Supporting information

Photochemical Synthesis of π-Extended Ullazine Derivatives as New Electron Donor for Efficient Conjugated D-A Polymers

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GENERAL METHODS

Chemical reagents were purchased from Sigma-Aldrich Co. Canada, Alfa Aesar Co., TCI America Co. or Oakwood Products Inc. and used as received. Solvents used for organic synthesis were purchased from Fisher Chemical Co., EMD Millipore Co. and CFS Chemical Co. as HPLC grade. These solvents were degassed, dried and purified with a Solvent Purifier System (SPS) (Vacuum Atmosphere Co., Hawthorne, USA). Anhydrous decahydronaphthalene (mixture of cis + trans) was used as received for photochemical reactions and other anhydrous solvents were bought from Sigma-Aldrich Co. Canada. All anhydrous and air sensitive reactions were performed in oven-dried glassware purchased from Synthware™ under positive nitrogen stream. Analytical thin-layer chromatographies were performed with silica gel 60 F254, 0.25 mm pre-coated TLC plates (Silicycle, Québec, Canada). Compounds were revealed by a 254 nm and/or 365 nm UV wavelength and/or aqueous K₂CO₃ and NaOH solution of potassium permanganate. Flash column chromatographies were performed with 230-400 mesh silica gel R10030B (Silicycle, Québec, Canada).
APPARATUS

Photochemical reactions were performed in a CCP-ICH2 Luzchem® photochemical reactor equipped with a thermostat and a heating mantle. Photochemical reactions were performed in a 100 mL quartz round-bottom flask bought from Chemglass®. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz (\(^1\)H) and 100 MHz (\(^{13}\)C). Chemical shifts were reported as values (ppm) relative to residual solvent peak. High resolution mass spectra (HRMS) were recorded with an Agilent 6210 Time-of-Flight (TOF) LC-MS apparatus equipped with an APPI ion source (Agilent Technologies, Toronto, Canada). Number-average (\(M_n\)) and weight-average (\(M_w\)) molecular weights were determined by size-exclusion chromatography (SEC) using a Varian Polymer Laboratories GPC220 equipped with an RI detector and a PL BV400 HT Bridge Viscometer. The column set consists of 2 PL gel Mixed C (300 × 7.5 mm) columns and a PL gel Mixed C guard column. The flow rate was fixed at 1mL min\(^{-1}\) using 1,2,4-trichlorobenzene (TCB) (with 0.0125% BHT w/v) as the eluent. The temperature of the system was set to 110 °C. All the samples were prepared at a nominal concentration of 1.0 mg mL\(^{-1}\) in TCB. Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vials were held at 110 °C with shaking for 1 h for complete dissolution. The solutions were filtered through a 2 mm porous stainless steel filter used with a 0.40 μm glass filter into a 2 mL chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards Easi-Vials PS-M from Varian Polymer Laboratories which were dissolved in TCB. UV-vis-NIR absorption spectra were recorded using a Varian Cary 500 UV-vis-NIR spectrophotometer using 1 cm path length quartz cells. For solid state measurements, the polymer solution (1.0 mg mL\(^{-1}\) in
chloroform) was spin coated on glass plates. Optical bandgaps were calculated from the onset of the absorption band. Cyclic voltammetry (CV) were recorded on a Solartron 1287 potentiostat using platinum wires as the working electrode and counter electrode at a scan rate of 50 mV s⁻¹. The reference electrode was Ag/Ag⁺ (0.01 M AgNO₃ in acetonitrile) in an anhydrous and argon-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in dry acetonitrile. Under these conditions, the oxidation potential of ferrocene was 0.09 V versus Ag/Ag⁺, whereas the oxidation potential of ferrocene was 0.41 V versus the saturated calomel electrode (SCE). The HOMO and LUMO energy levels were determined from the oxidation and reduction onsets (where the current starts to differ from the baseline) from the cyclic voltammogram assuming that the SCE is -4.71 eV in vacuum, as reported in the literature.
FABRICATION AND CHARACTERIZATION OF POLYMER SOLAR CELLS

Inverted BHJ solar cells were prepared on a commercial ITO coated glass substrate. The substrates were cleaned sequentially in ultrasonic baths with cleanroom detergent, deionized (DI) water, acetone and isopropyl alcohol. Prior to the fabrication, the ITO glass substrates were treated in a plasma-oxygen chamber (Spacemaker II sensor, Plasmatiic Systems, Inc, USA) for 5 min. First, a 20-30 nm ZnO thin film was made by spin coating a ZnO precursor solution (250 mg of zinc acetate, 69.0 µL of ethanolamine, and 2.91 mL of 2-methoxyethanol) onto the ITO glass at 5000 rpm for 40 s and then annealed at 250 °C on a hot plate in air for 1 h. Then, a 0.05 wt % polyethylenimine (PEI) in 2-methoxyethanol solution was spin-coated onto the ZnO layer and dried at 110 °C on a hot plate in air for 10 min. The blend solution was spin-coated over the ZnO layer and then dried at 130 °C for 90 s to make the active layer. All the blend solutions were prepared by dissolving the polymers (10 mg mL⁻¹) and PC₆₀BM (10 mg mL⁻¹) or PC₇₀BM (10 mg mL⁻¹) or ITIC (10 mg mL⁻¹) in chlorobenzene and stirring the mixtures on a hot plate in air at 60 °C overnight. Finally, MoO₃ (8 nm) and Ag anode (100 nm) were sequentially vacuum-deposited onto the active layer through a shadow mask on top of the active layer by thermal evaporation under high vacuum (1 × 10⁻⁷ Torr). Current versus potential curves (J-V characteristics) were measured with a Keithley 2400 Digital Source Meter under a collimated beam. Illumination of the cells was done through the ITO side using light from a 150 W Oriel Instruments Solar Simulator (model 16S, Solar Light Co., Philadelphia, PA) and a 200 W xenon Lamp Power Supply (Model XPS 200, Solar Light Co., Philadelphia, PA) with an AM 1.5G filter to provide an intensity of 100 mW cm⁻² calibrated by NREL certified Si photodiode (Model 1787-04, Hamamatsu Photonics K.K., Japan) and a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Japan).
NMR SPECTRA

Compound 1
Figure S1: $^1$H NMR spectrum of compound 1 in CDCl$_3$.

Figure S2: $^{13}$C NMR spectrum of compound 1 in CDCl$_3$.

Compound 2
Figure S3: $^1$H NMR spectrum of compound 2 in CDCl$_3$.

Figure S4: $^{13}$C NMR spectrum of compound 2 in CDCl$_3$.

**Compound 3**
Figure S5: $^1$H NMR spectrum of compound 3 in CDCl$_3$.

Figure S6: $^{13}$C NMR spectrum of compound 3 in CDCl$_3$.

Compound 4
Figure S7: $^1$H NMR spectrum of compound 4 in CDCl$_3$.

Figure S8: $^{13}$C NMR spectrum of compound 4 in CDCl$_3$.

Compound 5
Figure S9: $^1$H NMR spectrum of compound 5 in CDCl$_3$.

Figure S10: $^{13}$C NMR spectrum of compound 5 in CDCl$_3$.

**Compound 6**
Figure S11: $^1$H NMR spectrum of compound 6 in CDCl$_3$.

Figure S12: $^{13}$C NMR spectrum of compound 6 in CDCl$_3$.

**Compound 7**
Figure S13: $^1$H NMR spectrum of compound 7 in CDCl$_3$.

Figure S14: $^{13}$C NMR spectrum of compound 7 in CDCl$_3$.

**Compound 8**
Figure S15: $^1$H NMR spectrum of compound 8 in CDCl$_3$.

Figure S16: $^{13}$C NMR spectrum of compound 8 in CDCl$_3$.

**Compound 9**
Figure S17: $^1$H NMR spectrum of compound 9 in CDCl$_3$.

Figure S18: $^{13}$C NMR spectrum of compound 9 in CDCl$_3$.

**Compound 10**
Figure S19: $^1$H NMR spectrum of compound 10 in CDCl$_3$.

Figure S20: $^{13}$C NMR spectrum of compound 10 in CDCl$_3$.

**Compound 11**
Figure S21: $^1$H NMR spectrum of compound 11 in CDCl$_3$.

Figure S22: $^{13}$C NMR spectrum of compound 11 in CDCl$_3$.

Compound 12
Figure S23: $^1$H NMR spectrum of compound 12 in CDCl$_3$.

Figure S24: $^{13}$C NMR spectrum of compound 12 in CDCl$_3$.

Polymer P1
Figure S25: $^1$H NMR spectrum of P1 in TCE-$d_2$ at 383 K.

Polymer P2

Figure S26: $^1$H NMR spectrum of P2 in TCE-$d_2$ at 383 K.

Polymer P3
Figure S27: $^1$H NMR spectrum of P3 in TCE-$d_2$ at 383 K.

UV-VIS AND PHOTOLUMINESCENCE ANALYSIS
Figure S28: UV-vis absorption spectra of the compounds 4-7 (a) and 8-11 (b) in chloroform solution.
Figure S29: Photoluminescence spectra of the compounds 5, 7, 9 and 11 in chloroform solution.

SIZE-EXCLUSION CHROMATOGRAPHY
Figure S30: Size exclusion chromatography traces for P1 ($\bar{M}_n$: 12.5 kg mol$^{-1}$, $\bar{M}_w$: 22.5 kg mol$^{-1}$, dispersity index ($D$): 1.8, black trace), P2 ($\bar{M}_n$: 16.8 kg mol$^{-1}$, $\bar{M}_w$: 47.0 kg mol$^{-1}$, dispersity index ($D$): 2.8, red trace) and P3 ($\bar{M}_n$: 21.4 kg mol$^{-1}$, $\bar{M}_w$: 55.6 kg mol$^{-1}$, dispersity index ($D$): 2.6, blue trace).
Figure S31: Film Cyclic Voltammetry of P1.

Figure S32: Film Cyclic Voltammetry of P2.
Figure S33: Film Cyclic Voltammetry of P3.
Figure S34: AFM images obtained in tapping mode (5 \times 5 \mu m^2) of P1, P2 and P3 blend with PC_{60}BM films without DIO (on top) and with DIO (on the bottom).

Figure S35: AFM images obtained in tapping mode (5 \times 5 \mu m^2) of P3:ITIC blend film.
THERMAL GRAVIMETRIC ANALYSIS (TGA) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC) THERMAL ANALYSIS

Figure S36: TGA plots of P1, P2 and P3 at a scan rate of 10 °C min⁻¹ under nitrogen atmosphere.

Figure S37: DSC plots of P1, P2 and P3 at a scan rate of 20 °C min⁻¹ under nitrogen atmosphere.