

PCDTBT: From polymer photovoltaics to light-emitting diodes by side chain-controlled luminescence

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ABSTRACT:

Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT) is a copolymer composed of alternating thiophene-benzothiadiazole-thiophene (TBT) and carbazole (Cbz) repeat units widely used for stable organic photovoltaics. However, the solubility of PCDTBT is limited, which decreases polymer yield and makes synthesis and purification tedious. Here, we introduce a strategy to increase both solubility and luminescence by the statistical incorporation of additional hexyl side chains at the TBT unit (hex-TBT). An increasing amount of hex-TBT as comonomer from 0 to 100% enhances solubility, leads to backbone torsion and causes a blueshift in the absorption and emission spectra. While photovoltaic performance of both PCDTBT:P3HT blends and PCDTBT:PC₆₁BM blends decreases with increasing content of hex-TBT due to weaker and blue-shifted absorption, the luminescence properties can be systematically improved. Both photo- and electroluminescence (PL and EL) quantum efficiencies increase with increasing hex-TBT content. We further demonstrate solution-processed red polymer light-emitting diodes based on fully hexylated PCDTBT showing an EL quantum efficiency enhancement of up to 7 times and two orders of magnitude enhancement of brightness compared to standard PCDTBT. Fully hexylated PCDTBT shows a peak external quantum efficiency of 1.1% and a peak brightness of 2500 cd/m².

INTRODUCTION

Printed electronics have gathered considerable attention in academia and industry due to the possibility of low-cost, high-throughput manufacturing of flexible, light-weight and large-area optoelectronic devices such as organic field-effect transistors (OFET), organic photovoltaic cells (OPV) and organic light-emitting diodes (OLED).¹⁻³ To date, improved device performances have enabled this carbon-based technology to compete with its inorganic silicon-based counterpart in certain applications.^{4,5} Processability from solution essentially relies on solubilizing groups, whereby usually long, linear or branched alkyl side chains are attached to the rigid conjugated polymer backbone. While not only providing solubility, the side chains additionally influence film formation, structure formation, backbone torsion due to steric constraints,^{6,7} and backbone electronics *via* their donating or accepting character.^{8,9} Moreover, side chain engineering can also enable orthogonal processability for solution-based layer-by-layer deposition of optoelectronically active materials with complementary function,¹⁰⁻¹³ and therefore can drastically impact the optoelectronic properties of the resulting material. In addition, the position at which the side chains are attached to the conjugated backbone¹⁴ as well as the length and shape of the chain¹⁵ play an important role. Intramolecular interactions resulting from sterical hindrance between adjacent aromatic units generate backbone torsion, which is considered to be detrimental to electronic properties. For the biphenyl unit it was shown that the sterical interaction between two hydrogen atoms significantly prevents the aromatic rings from coplanarity, whereas a bithiophene unit is able to arrange almost coplanar.^{16,17} On those grounds, special attention on careful choice of appropriate side chains has to be paid.^{18,19}

The low-bandgap and thermally stable copolymer poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-

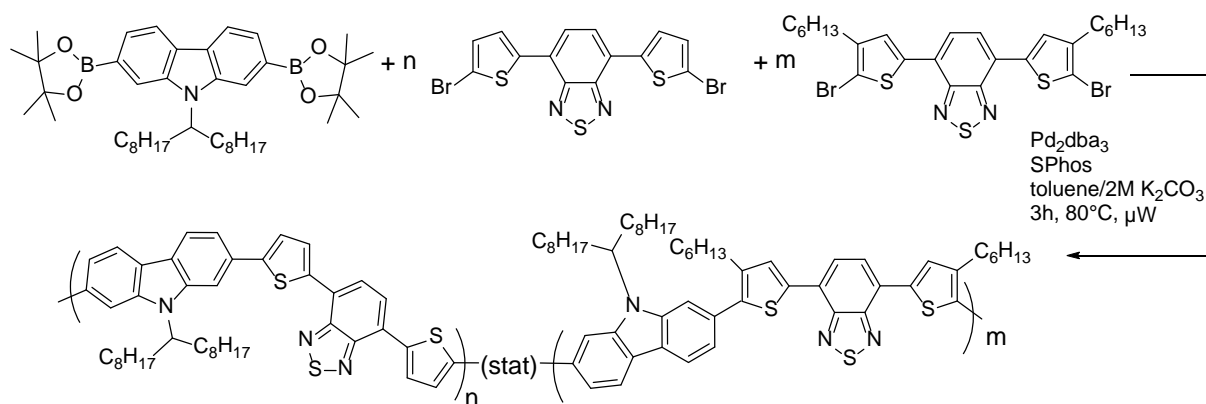
5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) has extensively been used in photovoltaic devices. The low lying HOMO level results in relatively high open-circuit voltages of about 0.9 V in combination with fullerene acceptors. Power conversion efficiencies (PCEs) of up to 7.9%²⁰ with fullerenes as acceptors, and solar cell operation lifetimes of up to 7 years have been reported.²¹ Also beneficial for charge injection is a face on orientation of the PCDTBT backbone in as-cast films.²² Due to the low-lying HOMO level of 5.5 eV, PCDTBT exhibits ambipolar character and can also be used as acceptor material in combination with strong donors such as P3HT.²³ Recently, we have shown that PCDTBT is prone to carbazole (Cbz) homocoupling defects which add to the two most important parameters molecular weight and dispersity.²⁴ Another crucial characteristic of PCDTBT is its limited solubility. This renders control over polymer yield, reproducibility and molecular weight (MW) to be difficult to achieve as a consequence of precipitation during polymerization, which in turn arises from the otherwise beneficial planarity of the backbone and the absence of solubilizing side chains at the TBT repeat unit.²⁵

Here, in order to balance solubility and planarity, we have synthesized a series of PCDTBT materials with additional and increasing amount of side chains at the thiophene units to investigate their effect on solubility, molecular weight as well as thermal, optical and electronic properties. While solar cell performance of PCDTBT:PCBM and PCDTBT:P3HT devices deteriorates with increasing side chain density, both photoluminescence (PL) and electroluminescence (EL) efficiencies are significantly improved with increasing hex-TBT content which, based on quantum chemical calculations, results in increased backbone torsion. Concomitantly, OLED brightness strongly increases as well, with hex-PCDTBT, which is the

fully hexylated analog of PCDTBT, exhibiting an EL quantum efficiency enhancement of up to 7 times compared to standard PCDTBT.

RESULTS AND DISCUSSION

A series of PCDTBT-based copolymers with increasing statistically incorporated hexyl side chain density was prepared *via* Suzuki polycondensation (SPC) by varying hexyl-substituted (hex-TBT) and unsubstituted TBT monomer feed ratio (Scheme 1) copolymerized with a Cbz comonomer. The use of microwave-assisted heating allowed short reaction times and high yields as reported recently by our group.^{26,27} The copolymers are referred to as **PX**, where X specifies the percentage of hex-TBT. **P0** refers to the classical PCDTBT with unsubstituted TBT repeat units and **P100** to hex-PCDTBT in which all TBT units are equipped with an *n*-hexyl group. **P100** has also been made recently using direct C-H activation polycondensation.²⁸



Scheme 1. Synthesis of PCDTBT with statistical incorporation of hexylated TBT.

While the chloroform fraction of **P100** exhibits excellent solubility in chloroform, **P0** dissolves slowly even at elevated temperatures. We found a strong, almost linear correlation between the

side chain density and the determined MWs of the chloroform fraction after purification and Soxhlet-fractionation (Table 1 and Figure S1).

Table 1. Overview of SEC data and optical parameters; *determined from SEC; #determined via absorption edge of thin film absorption spectra; §determined by UPS.

Polymer	M_n^* [kg/mol]	M_w^* [kg/mol]	D^*	T_g [°C]	Yield [%]	Abs _{max} [nm]	Em _{max} [nm]	$E_g^{\#}$ [eV]	HOMO [§] [eV]
P0	13.2	17.6	1.33	127	89	569	731	1.89	-5.34
P30	15.2	21.3	1.40	113	87	557	725	1.91	-5.38
P40	16.8	24.6	1.46	---	92	552	---	1.93	---
P50	20.5	34.9	1.70	111	93	551	712	1.96	-5.43
P60	23.7	52.0	2.19	---	92	540	---	1.98	-5.45
P70	24.2	54.2	2.24	---	89	535	---	2.00	---
P80	25.8	59.9	2.32	97	96	533	699	2.02	-5.48
P90	28.5	64.8	2.27	---	91	529	---	2.03	---
P100	42.6	87.6	2.06	93	93	523	669	2.05	-5.54

A quantitative incorporation of the TBT/hex-TBT feed ratio into the copolymer backbone could be confirmed by ¹H NMR spectroscopy (Figure S2). Thermal analyses, i.e. differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), revealed a lower glass transition temperature T_g for the hexyl-substituted derivatives. While **P0** shows a T_g of 127 °C, **P100** exhibits a glass transition temperature of 93 °C only. **P30**, **P50** and **P80** show a T_g of 113 °C, 111 °C and 97 °C, respectively (Table 1 and Figure S3). In addition, **P0** exhibits melting point T_m at 237 °C with a small melting enthalpy ΔH_m of 0.38 J/g, whereas melting transitions were not

detected for the other polymers. Thermogravimetric analysis did not show degradation of the polymers up to 400°C under an inert nitrogen atmosphere, as shown for **P0** and **P100** (Figure S4).

The absorption spectra of the copolymers measured in chlorobenzene solution show a gradual blue shift and weakening of the charge-transfer band absorption upon hex-TBT incorporation (Figure 1). The absorption maximum is shifted by 46 nm from 569 nm for **P0** to 523 nm for **P100** (Figures 1, S5 and S6). The origin for the blue shift by about 0.16 eV was found to be the lowering of the HOMO energy level, i.e. an increased in ionization energy, from -5.34 eV for **P0**, -5.38 eV for **P30**, -5.43 eV for **P50** and -5.48 eV for **P80** down to -5.54 eV for **P100** (see also Figure S7). The blue shift in absorption is accompanied with a blue shift of the emission spectra. While **P0** exhibits a maximum in emission at 731 nm, the emission of **P100** is shifted by 62 nm to 669 nm.

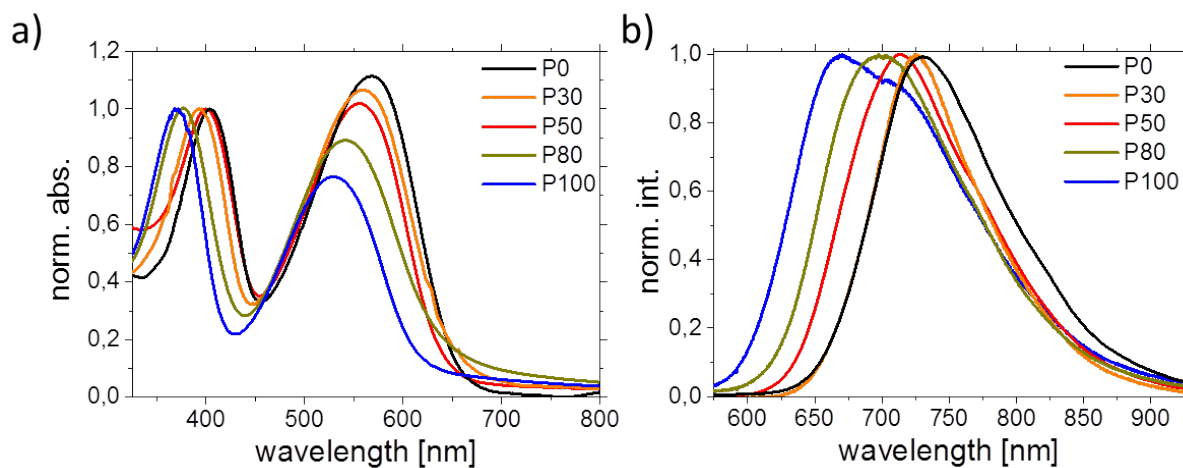


Figure 1. a) UV-vis absorption and b) emission spectra of the copolymers in chlorobenzene solution ($c = 0.02$ mg/ml).

A blue shift as well as a weakening of the CT band absorption upon increased hexyl side chain incorporation is clearly visible. Kim *et al.* reported a similar trend in absorption profile by investigating the polymers **P0** and **P100**.⁷ They claimed steric hindrance of the side chain and therefore weakened intramolecular interactions to be the origin of weakened absorption. Calculating torsion angles by density functional theory showed Cbz-TBT dihedral angles of 27° and 40 ° for **P0** and **P100**, respectively, when using methylated TBT as a model (Figure S8). Nevertheless, charge transport properties were reported to be unaffected by the presence of side chains, thus a tilted backbone. However, they did not test the performance of the polymers in optoelectronic devices such as OPV or OLED.

PCDTBT exhibits ambipolar properties and can be used as donor or acceptor material, depending on the complementary materials to be combined with.^{23,29,30} To investigate whether partially hexylated PCDTBT with enhanced yield and increased solubility exhibited similar performance compared to standard PCDTBT (**P0**), photovoltaic devices were fabricated using the set of PCDTBT as donor material in combination with PC₇₁BM as acceptor in a 1:4 ratio.³¹ *J-V*- and EQE-curves from PCDTBT:PC₇₁BM devices made in standard geometry (glass | ITO | PEDOT:PSS | polymer:PC₇₁BM | Al) are shown in Figure 2, OPV device characteristics are summarized in Table 2.

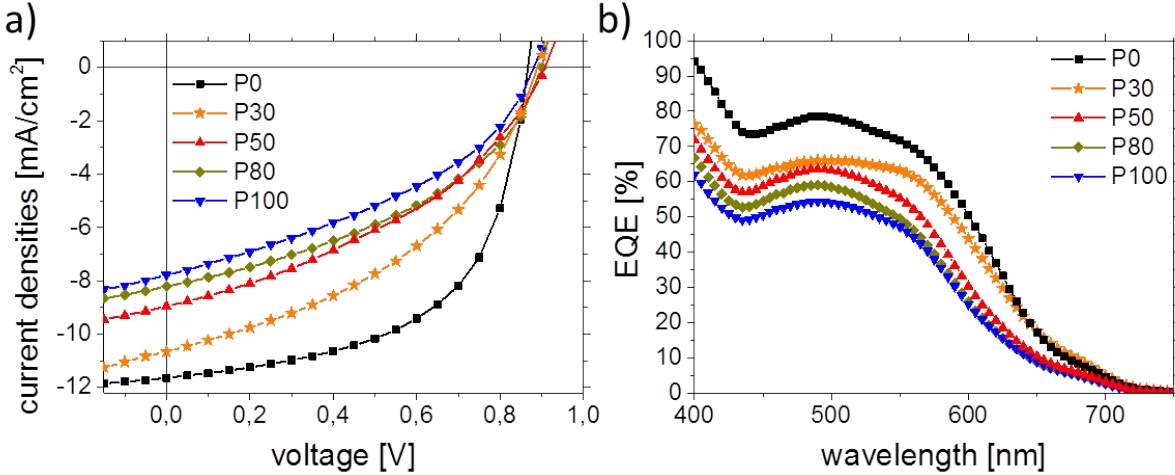


Figure 2. a) J - V - and b) EQE curves of OPV devices made from polymer:PC₇₁BM.

Table 2. OPV device characteristics of polymer:PC₇₁BM devices.

Polymer	Jsc [mA/cm ²]	Voc [V]	FF [%]	PCE [%]
P0	-11.66 ± 0.72	0.86 ± 0.03	55.2 ± 3.8	5.53 ± 0.59
P30	-10.65 ± 0.78	0.89 ± 0.02	39.3 ± 6.9	3.73 ± 0.71
P50	-9.14 ± 0.91	0.89 ± 0.02	37.5 ± 5.1	3.05 ± 0.46
P80	-8.26 ± 0.69	0.89 ± 0.04	41.0 ± 2.4	3.01 ± 0.50
P100	-7.81 ± 0.72	0.88 ± 0.02	38.5 ± 3.1	2.65 ± 0.61

A gradual decrease in the OPV power conversion efficiency (PCE) with increased degree of alkylation is observed. While the open-circuit voltage V_{OC} remains unaffected, both the short circuit current density J_{SC} and the fill factor FF decrease with increasing amount of hexylated TBT in the PCDTBT backbone. From the increasingly deeper HOMO level of hexylated PCDTBT a higher V_{OC} might have been expected, which is not the case. We speculate this experimental finding to result from an altered morphology, and therefore an altered interface in the active layer blend, due to the incorporation of additional side chains. In addition, different recombination dynamics in the bulk heterojunction as a consequence of a tilted polymer

backbone and thus more localized excitons for partially and fully hexylated PCDTBT might be another factor that cancels out the expected increase in V_{oc} of the respective OPV device. The short-circuit current densities as well as the fill factor are significantly affected by the incorporation of hexyl chains with J_{sc} values decreasing from -11.66 mA/cm^2 to -7.81 mA/cm^2 and FF values going from 55.2 % to 38.5 % for **P0** and **P100**, respectively. We explain the drop in J_{sc} primarily by the decreased CT band intensity in the absorption profile of the partially and fully hexylated polymers. However, as the FF is lowered at the same time, additional factors might be at play, which may arise from less efficient exciton diffusion to the interface and/or limited charge transport of free charges to the electrodes. The power conversion efficiencies (PCE) yield from 2.65 % for **P100** over 3.01 % (**P80**) and 3.05 % (**P50**) to 3.73 % (**P80**) and finally 5.53 % for **P0** underlining the negative influence of additional side chains attached to the thiophenes and the superior performance of the well-studied polymer PCDTBT. Although the MWs differ within the investigated series of polymers which potentially influence device performance, a clear trend can be extracted. For longer polymer chains, usually a better performance of OPV devices is found.^{24,25,32-35} We found this trend also for the terpolymers having the same composition but different MWs (Figure S9). Thus, the effect of additional hexyl side chains on the decrease of OPV performance is strongest. Using a P100 sample with comparable MW leads to even lower performance, which increases the discrepancy between P100 and P80 as shown in Figure 2 and Figure S9.

In addition, photovoltaic diodes using the set of PCDTBT-based polymers were tested in all-polymer solar cells combination with P3HT. In such a combination, PCDTBT acts as the electron acceptor with P3HT as donor counterpart. Previously, we observed that usage of a

hexylated TBT monomer in both PCDTBT^{29,30} as well as PF8TBT³⁶ prevents microphase separation in their corresponding block copolymers with P3HT. As the standard PCDTBT (**P0**) without side chains at the TBT repeat unit is poorly soluble with complicates processability especially for larger molecular weights²⁵, we envisioned that balancing the amount of hexyl side chains could lead to a controllable phase separation and hence domain size of PCDTBT:P3HT blends, with significantly increased solubility at the same time. Indeed, in thermally annealed thin films, AFM analysis indicated that domain sizes of ~1-2 μm were found for **P0**:P3HT films, which gradually decreased with increasing hex-TBT content. **P100**:P3HT as the other extreme showed smooth films with no discernible domain size, indicating enhanced miscibility (Figure S10). However, OPV device performance of all **PX**:P3HT blends was very poor, and hence this system was not further investigated with respect to solar cells (Figure S11 and Table S2).

Surprisingly, we observed that the photoluminescence quantum efficiency (PLQE) of PCDTBT strongly increased as the side chain content increases. Raising the side chain density from 0 % to 100 % enhanced the PLQE of spin-cast polymer films by about 3 times, from 6 % to 18 % (Figure 3a). This finding suggests that the classical PCDTBT made for photovoltaic applications may be transformed into a light-emitting polymer by a simple and straightforward side-chain engineering approach. We prepared solution-processed polymer OLEDs using a multi-layer structure (ITO/PEDOT:PSS/TFB/PCDTBT/TPBi/LiF/Al). For standard PCDTBT (**P0**), the maximum external quantum efficiency (EQE) was only 0.16 %. This value increased with increasing hex-TBT content. For hexyl PCDTBT with maximum side chain content (**P100**), the peak EQE was 1.1 % (Figure 3a and Table 3), showing efficient operation for a conventional fluorescent OLED. Detailed EQE versus current density curves are shown in Figure 3b.

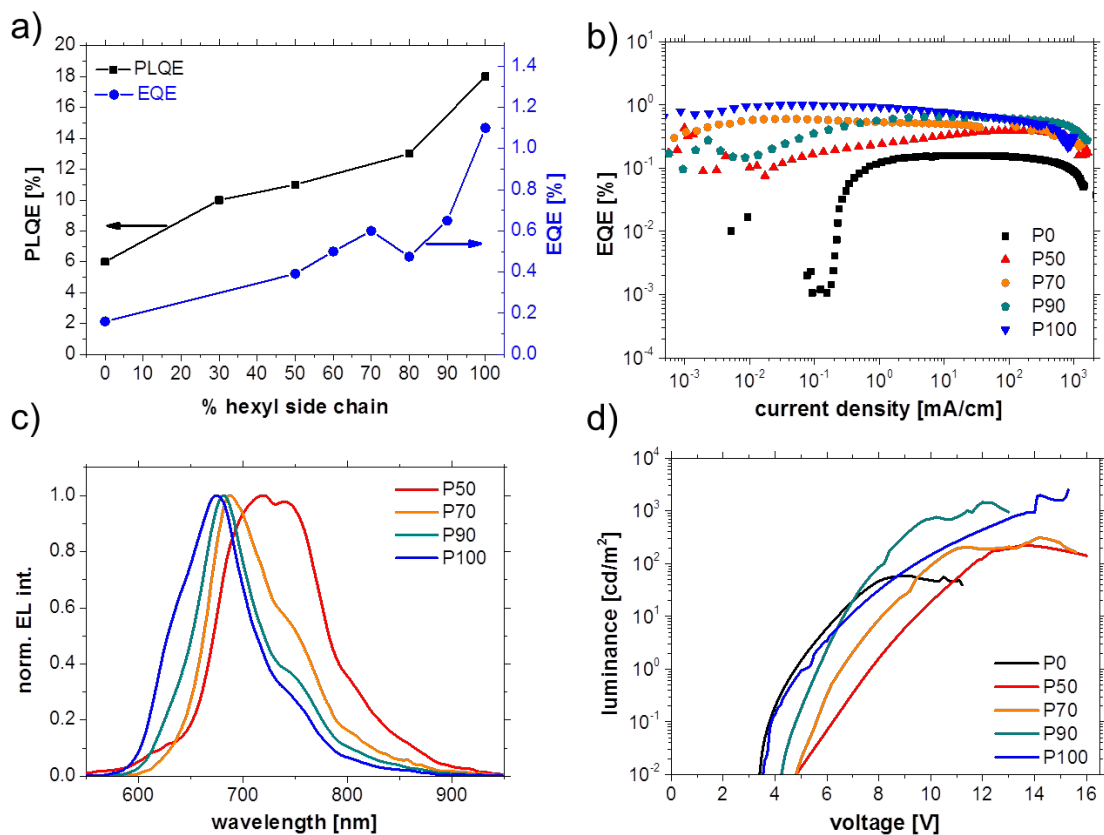


Figure 3. Luminescence characteristics. a) PLQE of thin films and EQE of devices with different polymer side chain content. b) EQE versus current density curves. c) EL spectra. d) luminance-voltage curves.

Table 3. Summary of device efficiency and luminance for polymers with various side chain content.

Polymer	Peak EQE	Max Luminance
	[%]	[cd/cm ²]
P0	0.16	60
P50	0.39	220
P60	0.50	280
P70	0.60	310
P80	0.48	425

P90	0.65	1460
P100	1.10	2500

The excellent stability of PCDTBT under OLED operation conditions (for both standard and hexyl) is reflected in the minimum efficiency roll-off at current densities of up to 10^3 mA/cm². At low current densities (<1 mA/cm²) the EQE is significantly lower for polymers with lower side chain densities. In contrast, devices made with side chain-rich polymers exhibit flatter EQE curves across a wider range of current densities (Figure 3b), indicating improved charge balance under these conditions. Similar to absorption and photoluminescence, a blue-shift of electroluminescence is observed for polymers with higher side chain densities (Figure 3c). The improved EQE and the blue-shifted emission of hexyl PCDTBT increase the luminance of the devices. Two orders of magnitude enhancement of brightness is observed when comparing the polymer with maximum side chain content to the standard PCDTBT (Figure 3d). A peak luminance of 2500 cd/m² is achieved for the brightest polymer (Table 3). The turn-on voltages of these devices do not follow the trend as one would expect from the matching of the HOMO levels of the emissive polymers with that of the TFB (5.3 eV). We speculate that this could be related to an improvement of interfacial quality between the higher-molecular weight, side chain-rich **P100** with the TFB. The EQE (1.1%) of our best hexyl PCDTBT (**P100**) OLED is still lower compared to the most efficient fluorescent red polymer OLEDs whose peak EQEs are 2.3% for a single polymer emitter, and 5.5% for a host-dopant-type polymer blend.^{37,38} However, we note that the slow efficiency roll-off under higher currents enabled by our stable hexyl PCDTBT polymers offers a potential advantage, and we expect the EQE and brightness to improve further when the emissive properties (PLQEs) of our polymers are fully optimized.

As demonstrated above, increasing the side chain density results in improved LED performance, while the efficiency of polymer:fullerene solar cells is reduced at the same time. Considering that the addition of side chains introduces backbone torsion and thus localization of excitons, side chain engineering may be used as a general design principle in conjugated polymers for light-emitting applications. Strongly localized excitons are detrimental for organic photovoltaics, where exciton delocalization is desirable to increase the probability for their subsequent dissociation into free charge carriers. In contrast, for OLED operation, localized excitons undergo radiative recombination more efficiently, possibly assisted by their hindered migration to luminescence-quenching sites due to the higher density of side chains and more balanced charge transport. Further optimization of OLED performance may be achieved by fine-tuning device architecture and OLED preparation as well as further variation of the nature of side chains.

CONCLUSION

In this work, we have studied a series of PCDTBT derivatives with systematically varied hexyl side chain density at the TBT comonomer. Solubility is drastically increased with increasing side chain density. Both absorption and emission blue shift as a result of increased backbone torsion, which weakens the intramolecular CT transition. Organic solar cells using a series of PCDTBT derivatives with consistently varied side chains density show decreased performance with higher hexyl chain density compared to the classical PCDTBT with un-substituted TBT units as a result of reduced absorption and likely reduced exciton diffusion. However, the luminescence properties have a strong positive dependence on side chain density, leading to strongly enhanced PL and EL quantum efficiencies. We have shown that solution-processed polymer red light-emitting diodes based on hexyl-PCDTBT (**P100**) exhibit an EL efficiency enhancement of up to

7 times compared to standard PCDTBT (**P0**), a peak external quantum efficiency of 1.1 %, and a peak brightness of 2500 cd/m². The increased torsion the polymer backbone due to a higher side chain density is beneficial for exciton localization, which improves the luminescence performance. Further optimization may be achieved by fine-tuning device architecture, preparation as well as further variation of the nature of side chains. Our results show that a photovoltaic polymer can be tailored into a light-emitting polymer by side-chain engineering.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge via the Internet at <http://pubs.acs.org>. Materials, Experimental Details, Figure S1-S12, and Tables S1-S3.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡ Florian Lombeck and Dawei Di contributed equally to the preparation of this manuscript.

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Table of contents figure TOC

