



Photo- and electroluminescence of ambipolar, high-mobility, donor-acceptor polymers



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ABSTRACT

Donor-acceptor polymers with narrow bandgaps are promising materials for bulk heterojunction solar cells and high-mobility field-effect transistors. They also emit light in the near-infrared. Here we investigate and compare the photoluminescence and electroluminescence properties of different narrow bandgap (<1.5 eV) donor-acceptor polymers with diketopyrrolopyrrole (DPP), isoindigo (IGT) and benzodipyrrolidone (BPT) cores, respectively. All of them show near-infrared photoluminescence quantum yields of 0.03–0.09% that decrease with decreasing bandgap. Bottom-contact/top-gate field-effect transistors show ambipolar charge transport with hole and electron mobilities between 0.02 and 0.7 cm² V⁻¹ s⁻¹ and near-infrared electroluminescence. Their external quantum efficiencies reach up to 0.001%. The effect of polaron quenching and other reasons for the low electroluminescence efficiency of these high mobility polymers are investigated.

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1. Introduction

Donor-acceptor polymers based on diketopyrrolopyrrole (DPP) and other large core units (e.g. indigo, isoindigo, cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, indaceno[1,2-*b*:5,6-*b'*]dithiophene) have attracted considerable attention over the past few years [1]. Due to the donor-acceptor hybridization of alternating electron-rich and electron-poor repeat units and the extended HOMO and LUMO distribution along their backbone these polymers exhibit a narrow bandgap (HOMO-LUMO gap) of less than 1.5 eV. Consequently, they were initially pursued for their ability to absorb near-infrared light as the donor layer in bulk heterojunction photovoltaic cells [2]. Many of these semiconducting polymers also show field-effect mobilities above 1 cm² V⁻¹ s⁻¹ despite a lack of significant long-range order [3]. The origin of the high carrier mobility appears to be the reduction of torsional freedom and thus nearly disorder-free transport [4]. Due to their narrow bandgap and low-lying LUMO levels these polymers often show not only hole but also electron transport with comparable mobilities [5], which makes them

interesting candidates for ambipolar and also light-emitting field-effect transistors (LEFETs) [6]. Ambipolar LEFETs combine the high current and charge carrier densities of field-effect transistors with the emission properties of light-emitting diodes. However, due to their planar structure they allow for spatial control of the emission zone, complete recombination of holes and electrons in a single layer and thus maximized quantum efficiencies [7–9].

Although the photophysical properties of donor-acceptor polymers have been studied extensively with regard to absorption, exciton generation and charge separation [10], their properties as near-infrared (NIR) light emitters have only recently been considered for NIR light-emitting diodes [11–13]. Near-infrared light has many applications from telecommunication, night-vision to biological imaging. However, efficient organic NIR emitters, especially beyond 900 nm, are scarce. While there are many highly efficient organic emitters for visible light a significant drop of photoluminescence yield is observed for molecules that emit at wavelengths above 700 nm [14] and alternative solution-processable NIR emitters such as quantum dots and carbon nanotubes may need to be used [15–17]. High mobility polymers would be attractive for LEFETs if they could combine their high carrier mobilities with high emission efficiencies in order to achieve maximum exciton density and brightness [12,18,19]. The high

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mobilities found for many donor-acceptor polymers are promising but their emission properties are yet unknown.

Here we investigate the photoluminescence and electroluminescence properties of four exemplary donor-acceptor polymers (DPPT-TT, DPPT-BT, IGT-T and BPT-T) as shown in Fig. 1. All of these semiconducting polymers exhibit ambipolar charge transport with good mobilities [3,5,20,21]. They have different optical bandgaps and different donor and acceptor units that may change their emission properties. We use ambipolar LEFETs in a bottom-contact/top-gate geometry to obtain electroluminescence spectra and external quantum efficiencies (EQE) for these polymers at high current densities and find a strong dependence of photoluminescence (PL) and electroluminescence (EL) efficiencies on the HOMO-LUMO gap of the polymer. We discuss fast non-radiative decay and polaron quenching as possible origins for the observed low electroluminescence efficiencies.

2. Experimental

2.1. Materials

The semiconducting polymers DPPT-TT (poly(2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)diketopyrrolo[3,4-c]pyrrole-1,4-dione-*alt*-thieno[3,2-*b*]thiophene), $M_n = 23$ kg/mol, $M_w = 87$ kg/mol) and DPPT-BT (poly(2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)diketopyrrolo[3,4-c]pyrrole-1,4-dione-*alt*-benzo[*c*]1,2,5-thiadiazole), $M_n = 33$ kg/mol, $M_w = 87$ kg/mol) were purchased from Flexink Ltd. IGT-BT (poly((*E*)-4,4'-bis(2-octyldodecyl)[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'-dione-*alt*-benzo[*c*]1,2,5-thiadiazole), $M_n = 40$ kg/mol, $M_w = 60$ kg/mol) and BPT-T (poly(1,5-bis(2-octyldodecyl)-3,7-di(thiophen-2-yl)pyrrolo[2,3-*f*]indole-2,6-dione-*alt*-thiophene), $M_n = 34$ kg/mol, $M_w = 57$ kg/mol) were synthesized as described previously [20,21].

2.2. Film characterization

Polymer films and solutions were prepared as detailed in [supplementary information S1](#). Absorption spectra of thin films and solutions were recorded with a Cary 6000i UV/Vis/NIR absorption spectrometer (Varian). Near-infrared photoluminescence (PL) spectra were recorded with an Acton SpectraPro SP2358 spectrometer (grating 150 lines/mm) and a liquid nitrogen-cooled InGaAs line camera (PI Acton OMA V:1024 1.7). For PL quantum yield (QY) measurements a 785 nm laser beam was directed through the entrance port of an integrating sphere (Spectralon

coating) while polymer solutions in quartz cuvettes and thin film samples, respectively, were positioned in the center of the sphere. Quantum yield measurements were performed according to DeMello et al. [22]. The scattered laser light and PL signal were fiber-coupled to the spectrometer. Emission spectra were compared to PL spectra measured outside the sphere to account for reabsorption/reemission effects in the integrating sphere [23]. To verify the reliability of our QY measurements, we also estimated the QY of a well-known near-infrared standard IR-26 Dye (Acros Organics) in 1,2-dichloromethane. The obtained value of 0.15% was at the upper limit of reported values [24,25]. EL and PL spectra were corrected against the response of the detection system with a calibrated tungsten halogen lamp.

2.3. Light emitting transistor characterization

Bottom-contact (Cr/Au)/top-gate (Ag) field-effect transistors on glass with a PMMA or a hybrid (PMMA/HfO₂ [26]) dielectric were used. Detailed information about device fabrication can be found in the [supplementary information S1](#). Current-voltage characteristics were recorded with an Agilent 4156C Semiconductor Parameter Analyzer or a Keithley 2612A source meter. Gate dielectric capacitances were measured with an Agilent E4980A Precision LCR Meter.

Electroluminescence images were recorded with a thermoelectrically cooled 256 × 360 pixel InGaAs camera (Xenics XEVA-CL-TE3, 800–1600 nm). PL and EL spectra were obtained with the same spectrometer as described above. For PL measurements a 640 nm (20 mW) or a 785 nm (10 mW) laser diode (OBIS, Coherent Europe B.V.) were used for excitation. The laser was focussed onto the channel area through a near-infrared ×50 or ×100 objective (Olympus LCPLN50XIR, NA 0.65 with correction collar or LMPlan100XIR, NA 0.8), which also collected PL/EL emission. A cold mirror (750 nm) and a long-pass filter rejected scattered laser light. All PL and EL spectra were smoothed and normalized.

The total light output in the near-infrared was measured with a calibrated InGaAs photodiode (Thorlabs FGA21-CAL, active area 3.1 mm²) positioned underneath the transistor to enable collection of most of the emitted light. The silver gate electrode acted as a back mirror. The external quantum efficiency (EQE) defined as the number of outcoupled photons divided by the number of injected charges was calculated from the maximum photocurrent I_{diode} of the photodiode (at 0 V bias) during a sweep of the gate voltage for constant drain current (I_d) according to:

$$EQE = \frac{I_{diode}}{I_d} \cdot \frac{\int EL_{norm}(\lambda) d\lambda}{\int S(\lambda) \cdot EL_{norm}(\lambda) d\lambda} \cdot \frac{e}{hc} \cdot \frac{\int \lambda \cdot EL_{norm}(\lambda) d\lambda}{\int EL_{norm}(\lambda) d\lambda} \quad (1)$$

with $S(\lambda)$ as the wavelength-dependent sensitivity of the photodiode weighted by the normalized $EL(\lambda)$ spectrum of the respective polymer.

3. Results and discussion

3.1. Photoluminescence

For basic characterization the absorption spectra of dilute solutions, as-spun and annealed films were recorded (see [supplementary information S2](#)) but did not change much for any of the polymers. The absorption onset in solution was blue-shifted compared to the films in all cases, as is common for conjugated polymers. Yet, the shift was minimal and indicates either only small conformational changes of the polymer backbones from solution to the solid state or just increased π - π -stacking. In addition, DPPT-TT

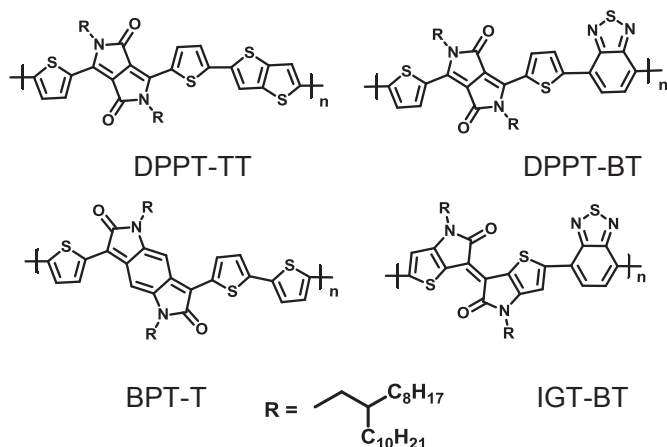


Fig. 1. Molecular structures of DPPT-TT, DPPT-BT, BPT-T and IGT-BT.

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