Supporting Information

Polypyridyl Complexes as Electron Transporting Materials for Inverted Bulk Heterojunction Solar Cells: The Metal Center Effect

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EXPERIMENTAL SECTION

Materials and Methods. Complexes 1-Ru, 2-Os, and 3-Fe were prepared according to published procedures.^{S1-S3} UV/Vis spectroscopy was carried out on guartz substrates using a Cary 100 spectrophotometer. Thicknesses were determined on silicon substrates by spectroscopic ellipsometry with an M-2000V variable angle instrument (J. A. Woollam Co., Inc.) with VASE32 software. Root mean square roughness ($R_{\rm rms}$) values were measured with Atomic force microscopy (AFM) using a Bruker multimode atomic force microscope, operating in a semicontact mode. Electrochemical measurements (i.e., cyclic voltammetry) were performed using a CHI660A potentiostat. The electrochemical measurements were performed in a three-electrode cell configuration consisting of a functionalized ITO substrate, Pt wire, and Ag wire as working, counter, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M) in CH₃CN was used as the supporting electrolyte. All measurements were carried out at room temperature. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal standard and was assigned an absolute energy level of -4.8 eV vs vacuum.^{S4} The corresponding HOMO energy levels were determined by eq. 1 (E_{0x}^{onset} = onset oxidation potential vs. Fc/Fc⁺, $E_{1/2}^{Fc} = 0.4 \text{ V}$). The optical band gap was calculated from the optical absorption spectra (the onset of the metal-to-ligand charge transfer (MLCT) bands of the monolayers). The LUMO energy levels were determined by eq 2 (E_g = optical band gap) (Table S1).

$$E_{HOMO} = (E_{Ox}^{\text{onset}} - E_{1/2}^{\text{Fc}}) + 4.8 \ (eV) \tag{1}$$

$$E_{LUMO} = E_{HOMO} - E_g (eV) \tag{2}$$

The surface coverage was calculated according to eq. 3 (A = maximal absorption intensity; ε = molar extinction coefficient).

$$\Gamma = \frac{A \cdot N_A \cdot 10^{-3}}{\varepsilon} \tag{3}$$

UPS measurements were carried out with a Kratos AXIS ULTRA system using a concentric hemispherical analyzer for photo-excited electron detection. UPS was measured with a helium discharge lamp, using He(I) (21.22 eV) and He(II) (40.8 eV) radiation lines.⁸⁵ The energy scale was referenced to the Fermi level measured on a bare Au substrate.^{86,87} The vacuum level was obtained from the secondary-electron cutoff (photoemission onset) measured in the low kinetic energy region of the He(I) spectra.^{86,87} Total energy resolution was less than 100 meV, as determined from the Fermi edge of an Au reference sample.

Self Assembled Monolayers (SAM) Formation. 15 mm \times 15 mm ITO-coated glass sheets (10 Ohm/sq, Kintec) were successively cleaned in acetone and isopropanol in an ultrasonic bath and exposed to UV-ozone for 30 min. Si and quartz slides were cleaned, and the SAMs were prepared according to published procedures.^{S1-S3}

Inverted OPV Device Fabrication. The photoactive blend was spun-cast on top of the SAM: (*i*) a P3HT/[60]PCBM mixture solution with a P3HT (4002-E, Rieke Metals) concentration of 15 mg/mL and [60]PCBM (99.5%, Nano-C) of 12 mg/mL in anhydrous chlorobenzene+4% v/v 1-chloronaphthalene; (*ii*) a P3HT/ICBA mixture solution with a

P3HT (4002-E, Rieke Metals) concentration of 20 mg/mL and ICBA (Nano-C) of 20 mg/mL in anhydrous chlorobenzene+4% v/v 1-chloronaphthalene; and (iii) a PTB7/[70]PCBM mixture solution with PTB7 (1-materials) concentration of 10 mg/mL and [70]PCBM (Nano-C) of 15 mg/mL in anhydrous chlorobenzene+3% v/v 1,8-diiodooctane. The solutions were stirred on a hot plate for 1 h before spin-coating at (i) 1000 rpm for 40 s, (ii) 800 rpm for 50 s, or (iii) 800 rpm for 60 s with a final film thickness of ~130 nm, ~210 nm and ~100 nm, respectively. The P3HT/[60]PCBM and P3HT/ICBA samples were then annealed on a hot plate at 120 °C for 10 min. in a glove box. The samples were then transferred into a vacuum chamber for MoO₃/Ag deposition by thermal-evaporation. At a pressure of $\sim 10^{-6}$ Torr, 8 nm of MoO₃ were deposited at 1 Å/s, followed by 120 nm of Ag deposited at 4-6 Å/s. MoO₃ powder (99.99% trace metals basis) and Ag slugs (99.999% trace metals basis) were purchased from Sigma-Aldrich. The device area was defined by the shadow mask used in the electrode deposition of 9.6 mm². The OPV devices were encapsulated with a cover glass using UV curable epoxy (Epoxy Technology, OG112-6) inside a glove box before exposing to air for measurement.

Inverted OPV Device Characterization. The current density-voltage (*J-V*) curves were obtained using a Keithley 2400 source-measure unit controlled by a Labview program. The photocurrent was measured under simulated AM1.5G irradiation (100 mW cm⁻²) using a xenon-lamp-based solar simulator (Newport 91160A 300W Class-A Solar Simulator, 2 inch \times 2 inch uniform beam) with an air mass 1.5 global filter. The light intensity was set using a NREL calibrated silicon photodiode with a KG3 color filter. External quantum efficiency (EQE) was measured using Newport's QE setup. Incident light from a xenon lamp (300 W) passing through a monochromator (Newport, Cornerstone 260) was focused on the active

area of the cell. The output current was measured using a current pre-amplifier (Newport, 70710QE) and a lock-in amplifier (Newport, 70105 Dual channel Merlin). A calibrated silicon diode (Newport 70356) was used as a reference. EQE data was integrated with ASTM G173 global reference spectrum to get the calculated J_{sc} .



Fig. S1 Ruthenium (1-Ru), osmium (2-Os), and iron (3-Fe) complexes used for the fabrication of the self-assembled monolayers (SAMs).



Fig. S2 Representative cyclic voltammograms of the following self assembled monolayers (SAMs) vs. Fc/Fc^+ : (a) **SAM1-Ru**, (b) **SAM2-Os**, and (c) **SAM3-Fe**. The measurements were carried out at room temperature in 0.1 M TBAPF₆/CH₃CN. ITO-coated glass, Pt wire, and Ag wire were used as working, counter, and reference electrodes, respectively.



Fig. S3 Dark *J-V* characteristics of inverted BHJ solar cells with the following photo-active blends: P3HT:[60]PCBM (blue), P3HT:ICBA (purple), and PTB7:[70]PCBM (black), deposited on a bare ITO.

References

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