Conjugated Polymers Bearing Iridium Complexes for Triplet Photovoltaic Devices

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The aim of this work is to investigate the effect of incorporating an iridium complex into a π-conjugated polymer backbone on photovoltaic properties such as charge generation, power conversion efficiency and external quantum efficiency (EQE). Poly(9,9-dihexylfluorene-co-2-phenylpyridine) (**1**) and poly(9,9-dioctylfluorene-co-tris(2-phenylpyridine) iridium (III))) (**2**) were synthesized using Suzuki polycondensation. Characterization was performed using NMR, UV−vis, photoluminescence, and time-resolved luminescence spectroscopy; gel permeation chromatography; elemental analysis; and photovoltaic devices. An increase in percent EQE for **2** over **1**, from 1.1 to 10.3, is attributed to the formation of the triplet state in (**2**), and by inference, longer diffusion lengths of the triplet exciton, compared to the singlet exciton that is formed in (**1**).

Introduction

The use of conjugated polymers as active materials in solar cells is an area of increasing interest.[1] This interest is motivated, in part, by their solution processability and low fabrication costs. An efficiency-limiting process in organic photovoltaic (PV) devices is the small diffusion length of the singlet exciton, which is determined by its mobility and lifetime. Hence much research is devoted to the formation of nanophase binary morphologies of donor (D) and acceptor (A) so that the singlet exciton has only to travel a short distant (tens of nm) to a D/A interface; the negative consequence is that electron and hole transport are compromised. A solution to this dilemma might be found with the formation of triplet excitons. Triplet excited states possess inherently longer lifetimes and triplet excitons are expected to possess longer diffusion lengths, thereby increasing the percentage of excitons that reach a donor/acceptor interface, i.e., increasing the efficiency of charge generation.

As part of the body of work on triplet-forming materials for PV devices, Köhler et al.[2] describe the photophysics of an organometallic polymer, Pt-poly yne blended with C_{60}, reporting that electron transfer occurs from the Pt-poly yne to C_{60} via triplet excitons. PV devices give external quantum efficiencies (EQE) up to 1.6% under monochromatic illumination. Shao et al.[3] report the performance of a bilayer device using 2,3,7,8,12,13,17,18-octaethyl-21H,23H-phorphineplatinum(II) (PtOEP) and C_{60} as the electron donor and acceptor, respectively. They report power conversion efficiencies (PCE) of 1.2%. Guo et al. report that photoinduced charge transfer from Pt-acetylide to C_{60} occurs via the triplet excited state (EQE = 9%, PCE = 0.27%),[4] as does photoinduced charge transfer in Pt acetylide triads end-capped with fullerene (EQE = 22%, PCE = 0.05%).[5] Yang et al. studied poly(fluorene) (PF) and poly(thiophene) (P3HT) blended with molecular Ir(mppy)$_3$ using CdSe as an acceptor,[6] and demonstrate an increase in the triplet exciton population, attributed to the increased rate of intersystem crossing (ISC) from the PF singlet state to the triplet state. The short-circuit photocurrent subsequently doubled and the open circuit voltage (V_{oc}) increased by 50% upon addition of the phosphor.

Blends of polymers and small molecules generally suffer from gross phase segregation, if not initially, then over a period of time;[7] however, this may be mitigated by chemically attaching the small molecule to the polymer backbone. This paper examines the effect of tethering an Ir complex to the main chain of a conjugated polymer; its role in enhancing triplet formation (as evidence by increased phosphorescence); and its effect on charge generation in photovoltaic devices by giving rise to longer lived excited states and longer exciton diffusion lengths. The work distinguishes itself from other reports in the field in that it is the first photovoltaic study where Ir complexes are covalently incorporated into a conjugated polymer.

Experimental Section

Materials and Chemicals. 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate), 9,9-dihexyl-2,7-dibromofluorene, 9,9-dioctyllfluorene-

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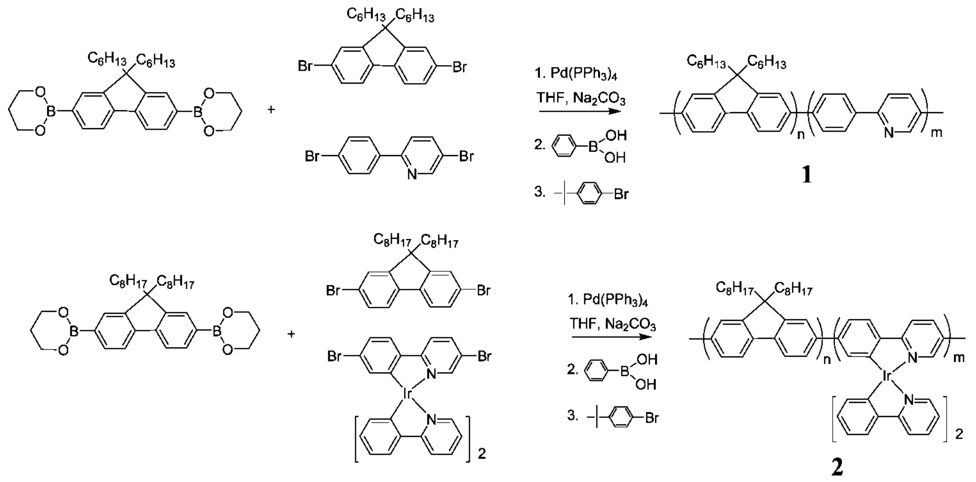
Scheme 1. Synthesis of 1 and 2



2,7-bis(trimethyleneborate), 9,9-dioctyl-2,7-dibromofluorene, 2,5-dibromopyridine, 4-bromophenylboronic acid, phenyl boronic acid, 2,5-dibromobenzene, 2-phenylpyridine, tetrakis(triphenylphosphine)-palladium ($Pd(PPh_3)_4$), iridium(III) chloride trihydrate, and iridium(III) acetylacetonate were purchased from either Aldrich or Strem. THF, ether, and chlorobenzene were dried and freshly distilled before use. Poly(styrene sulfonic acid)-doped poly(ethylenedioxythiophene) (PEDOT:PSS, Baytron VP Al 4063) was purchased from Bayer. PCBM was purchased from American Dye Source.

Poly(9,9-dihexylfluorene-co-2-phenylpyridine) (1). **1** was synthesized via Suzuki polycondensation according to Scheme 1.[16] 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) (0.324 g, 0.64 mmol), 9,9-dihexyl-2,7-dibromofluorene (0.159, 0.32 mmol), and 5-bromo-2-(4-bromophenyl)pyridine) (0.102 g, 0.32 mmol) were dissolved in THF (12.5 mL, deoxygenated), to which a solution of K_2CO_3 (2 M, 2 mL) was added, together with $Pd(PPh_3)_4$ (0.022 g, 3 mol % based on fluorene). The resulting mixture was sealed in a glass vial and heated for 2 days at 80 °C in an oil bath. End capping of the polymer was carried out as the last step in synthesis. Phenyl boronic acid (0.0039 g, 5 mol %) was added and the solution was heated (80 °C, 12 h). This was followed by the addition of bromobenzene (0.0067 g, 5 mol %) at the same temperature. Once cooled to room temperature, THF was removed and the residue dissolved in chloroform. This was followed by washing with water (3 times) and drying over anhydrous magnesium sulfate. After filtration, the volume of chloroform was reduced and the concentrated solution was passed through an alumina column. The volume of the resulting solution was again reduced and precipitated in methanol (~50 mL) to yield **1** (0.386 g, 68%). A weight average molecular weight (M_w) of 32 700 Daltons and a PDI of 2.0 was obtained. δ_H (600 MHz, $CDCl_3$, Me_4Si) 9.1 (1H, s), 8.20−7.75 (29 H, m), 2.13 (12 H, br. β-CH_2), 1.15−0.78 (66 H, m, CH_2 and CH_3). δ_C (150 MHz, $CDCl_3$, Me_4Si) 155.50, 152.13, 148.30, 140.52, 140.02, 135.10, 128.82, 127.58, 127.23, 126.18, 121.53, 120.27, 120.01 (aromatic) 55.35 (C_9-fluorene ring) 40.38, 31.49, 29.72, 23.86, 22.59, 14.06 (aliphatic). Anal. Calcd for $C_{86}H_{103}N$: C, 89.8; H, 9.0; N, 1.2. Found: C, 87.8; H, 9.0; N, 0.7.

Poly(9,9-dioctylfluorene-co-tris(2-phenylpyridine) Iridium-(III)) (2). was synthesized via Suzuki polycondensation according to Scheme 1.[15] 9,9-Dioctyllfluorene-2,7-bis(trimethyleneborate) (0.178 g, 0.32 mmol), 9,9-dioctyl-2,7-dibromofluorene (0.88, 0.16 mmol), and (5-bromo-2-(4-bromophenyl)pyridine))Ir(III)bis(2-phenylpyridine) (0.130 g, 0.16 mmol) were dissolve in THF (12.5 mL, deoxygenated), to which a solution of Na_2CO_3 (2 M, 2 mL) was added, together with $Pd(PPh_3)_4$ (0.011 g, 3 mol % based on fluorene). The resulting mixture was sealed in a glass vial and heated for 5 days at 80 °C in an oil bath. End capping of the polymer was carried out as the last step in synthesis. Phenyl boronic acid (0.002 g, 5 mol %) was added and the solution was heated (80 °C, 12 h). This was followed by the addition of bromobenzene (0.0068 g, 10 mol %), at the same temperature. Once cooled to room temperature, THF was removed, and the residue dissolved in chloroform. This was followed by washing with water (3 times) and drying over anhydrous magnesium sulfate. After filtration, the volume of chloroform was reduced, and the concentrated solution was passed through an alumina column. The volume of the resulting solution was again reduced and precipitated in methanol (~50 mL). The resulting solid was washed with acetone for 12 h to remove residual oligomer, yielding **2** (0.073 g, 51%). A weight average molecular weight (M_w) of 12 200 Daltons and a PDI of 1.4 was obtained. δ_H (600 MHz, $CDCl_3$, Me_4Si) 8.3−6.6 (m, aromatic H), 2.12 (12 H, br. β-CH_2), 1.16−0.81 (m, CH_2 and CH_3). δ_C (150 MHz, $CDCl_3$, Me_4Si) 151.79, 140.47, 140.00, 128.77, 127.20, 126.14, 121.47, 119.95 (aromatic) 55.32 (C_9-fluorene ring) 40.37, 31.78, 30.03, 29.21, 23.90, 22.60, 14.06 (aliphatic). Anal. Calcd for $C_{120}H_{142}N_3Ir$: C, 79.2; H, 7.9; N, 2.3. Found: C, 82.4; H, 9.1; N, 0.5. Iridium content (XRF) 5.3 wt %.

$[(ppy)_2IrCl]_2$ and $(ppy)_2Ir(BrPhPyBr)$ were synthesized according to a previously published procedure.[10]

5-Bromo-2-(4-bromophenyl)pyridine). was synthesized according to the published procedure.[17] 4-Bromophenylboronic acid (2.54 g, 12.7 mmol) and 2,5-dibromopyridine (3.00 g, 12.7 mmol) were added to a degassed solution of THF, to which a solution of Na_2CO_3 (2 M, 2 mL) was added, together with $Pd(PPh_3)_4$ (0.145 g, 1 mol % based on dibromopyridine). The resulting mixture was refluxed at 80 °C for 48 h. The reaction flask was cooled to room

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temperature and the solvent was removed, water was added to the residue (100 mL), followed by dilute HCl until the pH of the solution reached 5. The product was extracted with chloroform (3 × 30 mL), washed with water, and dried over anhydrous magnesium sulfate. Column chromatography was used to isolate the product (silica gel, hexane, and a mixture of hexane and ether, 50:2), which was recrystallized from a mixture of chloroform and hexane. Fluffy, white crystals were obtained (2.4 g, 60%). δ_H (500 MHz, $CDCl_3$, Me_4Si) 8.73 (1 H, d), 7.88 (1 H, dd), 7.85 (1 H, s), 7.83 (1 H, s), 7.59−7.61 (3 H, s). *m/z* (EI) 314.90, 312.80, 310.95 (M^+, 1:2:1, $C_{11}H_7NBr_2$ requires 314.98, 312.98, 310.98) 234.00, 231.90 (M^+- Br, $C_{11}H_7NBr$ requires 234.06, 232.06) 153.00 (M^+- 2Br, $C_{11}H_7N$ requires 153.06).

Characterization. Chloroform (spectro-grade, Caledon Laboratories Ltd.) was used to prepare solutions (4 mg/mL) for film casting. Films were spin-cast on either quartz or glass slides at 1000 rpm for 60 s, shortly before acquisition of absorption and photoluminescence spectra. NMR spectroscopy was performed using a 500 MHz Varian Inova500 spectrometer or a 600 MHz Brucker Avance QNP cryoprobe spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd. Mass spectrometry was performed using a Voyager DE Perceptive biosystems MALDI Spectrometer. Ir content was determined using a Kristalloflex 2H X-ray fluorescence (XRF) spectrometer made by Siemens. Samples were excited with Mo X-rays, operated at 40 kV and 5 mA. A calibration curve was made using $Ir(acac)_3$ as a standard and yttrium as an internal standard. Samples were prepared by drop casting films on ultra thin mylar sheets. Molecular weight determinations were performed using gel permeation chromatography (Waters model 1515 isocratic pump) calibrated against PS standards. Polymers were eluted with THF using a flow rate of 1 mL/min and monitored with a UV−vis detector (Waters 2487). Microwave synthesis was performed using an in-house modified Panasonic Inverter Microwave (model NN-S614). Absorption and fluorescence spectra were collected using Cary 3E and Photon Technology International (PTI) spectrophotometers, respectively. Quantum yield measurements were performed using an integrating sphere instrument from PTI. Emission lifetimes were measured using a time correlated single photon counting system. Cyclic voltammograms were measured on polymer films drop cast on glassy carbon electrode (1.5 mm diameter). The electrolyte was dissolved in acetonitrile (0.1 M Bu4NClO4). Pt wire was used for the counter electrode. The reference electrode consisted of Pt wire in acetonitrile (0.1 M tetrabutylammonium iodine, 0.05 M I_2). Potentials were measured against ferrocene/ferrocenium redox couple using a PAR potentiostat/galvanostat 263A at a scan rate of 50 mV/s.

PV devices were prepared in the following manner: ITO was patterned using concentrated HCl, followed by cleaning in isopropyl alcohol, acetone, a mixture of H_2O, H_2O_2, and NH_4OH (5:1:1 vol. ratio), prior to rinsing with H_2O. PEDOT:PSS (Baytron VP Al 4083) was spin-coated at 5000 rpm and annealed for 10 min at 140 °C. Polymer:PCBM blends (1:4 wt. ratio, ~15 mg/mL) in chlorobenzene were spin coated at 700 rpm in air. An Al layer was thermally evaporated on the polymer surface at a pressure $<2 \times 10^{-6}$ Torr, yielding thicknesses of 100 nm. Current−voltage characteristics were measured using a Keithley source meter (model 2400). Polymer thicknesses were determined using a KLA Tencor Alpha-Step IQ surface profiler. The active area of the device was ~10 mm^2. *I*−*V* curves were obtained using a solar simulator, supplied by Newport, equipped with a 300 W xenon lamp and a 1.5 a.m. filter at an irradiation intensity of 80 mW/cm^2. The reflection of light by the ITO was taken into account by placing a piece of ITO coated glass in front of the power meter when measuring the irradiation intensity.

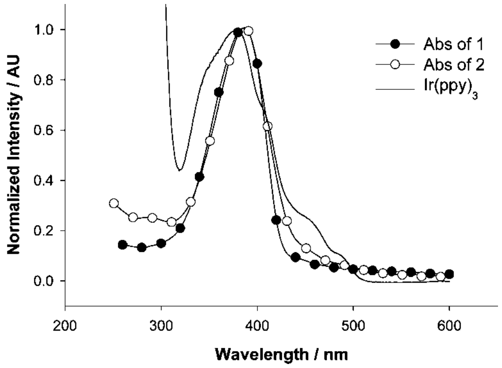

Figure 1. Absorption spectra of **1**, **2**, and $Ir(ppy)_3$.

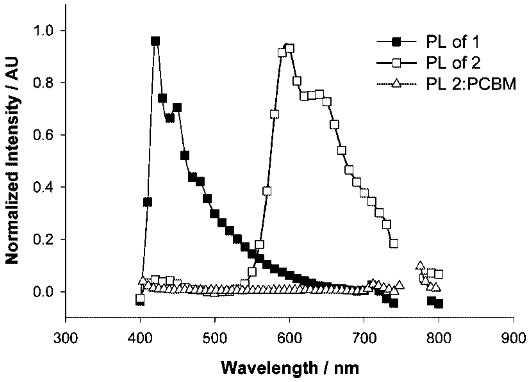

Figure 2. Photoluminescence spectra of **1**, **2**, and a **2**:PCBM blend (1:4 wt ratio). $\lambda_{ex} = 380$ nm.

Results and Discussion

Scheme 1 depicts the Suzuki polycondensation reaction that yielded polymers **1** and **2**. The feed ratio of dibromo-9,9-dialkylfluorene to 5-bromo-2-(4-bromophenyl)pyridine or (5-bromo-2-(4-bromophenyl)pyridine))Ir(III)bis(2-phenylpyridine) was 1:1. The molar feed ratio of iridium in the **2** was calculated to be 25%. X-ray fluorescence (XRF) spectroscopy determined the actual amount incorporated was 13 mol %. The weight average molecular weights of **1** and **2** were determined to be 32 700 and 12 200 Daltons with polydispersities of 2.0 and 1.4, respectively.

Absorption and photoluminescence spectra of films of **1** and **2** are shown in Figure 1 and 2, respectively. λ_{max} for both **1** and **2** occurs at ~385 nm, due to the absorption of the poly(fluorene-co-phenylpyridine) main chain. The longer absorption tail observed in **2**, between 400−450 nm, is due to absorption by the iridium complex. Figure 1 shows the absorption profile of $Ir(ppy)_3$, to further illustrate this point. The photoluminescence spectrum of **1** exhibits a maximum at 422 nm, whereas **2** exhibits a maximum at 596 nm (Figure 2). The former is due to fluorescence from the main chain, whereas the latter is due to phosphorescence from the iridium complex. The transient luminescent decay monitored at ~600 nm revealed the PL lifetime of **2** to be 0.26 μs (Figure 3, Table 1), indicating the triplet nature of the long wavelength emission. This result is consistent with previously reported lifetimes of iridium-bound conjugated polyfluorene copolymers, where it was shown that phosphorescence lifetimes decreased with increasing iridium content.[8] Fluorescent emission of **2** at 422 nm is very weak compared to its

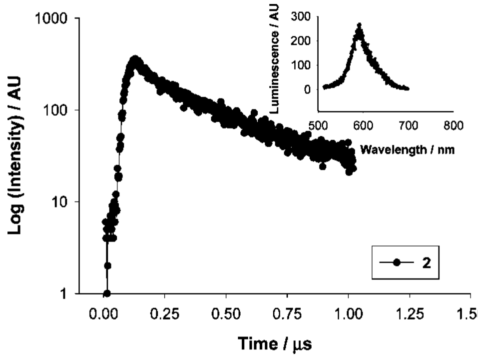

Figure 3. Transient luminescent decay of **2**. $\lambda_{ex} = 355$ nm. Inset shows the corresponding luminescence spectrum.

Table 1. Photophysical properties of 1 and 2

polymer	absorption λ_{max} (nm)	emission λ_{max} (nm)	Φ	τ (μs)
1	385	422	0.04	
2	385	596	0.02	0.26

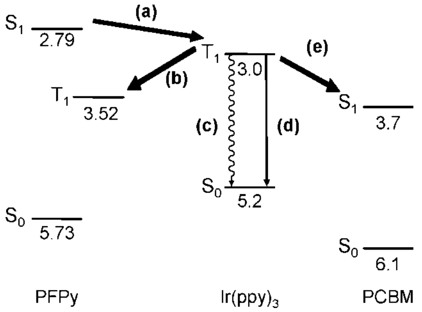

Figure 4. Energy level diagram showing (a) energy transfer from the PFPy main chain to the bound Ir complex, (b) triplet quenching of the Ir complex by the PFPy main chain, (c) concentration quenching of the triplet state, (d) phosphorescence of the Ir complex, and (e) photoinduced electron transfer (PET) from the Ir complex to PCBM.

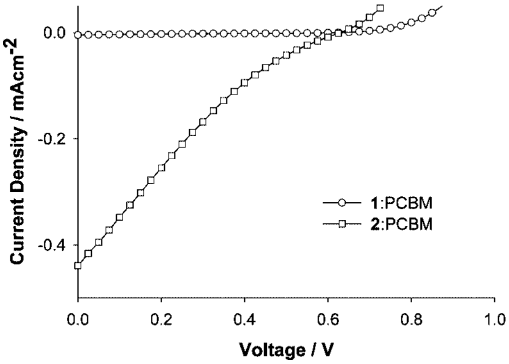

Figure 5. *I*−*V* curves obtained from **2**:PCBM (1:4) and **1**:PCBM (1:4) solar cells under AM 1.5 illumination (80 mW/cm^2). Device configuration: ITO|PEDOT:PSS| (**1** or **2**):PCBM| Al.

Table 2. Summary of Device Performance Data Plotted in Figure 5

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
1:PCBM	0.60	0.01	0.24	0.002
2:PCBM	0.63	0.44	0.19	0.07

phosphorescence, due to energy transfer from the polymer backbone to the iridium complex, as observed for analogous host−guest polymer systems in light emitting devices (LEDs).[9–11] Phosphorescence from **2** is completely quenched upon blending [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) into the film, as illustrated in Figure 2.

The quantum yield of fluorescence from **1** and phosphorescence from **2** was measured to be 0.04 and 0.02, respectively. Polymer **2** was designed to contain a significant amount of the iridium complex (25 mol %), to facilitate triplet exciton migration to an electron acceptor site. Hence the phosphorescence quantum yield of **2** is partially "concentration quenched"[12] or quenched by back energy transfer from the triplet state of the iridium complex by the triplet state of the polymer backbone. The quantum yield of **2** is much lower in magnitude than analogous poly(fluorene-co-thiophene) iridium complexes prepared with lower Ir content.[10]

Electronic energy levels of the compounds were estimated using a combination of absorption spectroscopy and cyclic voltammetry (CV). CVs of thin films deposited on a glassy-carbon working electrode were recorded at a scan rate of 50 mV/s and potentials were measured relative to the ferrocene/ferrocenium redox couple. Using the onset of the oxidation peak, the HOMO levels of **1** and **2** were estimated to be 5.73 and 5.68 eV (± 0.05), respectively. Using the onset of the absorption spectra, the band gap was estimated to be 2.94 and 2.88 eV (± 0.05), resulting in a LUMO level estimation for **1** and **2** of 2.79 and 2.80 eV (± 0.10), respectively. The HOMO levels were within 0.05 eV of each other and assumed to be similarly dominated by the poly(fluorene-co-phenylpyridine) backbone. The HOMO and LUMO levels of **1** are depicted in Figure 4. The triplet energy gap of the polymer was estimated using the following equation: $T_1 = (1.13\ S_1 - 1.43) \pm 0.25$ eV.[13] Given the similarity of the energy levels, it is expected that PV devices prepared from **1** and **2** blended with PCBM will possess similar open circuit potentials.

Figure 4 demonstrates representative processes that may occur upon excitation of **2** in the presence of PCBM. Energy transfer from poly(fluorene-alt-pyridine) (PFPy) to the phosphorescent group, Ir(ppy)$_3$, is depicted as process (a). The triplet excited state may be quenched by the polymer backbone (b), by concentration quenching (c), or by electron transfer to PCBM (e), the latter being essential for PV activity. The relative rates of these photophysical processes determine the fate of the triplet state. For an analogous system, polyspirobifluorene and a substituted derivative of Ir(ppy)$_3$, the rate of (b) occurs within ~10 ns.[14] Rates of photoelectron transfer (process (e)) typically occur in the ps time domain,[5] i.e., 3 orders of magnitude faster. It is thus believed that self-quenching of the Ir(ppy)$_3$ triplet state in **2** by the main chain is unlikely to compete with electron transfer, if the triplet exciton can reach an electron acceptor site. Therefore, in contrast to highly phosphorescent polymers of similar structure, designed for LED applications, the triplet energy level of the conjugated polymer is deemed to be of less significance in the design of such polymers. As discussed above, PL from a **2**:PCBM blend (1:4 wt ratio) shown in Figure 2 is completely quenched, which is indicative of electron transfer from the excited-state polymer to PCBM.

Photovoltaic devices were fabricated by blending **1** and **2** with PCBM in order to examine the effect of triplet formation on charge generation as observed by the PV response.

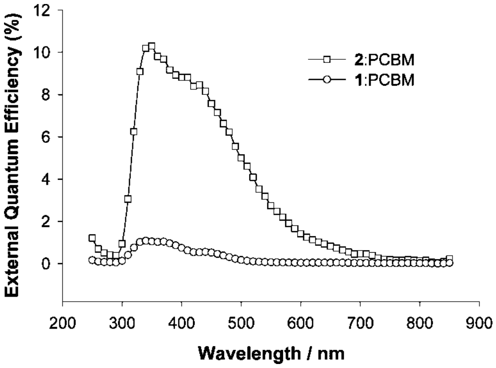

Figure 6. External quantum efficiency (EQE) of **2**:PCBM (1:4) and **1**:PCBM (1:4) versus wavelength. Device configuration: ITO| PEDOT:PSS| Polymer: PCBM| Al.

Although the solar PV efficiencies of devices based on **1** and **2** are much lower than current state-of-the-art devices,[15] **2** clearly exhibits an improved device performance as shown in Figure 5 and listed in Table 2. The short circuit current densities (J_{sc}) are 0.01 and 0.44 mA/cm^2 for devices prepared with **1** and **2**, respectively, and the power conversion efficiency improves from 0.002 for **1** to 0.07% for **2**. The fill factors of the two systems, while relatively low, are similar, which indicates that that the overall cell resistances to charge transport, once charges are formed, are similar, and that this is unlikely to account for the differences in photovoltaic efficiency.

External quantum efficiencies (EQE) of the devices are shown in Figure 6. Incorporating the Ir complex into the polymer increases the EQE by approximately a factor of 10, from 1.1 to 10.3%. The maximum EQE observed at ~350 nm is attributed to absorption by the poly(fluorene-co-phenylpyridine) main chain, and the small peak observed at ~715 nm is attributed to absorption by PCBM. An approximation of the internal quantum efficiency (IQE), i.e., the conversion efficiency of photons absorbed to current produced, was obtained by dividing the EQE by the light absorbed in the device. The absorption of **1** and **2** at 350 nm is 0.62 and 0.59, respectively, from which it is calculated that 76 and 74% of the incident irradiation is absorbed. The reflection by the ITO was estimated to be ~20% at 350 nm. IQEs were estimated to be 2.0 and 19.0% for **1** and **2**, respectively.

Conclusions

In summary, we demonstrate that introducing triplet forming Ir complexes into the polyfluorene-based polymer blended with an electron acceptor considerably enhances solar cell conversion efficiencies. Excitation of **2** is followed by ISC to the triplet state, which phosphoresces unless it dissociates at a D−A interface. The improved performance of **2** over **1** is believed to be due to the formation of the triplet state, and by inference, the longer diffusion length of the triplet exciton, compared to the singlet exciton formed in **1**. Power conversion efficiencies are lower than many polymer:PCBM systems based on singlet exciton charge generation, but this is mainly due to the unfavorable absorption cross-section of **2**. Further improvements in conversion efficiencies are expected upon optimizing the iridium content in the system and choosing a main chain that possess an absorption spectrum that overlaps more fully with the solar spectrum.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR data and GPC data for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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