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PAPER

A straightforward route to electron transporting conjugated polymers†

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We report a straightforward synthetic method to generate solution processable electron transporting polymers with low band gap and wide absorption range from readily available acceptor monomers. We show the efficacy of this approach using widely used electron acceptor 2,1,3-benzothiadiazole. The polymers have absorption up to 750 nm with electron mobility comparable to PCBM.

Electron transporting polymers with wide absorption are needed in all polymer solar cells to achieve maximum absorption in the solar spectrum.¹⁻⁹ Currently, the electron transporting conjugated polymers that are widely used in all polymer solar cells are limited to poly(benzimidazobenzophenanthroline (BBL), poly[2methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene) phenylene] (CN-PPV) and rylene diimide based polymers.^{1-6,10,11} In addition to the wide absorption window, optimal frontier energy levels offset and a balanced charge transport between hole and electron transporters is also needed to achieve maximum photovoltaic efficiency.^{5,6,12} However, at present time, there are not many π conjugated electron transporters to complement and exploit the existing wide variety of hole transporting polymers for solar energy conversion.^{1-3,13-15} Thus, there is a need for a synthetic strategy to rapidly generate electron transporting π -conjugated solution processable polymers from readily available monomers.

Recently, there has been a widespread interest in developing donor-acceptor polymers for lowering the band gap and widening the absorption window of hole transporting polymers.^{1-3,13-19} This has resulted in a wide-array of acceptor moieties. Conjugated homopolymers of an acceptor unit could be electron transporting with interesting optoelectronic properties.²⁰⁻²⁴ But, not many of them are synthesized because the synthesis is specific to a few monomers and cannot be readily extended to other acceptor monomers. Moreover, most of the conjugated homopolymers of an acceptor monomer have high band gap, narrow absorption range and low solubility in common organic solvents.²²⁻²⁴ Although a conjugated alternating copolymer of two acceptor monomers was reported recently,²¹ at the present time, there is no general strategy to generate solution processable, low band gap conjugated polymers of a single acceptor monomer. Herein, we report a straightforward synthetic route *via* Stille coupling to generate solution processable low band gap conjugated polymers from readily available acceptor monomers. We demonstrate the efficacy of our approach using widely used electron acceptor, 2,1,3-benzothiadiazole and commercially available *trans*-1,2-bis(tri-*n*-butylstannyl)ethylene. The polymer shows electron mobilities that are comparable to that of phenyl-C₆₁-butyric acid methyl ester (PCBM),^{25,26} the widely used electron transporter in organic solar cells. We believe that our method can be readily extended to a wide array of acceptor monomers to rapidly generate electron transporting polymers.

We chose 2,1,3-benzothiadiazole as our monomer and electron accepting moiety because of the ready availability of the monomer as it is widely used to synthesize donor–acceptor alternating conjugated copolymers.^{2,3,16–19} **PBTDV1** and **PBTDV2** (poly-(benzothiadiazole vinylene)) were synthesized through a Stille coupling²⁷ of dihalo 2,1,3-benzothiadiazole and *trans*-1,2-bis(tri*n*-butylstannyl)ethylene (Fig. 1 and 2). The synthesis of monomers **1** and **3** is shown in the ESI.^{†18} The synthesis of **3** from **2** was not successful under commonly employed iodinating conditions (see ESI, Table S1[†]) and required mild and active iodinating conditions.

After screening various conditions for polymerization (see ESI, Tables S3 and S4[†]), we found that the polymers with desired molecular weights can be obtained if $Pd(PPh_3)_4$ was a catalyst. We found no appreciable differences in the molecular weight or



Fig. 1 Chemical structures of the polymers synthesized in this study and their solution in chloroform.

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[†] Electronic supplementary information (ESI) available: GPC, cyclicvoltammetry, WAXS, photocurrent transients data and synthesis of monomers and polymers along with the other attempted synthetic conditions are presented. See DOI: 10.1039/c2jm32217j



Fig. 2 Key steps in the synthesis of polymers.

the reaction time if the monomer was an aryl bromide or an aryl iodide. In order to probe the effect of the vinylene linker, we also synthesized conjugated polymers, PBTD1 and PBTD2 (poly-(benzothiadiazole)), containing 2,1,3-benzothiadiazole alone. Conjugated polymers made of a single electron deficient unit are rare and most of them are not solution processable.^{22,24} PBTD1 and PBTD2 are the first reported solution processable conjugated polymers containing 2,1,3-benzothiadiazole alone. These polymers were synthesized using a palladium-mediated Suzuki coupling of the benzothiadiazole dihalide monomer with the commercially available diborate BTD (Fig. 2). The Suzuki coupling, to yield polymers, required a binary or ternary solvent mixture, the highly active Pd('Bu₃P)₂ catalyst, and a strong base such as LiOH · H₂O. The solvents for the polymerization were chosen based on the activity of the catalyst and the solubility of the polymer in that solvent. In general, palladium catalysts are highly active in polar solvents such as di-n-butylether and conjugated polymers are soluble in 1,2-dichlorobenzene. The polymerization was not successful with less active but widely used Pd(PPh₃)₄ catalyst for Suzuki coupling (see ESI, Table S2⁺ for other attempted polymerization conditions). Much like in **PBTDV1** and **PBTDV2**, we did not find any significant difference in the reaction time if the monomer was an aryl bromide or an aryl iodide. The synthesis of PBTDV1 and PBTDV2 involves the condensation of a dihalo derivative of 2,1,3-benzothiadiazole with commercially available *trans*-1,2-bis(tri-n-butylstannyl) ethylene. Since dihalo derivatives of many acceptor monomers are already known, this strategy can be readily extended to a wide range of acceptor monomers.

The thin film UV-Vis absorption spectra of all the polymers are shown in Fig. 3. The thin films absorption range for **PBTD1** and **PBTD2** is 250–400 nm. The large band gap and narrow absorption range of these polymers might be due to the sterics between the neighbouring repeat units, leading to a twist and thereby disrupting the π - π conjugation along the polymer backbone, consistent with our expectation. **PBTDV1** and **PBTDV2** with the vinylene linkers have the absorption range of 250–735 nm with the absorption maximum around 580 nm and shoulders at 630 nm and 680 nm. The optical band gap of **PBTDV1** and **PBTDV2** was found to be 1.68 eV, which is 1.0 eV less than for **PBTD1** and **PBTD2** (Table 1). The lowering of the band gap clearly indicates that the vinylic spacer unit facilitates the reduction in sterics between neighboring benzothiadiazole units, and thus enhancing the π - π conjugation along the



Fig. 3 Thin film UV-Vis absorption spectra of polymers.

polymer backbone. There is also an increase in the absorption range of alternating polymers compared to their non-vinylene counterparts. We found that there was no appreciable difference between the solution and thin film absorption for all the polymers (ESI, Fig. S1[†]). The vinylene polymers, **PBTDV1** and **PBTDV2**, exhibit a vibronic structure in the absorption spectra of both solution and thin film. Since the presence of vibronic structure in the absorption spectrum is an indication of interchain π - π interactions,²⁸⁻³⁴ we believe that the vinylene polymer may be aggregating in solution. On the other hand, no vibronic structure was observed in the absorption spectra for **PBTD1** and **PBTD2** indicating the absence of inter-chain π - π interactions. This might be due to the twist in the polymer backbone caused by the sterics. Interestingly, the side chains have negligible effect on the optical properties of all the polymers.

The redox properties of the polymers are shown in Fig. S2⁺ and their frontier energy levels are determined using established protocols.35,36 The frontier energy levels, electrical and optical band gap values of the polymers are tabulated in Table 1. PBTD1 showed no oxidation peak thus, HOMOelec and LUMOopt cannot be determined. The vinylene polymers PBTDV1 and PBTDV2 are much easier to oxidize and reduce compared to **PBTD1** and PBTD2. This is expected because the charges in the vinylene polymers can be better stabilized because of the increased delocalization along the conjugated polymer backbone. This observation once again is consistent with the vinylic spacer unit facilitating the π - π conjugation along the polymer backbone by reducing the steric interactions between the neighboring repeat units. PBTDV1 and PBTDV2 have optimal frontier energy levels offset with respect to many low band gap hole conductors such as P3HT, PCPDTBT,¹⁹ PBDTTT-CF,³⁷ and PBnDT-FTAZ,¹⁷ making them promising candidates for use as electron conductors in all polymer solar cells (Fig. S6[†]). Wide angle X-ray scattering (WAXS) was recorded for the polymers and the data are shown in Fig. S3.† PBTD2 and PBTDV2 polymers with octyloxy side chains exhibit peaks at 2.25 nm and 2.28 nm, respectively. This distance correlates well with the expected octyloxy-octyloxy inter-chain distance. On the other hand, PBTD1 and PBTDV1 polymers exhibit peaks at 3.25 nm and 3.45 nm, respectively, which are smaller than the expected tetradecyloxy side chain packing distance of 4.3 nm. The simulation

$M_{\rm w}(M_{\rm w}/M_{\rm n})^a$ (kDa)	$E_{g}^{\mathrm{opt}}\left(\mathrm{eV} ight)$	$\lambda_{\max}^{\text{film}}$ (nm)	$\operatorname{HOMO}^{\operatorname{elec}}\left(\operatorname{eV}\right)^{d}$	$LUMO^{elec} (eV)^d$	LUMO ^{opt} (eV) ⁶
79.1 (1.2)	2.69	411	_	-2.93	_
16.2 (1.1)	2.69	396	-5.96	-3.03	-3.27
19.2 (1.8)	1.68	584 (633, 686) ^{c}	-5.45	-3.42	-3.77
15.0 (1.6)	1.68	579 (627 675) ^e	-5.24	-3.45	-3.59
	$\frac{M_{\rm w}(M_{\rm w}/M_{\rm n})^a \text{ (kDa)}}{79.1 (1.2)}$ 16.2 (1.1) 19.2 (1.8) 15.0 (1.6)	$M_w(M_w/M_n)^a$ (kDa) E_g^{opt} (eV) 79.1 (1.2) 2.69 16.2 (1.1) 2.69 19.2 (1.8) 1.68 15.0 (1.6) 1.68	$M_{\rm w}(M_{\rm w}/M_{\rm n})^a$ (kDa) $E_{\rm g}^{\rm opt}$ (eV) $\lambda_{\rm max}^{\rm film}$ (nm) 79.1 (1.2) 2.69 411 16.2 (1.1) 2.69 396 19.2 (1.8) 1.68 584 (633, 686)^c 15.0 (1.6) 1.68 579 (627 675)^c	$M_{\rm w}(M_{\rm w}/M_{\rm n})^a$ (kDa) $E_{\rm g}^{\rm opt}$ (eV) $\lambda_{\rm max}^{\rm film}$ (nm)HOMO^{\rm elec} (eV)^d79.1 (1.2)2.6941116.2 (1.1)2.69396-5.9619.2 (1.8)1.68584 (633, 686)^c-5.4515.0 (1.6)1.68579 (627 675)^c-5.24	$M_{\rm w}(M_{\rm w}/M_{\rm n})^d$ (kDa) $E_{\rm g}^{\rm opt}$ (eV) $\lambda_{\rm max}^{\rm film}$ (nm)HOMO ^{elec} (eV)^dLUMO ^{elec} (eV)^d79.1 (1.2)2.694112.9316.2 (1.1)2.69396-5.96-3.0319.2 (1.8)1.68584 (633, 686)^c-5.45-3.4215.0 (1.6)1.68579 (627 675)^c-5.24-3.45

^a GPC (THF) with respect to polystyrene standards. ^b Shows a small molecular weight peak in GPC (see ESI, Fig. S5†). E^{opt}_g: calculated from the onset of thin film UV-Vis absorption spectra. ^e Shoulders in absorption spectra. ^d Calculated from cyclic voltammetry. ^e Calculated from HOMO^{elee} + E^{ort}_{opt}.

of polymer packing on Cerius2 for the corresponding interchain packing indicated partial interdigitation between side chains (see Fig. 4). Side chain interdigitation is commonly observed in many semiconducting conjugated polymer packing.^{1,31,32,34,38} Side chain interdigitation decreases the distance between polymer backbones and can enhance the charge transport.

 Table 1
 Summary of physical properties of polymers

The electron mobilities of PBTDV1 and PBTDV2 are determined using time of flight (ToF) technique.³⁹ We chose ToF to measure the mobility because the charge transport occurs across the polymer film in a device configuration similar to organic



Fig. 4 Illustration of a simulated packing (using Cerius2) of the side chains in **PBTDV1**



Fig. 5 Time of flight electron mobilities of polymers as a function of the applied electric field.

the polymer solutions onto ITO coated glass slides followed by the thermal evaporation of aluminum on top of the polymer film. In ToF, a short laser pulse incident on a sample generates a thin sheet of charge carriers. Transit time (t_{TR}) , time to migrate the generated charge carriers across the sample under the influence of an applied electric field (E), is determined. The photocurrent transient of polymers (PBTDV1 and PBTDV2) at various applied fields is shown in Fig. S7[†] and the shape of photocurrent transit is characteristic of dispersive transport.³⁹ Charge carrier mobility (μ) was determined using the following equation: $\mu = L/(Et_{TR})$, where L is the film thickness. Electron mobilities of the polymers at various applied fields are shown in Fig. 5. PBTDV1 and PBTDV2 exhibit high electron mobilities of 10⁻³ cm² V⁻¹ s⁻¹, comparable to those of PCBM and F8BT thin films.^{25,26,40} A slight increase in the electron mobility was observed with a decrease in inter-chain distance from PBTDV1 (3.45 nm) to **PBTDV2** (2.25 nm). The dispersive charge transport is explained by a variation of local transport rates due to a high spatial and/or energetic disorder in the material.⁴¹ Each dataset is averaged over 128 photocurrent transients generated by the light pulses. In organic photovoltaics there should be a balance in charge transport between hole and electron transporters.⁴² The hole mobility of most of the conjugated polymers used in organic photovoltaics is on the order of 10^{-2} to 10^{-5} cm² V⁻¹ s⁻¹ making PBTDV1 and PBTDV2 excellent electron transporters for organic photovoltaic devices. In order to determine the hole mobilities, the polarity of the applied field was changed. However, negligible photocurrent transients were observed in this configuration, indicating that the hole mobility could be several orders of magnitude lower than the electron mobility.

photovoltaic devices. The samples were prepared by drop casting

In conclusion, we have shown that a poly(arylene vinylene) derivative of an acceptor unit such as 2,1,3-benzothiadiazole is a good electron transporter ($\mu_e \sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) with low band gap and broad absorption range (250-735 nm). Electron transporting properties of PBTDV1 and PBTDV2 indicate that the vinyl spacer indeed maintains the electron affinity of 2,1,3benzothiadiazole unlike other donor-acceptor polymers^{2,3,16-19} of 2,1,3-benznothiadiazole that exhibit hole transporting properties. Moreover, the vinyl spacer also reduces the band gap and widens the absorption range of PBTDV1 and PBTDV2 compared to the conjugated homopolymers of 2,1,3-benzothiadiazole (PBTD1 and PBTD2). The synthesis of PBTDV1 and PBTDV2 involves the condensation of a dihalo derivative of 2,1,3-benzothiadiazole with commercially available trans-1,2bis(tri-n-butylstannyl)ethylene. Since dihalo derivatives of many acceptor monomers are already known, this strategy can be readily extended to a wide range of acceptor monomers to

generate solution processable electron transporting polymers with low band gap and wide absorption range.

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