponding software. The cyclic voltammetry experiments were done using a glass cell with Teflon top under an Argon atmosphere. A three-electrode setup comprised of a glassy carbon-disc working electrode, platinum mesh counter electrode, and a silver quasi reference was used. The sample was dissolved in distilled acetonitrile at a concentration of 0.6 mM with 100 mM tetrabutylammonium hexafluorophosphate as supporting electrolyte. The silver quasi reference was calibrated using the ferrocenium/ferrocene (Fc^+/Fc) couple with Fc^+/Fc = 0.45 V vs. SCE. All scans were taken at 100 mV s^{-1}.

Electrochemical Determination of Current Efficiency. Following a previously reported procedure (1), a pseudo Clark electrode was held in close proximity to the TiO_2 electrode to collect photoelectrochemically generated oxygen. An 80% collection efficiency Pt electrode was calibrated at −490 mV vs. Ag/AgCl (this potential was chosen to maximize the oxygen collection efficiency while minimizing the current from hydrogen evolution) to reduce the oxygen generated from a facing Pt electrode held at +1200 mV vs. Ag/AgCl. The measurements were taken in 37.5 mM Na_2SiF_6-$NaHCO_3$ (1:1.5) silicate buffer (pH 5.8) containing 0.1 M $LiClO_4$ as the supporting electrolyte under a blanket of Ar gas. The calibrated collecting electrode was then assembled with the photoelectrode, in the same configuration as the Pt generator electrode, and then it was connected to the bipotentiostat. The photoelectrode and Pt collector electrode were held at 0 mV and −490 mV vs Ag/AgCl, respectively. The Faradaic efficiency of oxygen generation was calculated to be 87% and 86% for 3P-Ru dye +**1**-$IrO_x \cdot nH_2O$ (Fig. S2-*A*) and 3P-Ru dye +**2**-$IrO_x \cdot nH_2O$ (Fig. S2*B*), respectively.

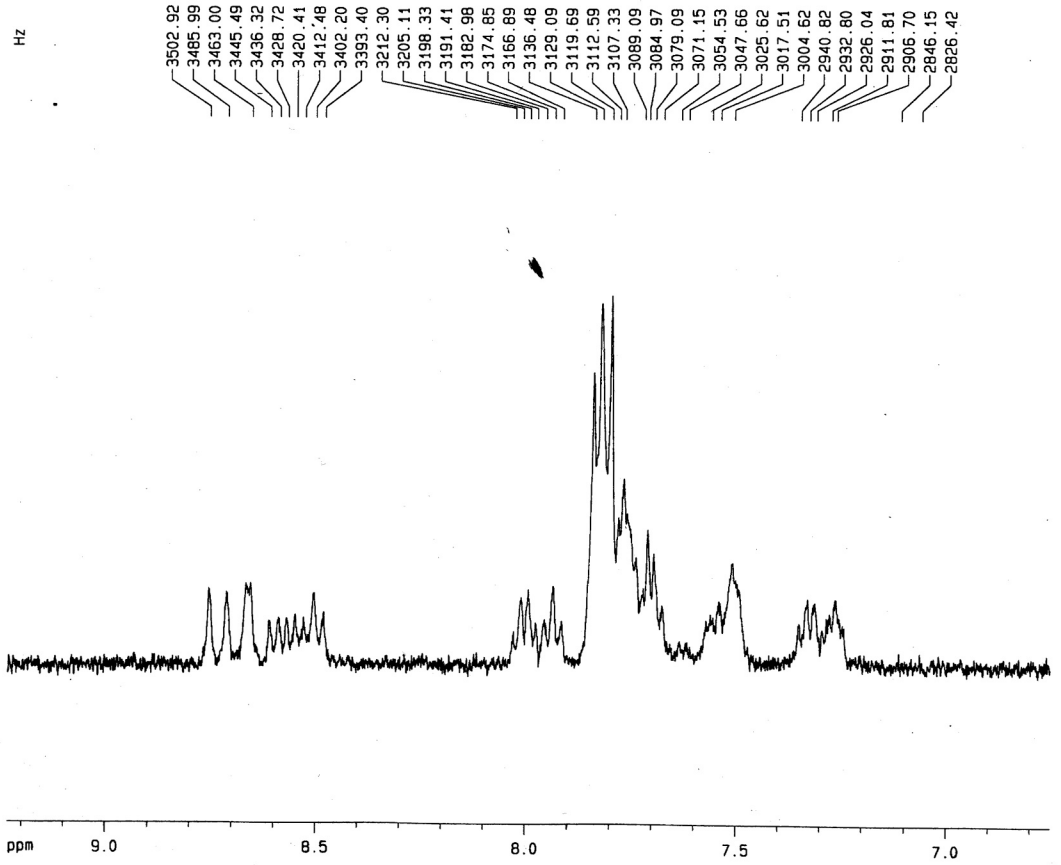


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Fig. S1. ^{1}H NMR spectrum of 3P-Ru.

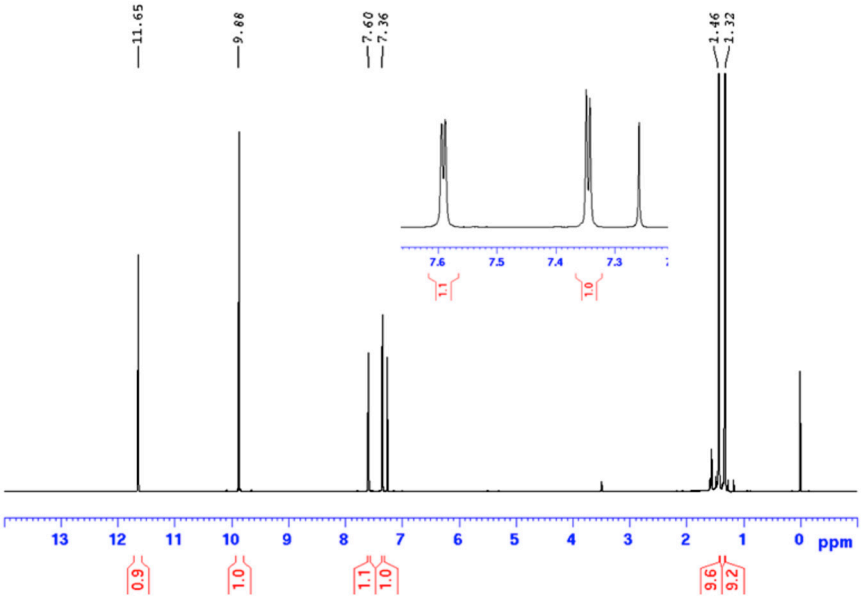


Fig. S2. ^{1}H NMR spectrum of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 400 MHz, $CDCl_3$, 25 °C.

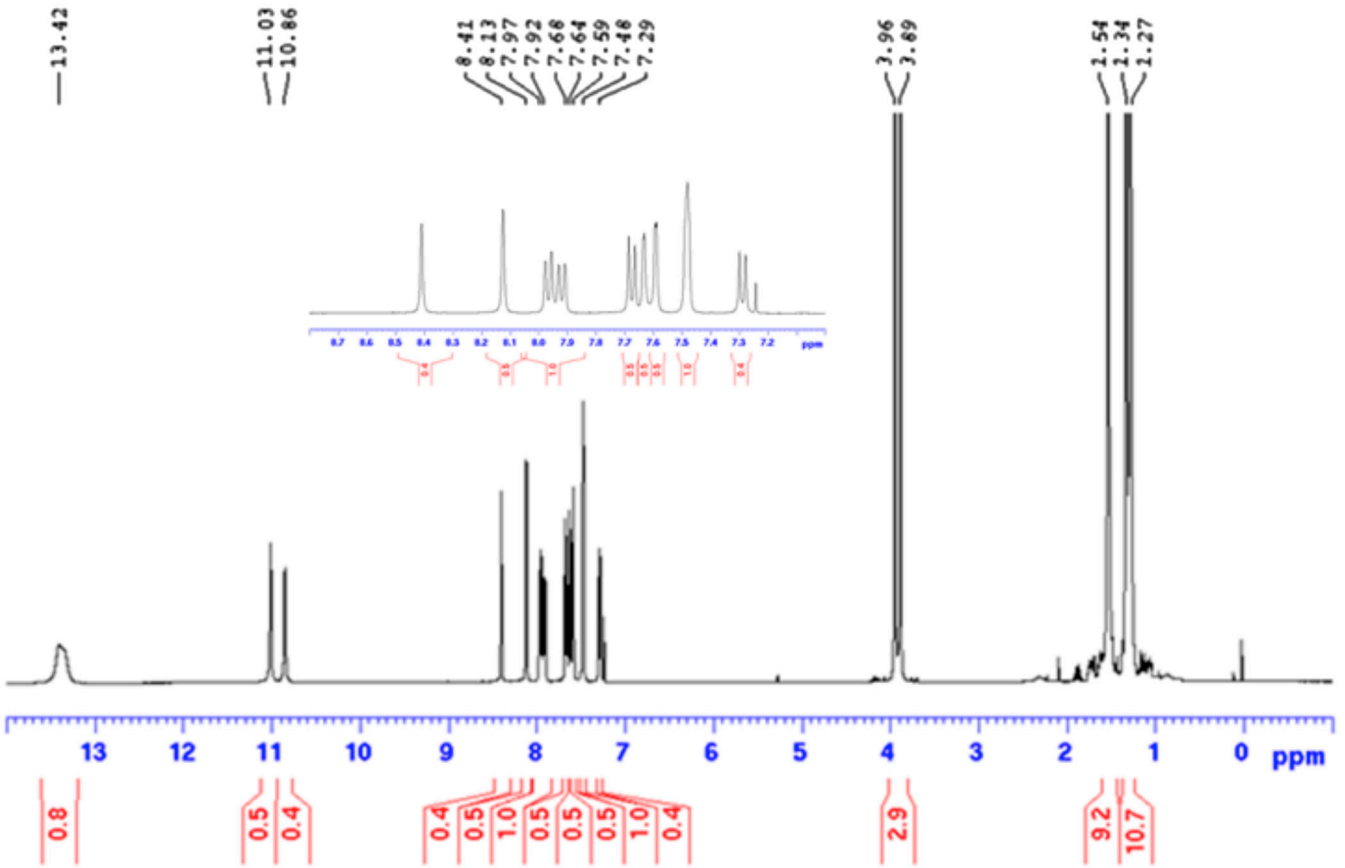


Fig. S3. ^{1}H NMR spectrum of 2-(3′,5′-di-*tert*-butyl-2′hydroxyphenyl)-5-carbomethoxybenzimidazole, 400 MHz, $CDCl_3$, 25 °C.

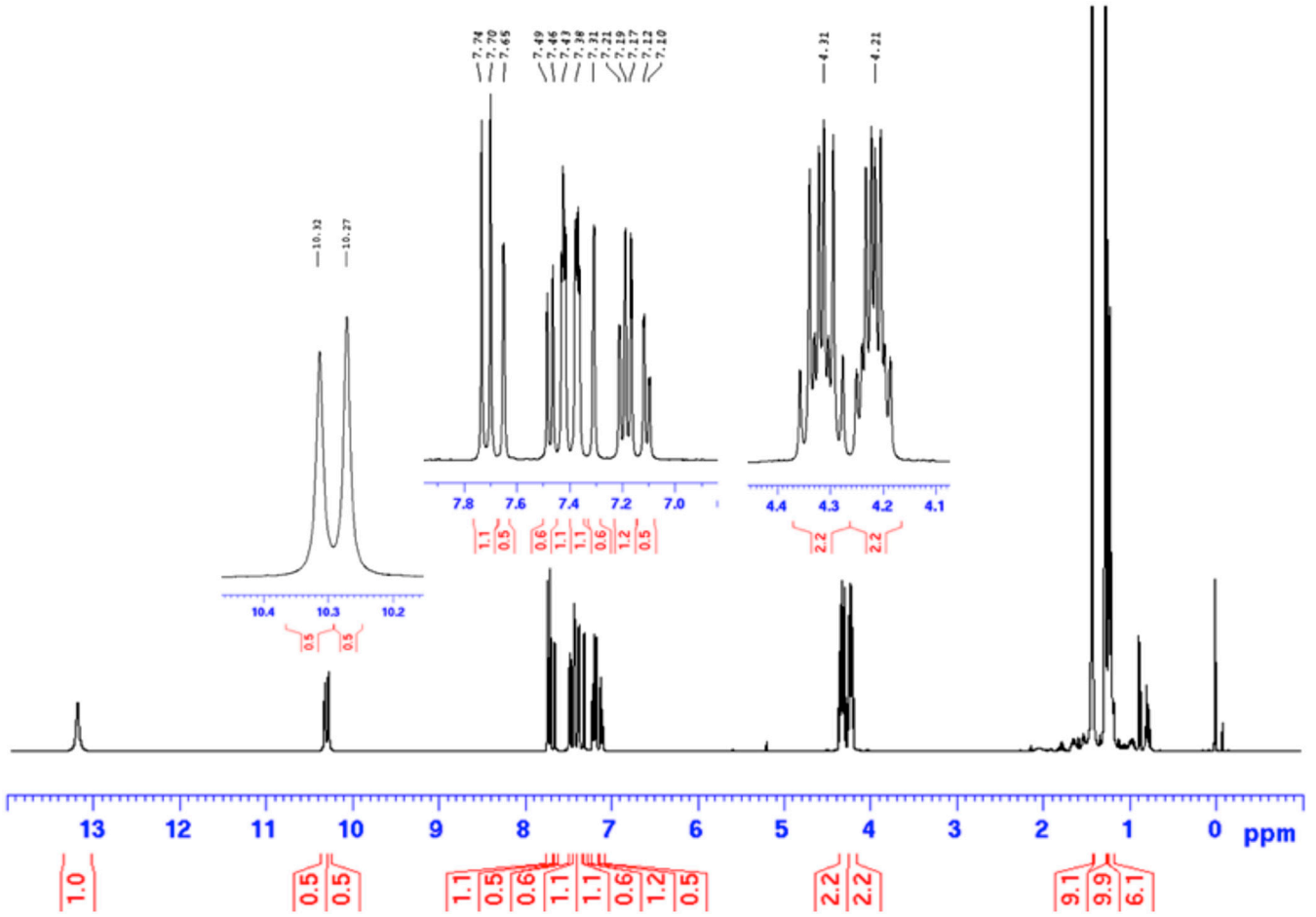


Fig. S4. ^{1}H NMR spectrum of the target compound, 400 MHz, $CDCl_3$, 25 °C.

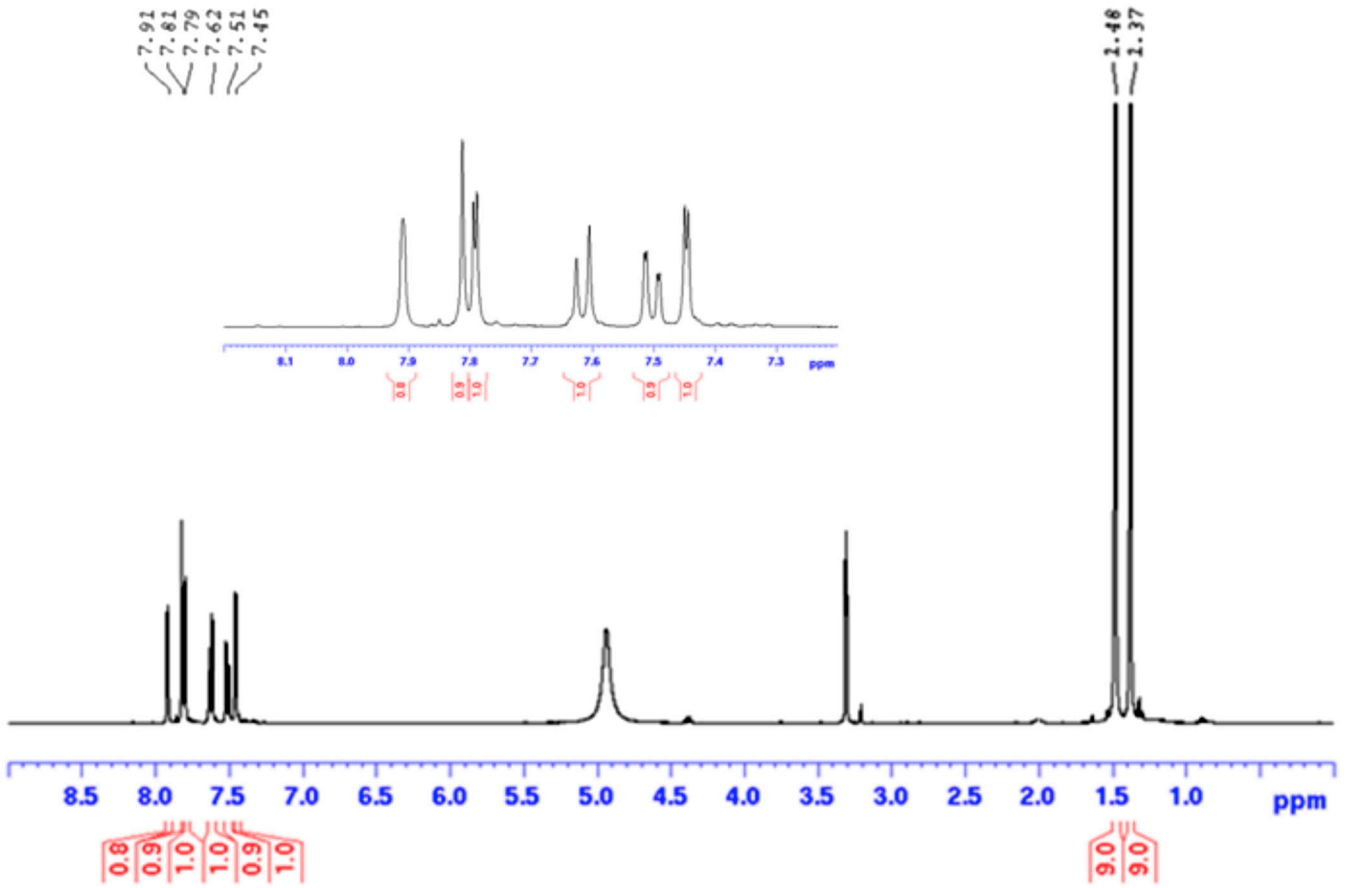


Fig. S5. ^{1}H NMR spectrum of the target compound, 400 MHz, CD_3OD, 25 °C.

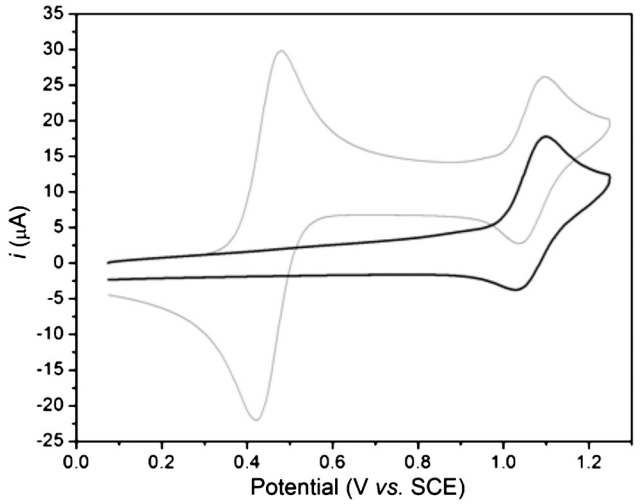


Fig. S6. Cyclic voltammograms showing the first oxidation of benzimidazole-phenol mediator (black) and a scan, after the addition of ferrocene (gray). The midpoint potential for the oxidation of the benzimidazole-phenol occurs at 1.06 V vs. SCE with a peak separation of 70 mV.

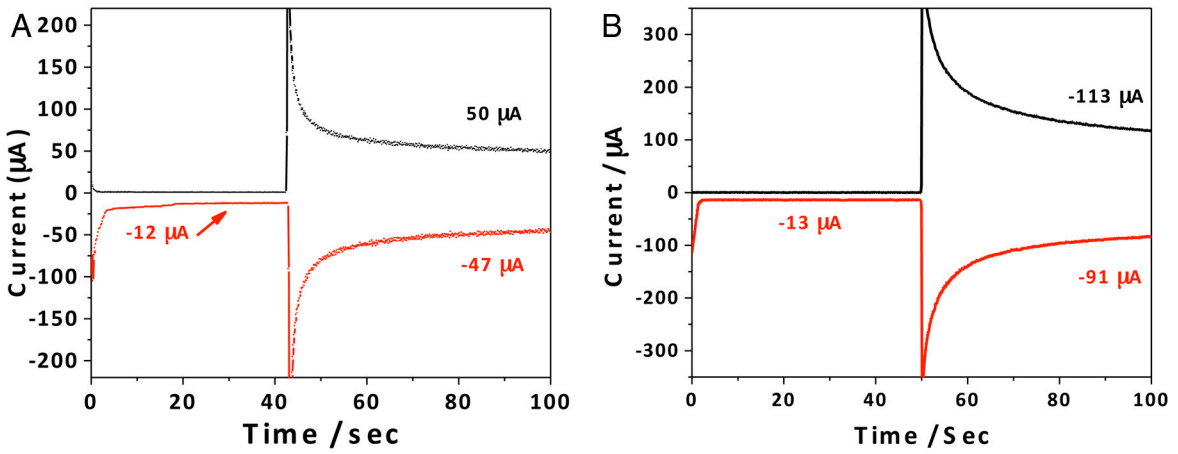
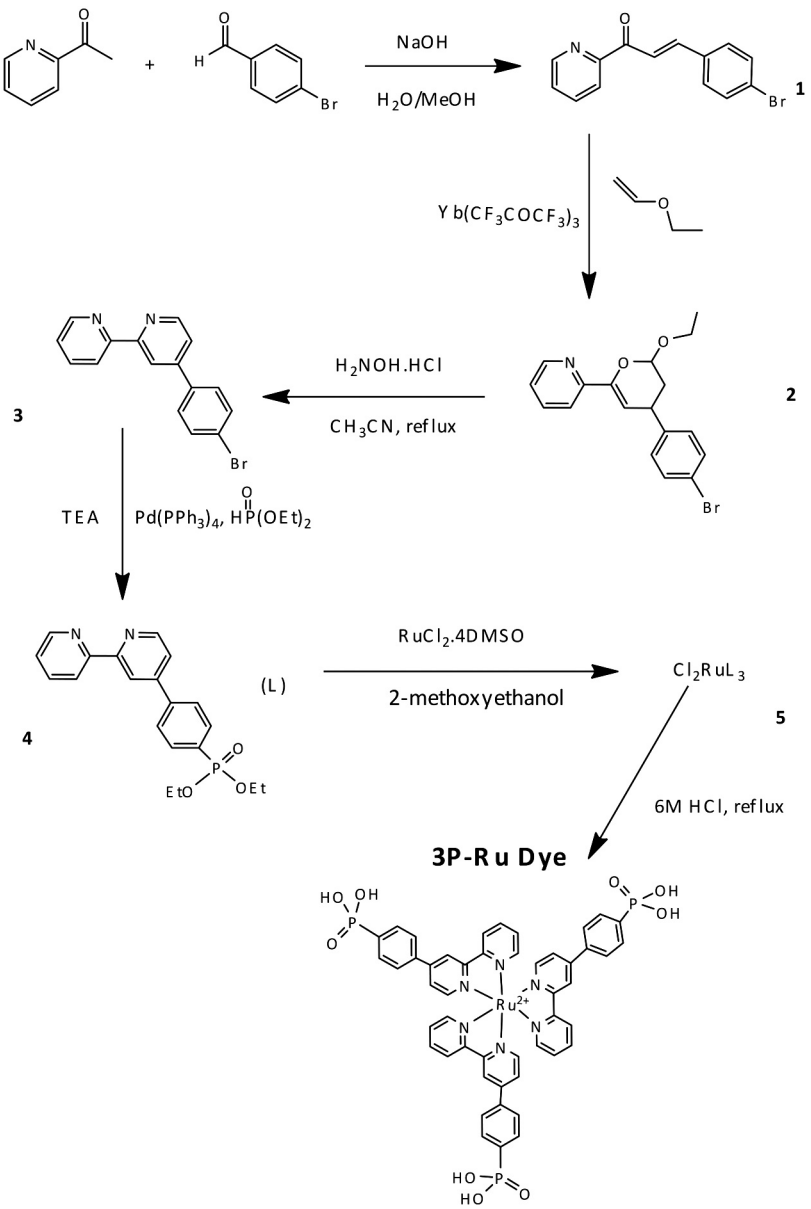


Fig. S7. Generator-collector current measurements with illuminated $TiCl_4$-treated TiO_2 photoelectrodes sensitized by (*A*) 3P-Ru dye +**1**-$IrO_x \cdot nH_2O$ nanoparticles (2.3 cm^2) and (*B*) 3P-Ru dye +2-$IrO_x \cdot nH_2O$ nanoparticles (1.8 cm^2) at 0 mV vs. Ag/AgCl, with the Pt collector electrode at −490 mV vs. Ag/AgCl.



Scheme S1. Synthesis of 3P-Ru dye.