Electronic supplementary information

Thia- and selena-diazole containing polymers for near-infrared light-emitting diodes

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Contents

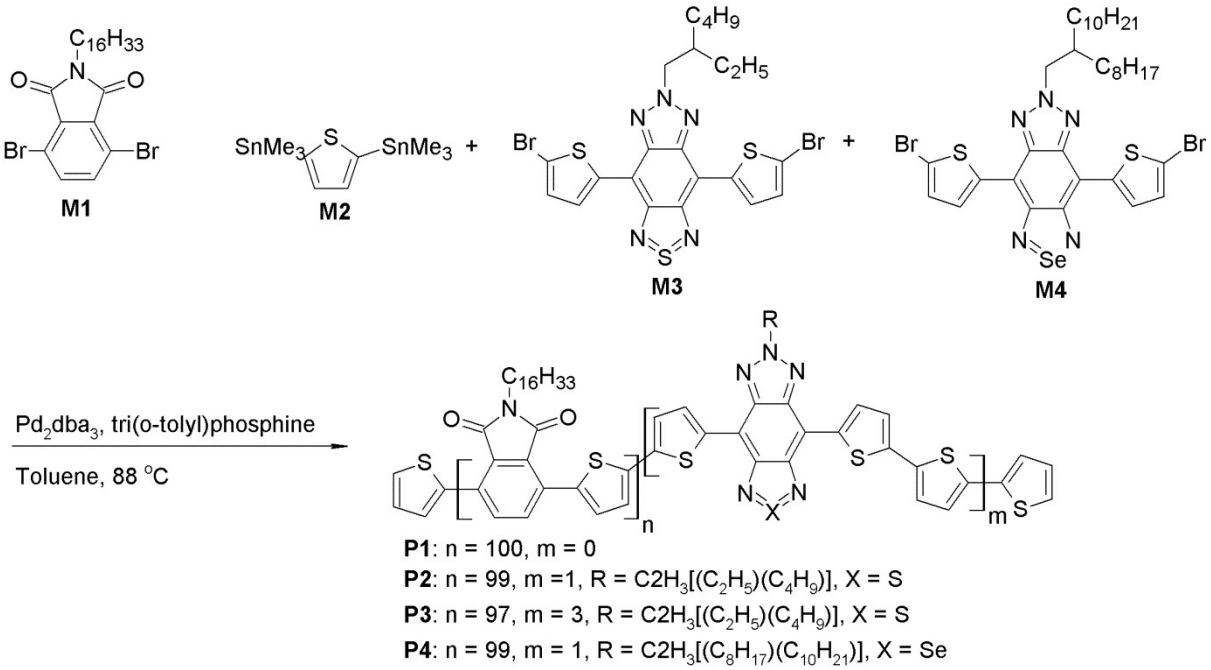
1. Experimental details

^{1}H-NMR spectra were measured on an automated Agilent (Varian) MR 400 MHz spectrometer (equipped with "one-probe") with $CDCl_3$ as the solvent. In all cases, the peak values were calibrated relative to tetramethylsilane. Size exclusion chromatography (SEC) was performed on a Waters Alliance GPCV2000 with refractive index detector columns: Waters Styragel HT GE x 1, Waters Styragel HMW GE x 2. The eluent was 1,2,4-trichlorobenzene. The operating temperature was 135 ˚C, and the dissolution time was 2 h. The concentration of the samples was 0.5 mg/mL, which were filtered through a 0.45 µm metal filter prior to analysis. The molecular weights were calculated relative to calibration with polystyrene standards. UV-Vis-NIR absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA7 Thermo Graphic Analyzer. A temperature range of 25-600 ˚C was used with a heating rate of 10 ˚C/min. Differential scanning calorimetry (DSC) measurements were done on a Perkin Elmer Pyris over a temperature range of 30-250 °C using a heating/cooling rate of 10 °C/min. Values from the 2nd scan were reported. Square-wave voltammetry (SWV) measurements were carried out on a CH-Instruments 650A Electrochemical Workstation. Experiments were performed in a three-electrode cell using platinum wires as both the working electrode and the counter electrode, and a Ag/Ag^+ reference electrode calibrated to the Fc/Fc^+ redox couple. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu4NPF6) in anhydrous acetonitrile was used as supporting electrolyte. The polymers were deposited onto the working electrode from chloroform solution. In order to remove oxygen from the electrolyte solution, the system was bubbled with nitrogen prior to each experiment. The nitrogen inlet was then placed above the liquid surface and left there during the scans. The HOMO/LUMO levels were estimated from onset and peak potentials of the third scan using the equation HOMO/LUMO = -($E_{ox/red}$ +5.13) eV).[1]

All the optical measurements reported are taken in the solid state. We prepared thin films (100 nm) of polymers by spin-coating (2 krpm) a 1.5 wt % chloroform solution over a Spectrosil fused silica substrate. The steady-state photoluminescence (PL) spectra were recorded after exciting the PL with a 405 nm diode laser with an ANDOR Shamrock spectrograph coupled with an ANDOR Newton CCD unit. Time-resolved PL measurements were carried out with a time-correlated single photon counting (TCSPC) spectrometer using a pulsed diode laser (Edinburg Instruments-EPL-375) at 371 nm as excitation source and a cooled photomultiplier (Becker & Hickl PMC-100-1) coupled to a monochromator and TCSPC electronics (Edinburg Instrument Lifespec-ps TCC-900 PC card) to detect and to process the luminescence signal with a temporal resolution of ~200 ps. The photoluminescence quantum efficiency (PLQE) was measured using an integrating sphere method.[2] The

polymers were also tested in PLED devices as the active layer. PLEDs were fabricated by spin-coating (4 krpm) a 2.8 wt. % dispersion in water of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)[3] (PEDOT:PSS, Sigma Aldrich) to a thickness of a 80 nm over an ITO-coated glass pre-treated with oxygen plasma a (10 min at 10.2 W).[4] The substrates were then baked at 150°C for 10 min in a nitrogen atmosphere to remove residual water. The active layer was deposited by spin-coating (2 krpm) a 1.5 wt. % chloroform solution to obtain a thickness of 100 nm. Ca/Al electrodes (30 nm/150 nm respectively) were thermally evaporated under vacuum 10^{-6} mbar) on top of the active layer. We fabricated eight devices per polymer. Current-voltage-radiance characteristics were measured with a Keithley 2004 source meter and a calibrated Si photodiode (wavelength range of 200-1100 nm) coupled with a Keithley 2000 multimeter, electroluminescence (EL) spectra were taken with the ANDOR spectrometer described above.

2. Materials



Scheme S1. Synthesis of polymers **P1**-**4**.

Compounds **A**,[5] **B**,[6] **M1**[7] & **M3**[7] and polymer **P1**[7] were synthesized according to previously published procedures. Compound **M2** was purchased from Solamer Chemical Company and used as received. All other reagents and solvents were purchased from Aldrich Chemical Company and used as received. All reactions were performed under nitrogen unless noted.

1. To a dry 500 mL round-bottomed flask was added 4.38 g (15.82 mmol) of **A**, 6.86 g (18.98 mmol) of **B** and 60 mL of DMF. The reaction was stirred until everything dissolved. Then 4.37 g (31.64 mmol) of K_2CO_3 was added and the reaction was stirred at 90 °C for 3 h. Upon cooling the reaction was poured into 200 mL of 2 M HCl and extracted with diethylether. The combined ether layers were washed 1 x 50 mL with 1 M HCl and 1 x 50 mL with brine, dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2, starting with Pet Ether switching to 4:1 Pet Ether:DCM) yielded 6.08 g (69 %) of a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 7.43 (s, 2H), 4.67 (d, J = 7.3 Hz, 2H), 2.34 (sp, J = 5.7 Hz, 1H) 1.33-1.23 (m, 32 H), 0.89-0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.85, 129.63, 110.20, 61.36, 39.23, 32.14, 32.11, 31.38, 29.97, 29.88, 29.85, 29.81, 29.79, 29.67, 29.56, 29.53, 26.24, 22.90, 14.33 (3 overlapping alkyl C's).

2. To a dry 500 mL 2-neck round-bottomed flask equipped with an addition funnel was added 125 mL of DCM (dried over $MgSO_4$) and 5.87 mL (66.3 mmol) of CF_3SO_3H (d = 1.696g/mL). Then 1.37 mL (33.1 mmol) of fuming nitric acid (d = 1.52 g mL) was added and the mixture was stirred for 50 minutes at room temperature. During this time a white crystalline solid precipitated out of the solution. Next, 4.62 g (8.29 mmol) of **1** dissolved in 40 mL of dry DCM was added to the addition funnel and then added drop-wise to the reaction

mixture over 2-3 minutes. The reaction was stirred overnight (~ 12-14 h) at room temperature. Then the mixture was poured into 100 mL of cold H_2O and extracted with DCM. The combined DCM layers were washed with saturated sodium bicarbonate and dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure. Column chromatography (SiO_2, 2:1 Pet Ether:DCM) yielded 4.24 g (79 %) of a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 4.76 (d, J = 7.0 Hz, 2H), 2.33 (sp, J = 5.5 Hz, 1H), 1.39-1.25 (m, 32H), 0.87 (t, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.33, 142.09, 107.42, 62.38, 39.51, 32.13, 32.06, 31.36, 29.92, 29.89, 29.86, 29.80, 29.68, 29.63, 29.57, 29.54, 29.45, 26.24, 22.90, 14.32 (2 overlapping alkyl C's).

3. To a 100 mL round-bottomed flask was added 1.06 g (1.64 mmol) of **2** followed by 39 mL of AcOH. The mixture was stirred until everything dissolved. Then 1.10 g (19.6 mmol) of Fe powder was added and the reaction was stirred at 40 °C for 1 h. Upon cooling the reaction was poured into 100 mL of H_2O and extracted with $CHCl_3$. The combined organic layers were washed with water, saturated sodium bicarbonate, water and dried over anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure. Column chromatography (SiO_2, DCM) yielded 0.91 g (95 %) of a white/brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 4.53 (d, J = 7.4 Hz, 2H), 4.10 (br s, 4H), 2.27 (sp, J = 5.7 Hz, 1H), 1.29-1.22 (m, 32H), 0.89-0.85 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.22, 135.98, 92.48, 60.44, 39.11, 32.12, 32.07, 31.39, 30.03, 29.81, 29.80, 29.68, 29.63, 29.54, 29.55, 26.25, 22.89, 22.86, 14.32, 14.31 (2 overlapping alkyl C's). MS (MALDI): calcd for $C_{26}H_{45}Br_2N_5$ ($M+H^+$) 587.5, found 587.1.

4. To a 50 mL 2-neck round-bottomed flask equipped with a condenser, was added 1.00 g (1.70 mmol) of **3** and 10 mL of absolute EtOH. The reaction mixture was heated to reflux. Then a solution of 0.20 g (1.80 mmol) SeO_2 in 3.5 mL of water was added to the reaction mixture and the reaction was stirred at reflux for 3 h. Upon cooling 30 mL of water was added to the reaction and dark purple solid was collected by filtration and washed with water. Column chromatography (SiO_2, DCM) yielded 0.84 g (74 %) of a dark purple solid. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 4.79 (d, J = 7.3 Hz, 2H), 2.48 (sp, J = 5.7 Hz, 1H), 1.41-1.23 (m, 32H), 0.88-0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.53, 146.27, 99.80, 63.11, 39.47, 32.08, 32.03, 31.48, 29.94, 29.78, 29.77, 29.60, 29.50, 29.42, 26.25, 22.86, 22.83, 14.31, 14.28 (2 overlapping alkyl C's). MS (MALDI): calcd for $C_{26}H_{41}Br_2N_5Se$ (M^+) 662.4, found 661.9.

5. To a 25 mL 2-neck round-bottomed flask was added 0.296 g (0.447 mmol) of **4**, 0.0041 g Pd_2dba_3 (0.0045 mmol) and 0.0109 g (0.0358 mmol) tri(o-toyl)phosphine. Then the flask was then subjected to 4 x vacuum/N_2 backfill cycles. Next, 0.384 g (1.03 mmol) of 2-tributylstannylthiophene was added followed by 10 mL of degassed toluene and the reaction was stirred at 90 °C overnight. The solvent was then removed under reduced pressure and the residue was purified by column chromatography (SiO_2, Hex:DCM 1:1) yielding 0.140 g (47 %) of a dark blue solid. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 8.79 (dd, J = 0.8 Hz, 3.8 Hz, 2H), 7.60 (dd, J = 0.9 Hz, 5.1 Hz, 2H), 7.26 (dd, J = 3.9 Hz, 5.1 Hz, 2H), 4.76 (d, J = 6.6 Hz, 2H), 2.38 (sp, J = 6.0 Hz, 1H), 1.41-1.22 (m, 32H), 0.88-0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.28, 143.58, 138.08, 131.39, 130.00, 127.68, 112.34, 61.57, 39.44, 32.11, 32.09, 31.80, 30.09, 29.87, 29.84, 29.79, 29.54, 29.52, 26.54, 22.89, 22.87, 14.33, 14.31 (3 overlapping alkyl C's). MS (MALDI): calcd for $C_{34}H_{47}N_5S_2Se$ (M^+) 668.9, found 669.0.

M4. To a 100 mL round-bottomed flask was added 0.13 g (0.19 mmol) of **5** followed by 35 mL of DMF. The solution was degassed with nitrogen for 30 minutes. Then 0.076 g (0.43 mmol) of N-Bromosuccinimide was added and the reaction was stirred in the dark for 24 h. The solution was then poured into 150 mL of water and extracted with DCM. The combined organic layers were then washed 3 x with brine and dried over anhydrous magnesium sulfate. The solution was then filtered and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2, Hex:DCM 1:1) yielding 0.09 g (56 %) of a dark purple solid. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 8.31 (d, J = 4.2 Hz, 2H), 7.11 (d, J = 4.2 Hz, 2H), 4.62 (d, J = 6.6 Hz, 2H), 2.26 (sp, J = 6.1 Hz, 1H), 1.40-1.22 (m, 32H), 0.88-0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.23, 142.63, 139.50, 131.36, 130.46, 118.63, 111.14, 61.45, 39.39, 32.14, 32.11, 31.76, 30.13, 29.91, 29.87, 29.82, 29.57, 29.56, 26.50, 26.49, 22.91, 22.89, 14.36, 14.34 (2 overlapping alkyl C's). MS (MALDI): calcd for $C_{34}H_{45}Br_2N_5S_2Se$ (M^+) 826.7, found 826.8.

2.1 General procedure for the preparation of polymers.

To a 50 mL 2-neck round bottom flask was added 1 eq (~ 200-300 mg) of **M2**, 0.99 or 0.97 eq of **M1** and 0.01 or 0.03 eq of **M3** or **M4** followed by 0.01 eq of Pd_2dba_3 and 0.08 eq of tri(o-tolyl)phosphine. The flask was then subjected to 6 x vacuum/nitrogen backfill cycles. Then ~ 10 mL of degassed toluene was added and the flask was placed in a pre-heated oil bath at 88 °C and stirred. As the reaction progressed, the solution fluorescence

went from green to yellow to yellow/orange. When the polymerization became more viscous and precipitate was seen (~ 10-15 minutes for **P1**-**P3**, ~ 2 h for **P4**), the reaction mixture was immediately precipitated into ~200-250 mL of methanol and an orange or orangeish brown solid was collected by filtration. Then the polymer was dissolved in 100 mL of $CHCl_3$ and stirred with an aqueous solution of sodium diethyldithiocarbamate trihydrate (5 g in 100 mL H_2O) at reflux for 4 h. Then the $CHCl_3$ layer was separated, washed 3 X with water, concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and $CHCl_3$ (overnight, ~15-20 h). Then the $CHCl_3$ solution was concentrated, precipitated into 200 mL of methanol and an orange or orangeish brown solid was collected by filtration.

2.2 General procedure for the end-capping of polymers

To a 100 mL flask was added 1 eq (100-150 mg) of polymer, 0.01 eq of Pd_2dba_3 and 0.08 eq of tri(o-tolyl)phosphine. The flask was then subjected to 6x vacuum/nitrogen backfill cycles. Then a minimum amount of degassed $CHCl_3$ was added to dissolve the polymer (~15-30 mL). Next, 1.2 eq of 2-bromothiophene was added and the solution was refluxed for ~ 1 h. Then 1.4 eq of 2-tributlystannylthiophene was added and the solution was refluxed for ~ 1h. Upon cooling the mixture was precipitated into MeOH (~ 200-300 mL) and the polymer was collected by filtration. Then the polymer was dissolved in 100 mL of $CHCl_3$ and stirred with an aqueous solution of sodium diethyldithiocarbamate trihydrate (5 g in 100 mL H2O) at reflux for 4 h. Then the $CHCl_3$ layer was separated, washed 3 X with water, concentrated and precipitated into 200 mL of methanol. The polymer was then collected by filtration, placed in a thimble and subjected to Soxhlet extraction with methanol, acetone, hexane and $CHCl_3$ (overnight, ~15-20 h). Then the $CHCl_3$ solution was concentrated, precipitated into 200 mL of methanol and an orange or orangeish brown solid was collected by filtration.

2.3 Polymer data post end-capping

P1 (85 % overall yield) ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 7.89 (br s, 2H), 7.85 (br s, 2H), 3.71 (br, 2H), 1.70(br, 2H), 1.34-1.24 (br, 26H), 0.87 (br t, J = 6.8 Hz, 3H). GPC: M_n =8.1 kg/mol, M_w = 13.6 kg/mol, PDI = 1.7. TGA (N_2) T_{d99} = 390 ˚C, T_{d95} = 478 ˚C. DSC: No transitions observed. HOMO: - 6.05 eV, LUMO: - 3.45 eV.

P2 (87 % overall yield) ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 7.89 (br s, 2H), 7.85 (br s, 2H), 3.71 (br, 2H), 1.70(br, 2H), 1.34-1.24 (br, 26H), 0.86 (br t, J = 6.8 Hz, 3H). GPC: M_n =9.5 kg/mol, M_w = 17.4 kg/mol, PDI = 1.8. TGA (N_2) T_{d99} = 307 ˚C, T_{d95} = 463 ˚C. DSC: No transitions observed.

P3 (94 % overall yield) ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 7.89 (br s, 2H), 7.85 (br s, 2H), 3.71 (br, 2H), 1.70 (br, 2H), 1.34-1.24 (br, 17H), 0.86 (br t, J = 6.8 Hz, 3H). GPC: M_n =15.1 kg/mol, M_w = 30.3 kg/mol, PDI = 2.0. TGA (N_2) T_{d99} = 414 ˚C, T_{d95} = 475 ˚C. DSC: No transitions observed.

P4 (33 % overall yield) ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ (ppm): 7.89 (br s, 2H), 7.85 (br s, 2H), 3.71 (br, 2H), 1.70 (br, 2H), 1.34-1.24 (br, 17H), 0.87 (br t, J = 6.8 Hz, 3H). GPC: M_n =12.1 kg/mol, M_w = 23.5 kg/mol, PDI = 1.9. TGA (N_2) T_{d99} = 364 ˚C, T_{d95} = 492 ˚C. DSC: No transitions observed.

3. Electrochemistry

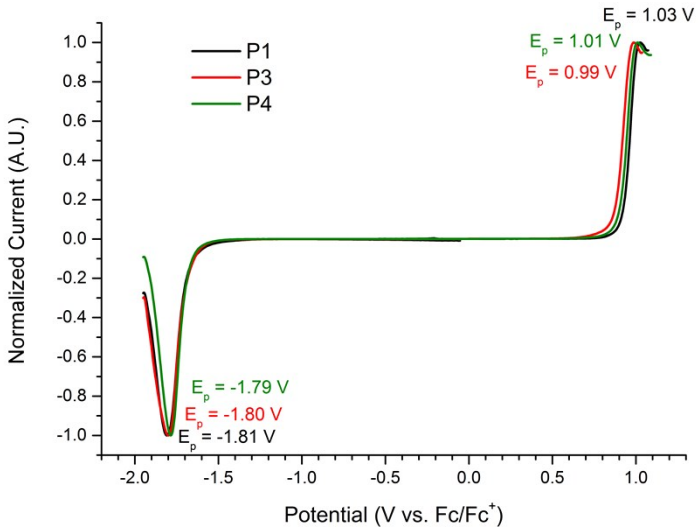


Figure S1 Square-wave voltammetry for polymers P1, P3 and P4.

4. Optical properties

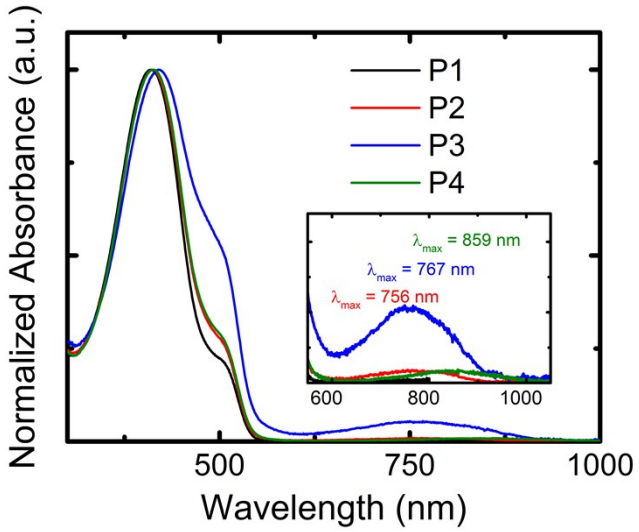


Figure S2 Absorption spectra for polymers **P1-4** in $CHCl_3$

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