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Effects of Different Bridges of A Series of c-Donor-nc-Bridge-cf-Acceptor Type Block Copolymers for Potential Solar Cell Applications

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Abstract: A series of c-D-nc-B-cf-A (or DBpfA, p=0,1,2,4,6) type of block copolymers has been designed, synthesized, and systematically studied for photo induced charge separations; where c-D is an electron-donating conjugated block, nc-B is a non-conjugated bridge unit, and cf-A is an electron-accepting conjugated and fluorinated block. A series of photoluminescence quenching measurements with and without different bridge units were evaluated for DBpfA. This study highlights the chemical molecular bridge effects on the optoelectronic property of the DBpfA type block copolymer. Specifically, the DB_1fA block copolymer (where only one methylene unit is present in the bridge unit) appears exhibiting the best optoelectronic performance. DfA block copolymer (without any bridge unit) exhibits photoluminescence quenching and optoelectronic property that is between the shortest and longest bridge units, and this can be explained by the calculated four stable state twisting angles (most stable state is at a seventeen degree twist) between conjugated donor and conjugated acceptor blocks. The optoelectronic properties appear following the PL quenching nicely.

Keywords: Conjugated donor and acceptor blocks, bridges, donor-acceptor interfaces, photo induced charge separations, optoelectronics, energy conversion, solar cells.

INTRODUCTION

Organic molecular photo induced charge separation based on an electron donor and acceptor for bi-layer – hetero- junction solar cell was reported in 1986 [1]. Polymeric materials based on electron accepting and donating conjugated block copolymers are very attractive in a range of polymer based optoelectronic applications such as photo detectors, solar cells, *etc* [2]. Fast photo induced charge separation and slow charge recombination rates are essential on power conversion efficiency (PCE). Polymer based optoelectronic devices exhibit inherent advantages such as lightweight, low-cost, and flexibility [3-4]. It has been established that polymer photoelectric process includes major or at least five critical steps: 1) photon absorption and Frenkel type exciton generation; 2) exciton diffusion toward an electron donor/acceptor interface; 3) exciton dissociation at the electron donor/acceptor interface or charge carrier generation; 4) charge carrier transport towards their respective electrodes; and 5) charge collection at the electrodes [2-3]. In addition, higher absorption coefficients (as compared to inorganics) have been observed in organic and polymeric semiconductors, therefore it opens up vast opportunities for the manufacture of extremely thin solar sheets or films to save large number of materials in a production [5]. Where conjugated donor and acceptor blocks are covalently attached by non-conjugated bridge chain it is expected that different donor and acceptor blocks could incur phase separation on the nanometer scale. This kind of ordered material has already been known in many block copolymers [6]. It was also known that there were no stable photo induced charge separations in many D/A co-polymers where the both blocks (donor & acceptor) are directly and covalently linked without any non-conjugated bridges and without any twists, possibly due to the ultra-fast charge recombination [7]. Fundamental questions are: what is an optimal chemical structure and what is the role of the bridge in a DBA type block copolymer where the photo induced charge separation is fast but charge recombination is slow.

In a donor-bridge-acceptor (or DBA) type of block copolymer system [8-9], photo excited electron (via step 1) are being transferred from the D to A via the bridge unit B (step 2), and that the charge recombination of step 3 is typically much slower than steps 1 and 2 [3]. Several factors could affect the process, such as photo induced electron transfer (or exciton dissociation) rates, or electron transfer driving and counter-driving forces in energy domain, electron transfer associated molecular reorganization energies, distances and molecular shapes between the charge transfer units [3, 10-12]. Here we report the design and synthesis of a series of DBpfA, where the bridge unit B varies from six methylene units down to zero methylene unit (DfA). Such systems could enable an

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opportunity to study the correlation of photo induced charge separation versus bridge unit size.

EXPERIMENTAL

Starting Materials, Instrumentation, and General Methods

All reagents, starting chemicals and solvents were purchased from commercial sources (Sigma-Aldrich, Fisher-Scientific and VWR) and were used without further purification unless noted otherwise. A Bruker (USA) Advance 300MHz spectrometer with TMS as the internal reference was used to obtain NMR spectra. UV-Vis spectra were measured on a Perkin Elmer Lambda 1050 Spectrophotometer (USA). Differential scanning calorimetric (DSC) and thermal gravimetric analysis (TGA) data were collected on Perkin Elmer DSC- 6 and TGA-6 systems (USA). Elemental analyses results were measured at Atlantic Microlab Inc (USA). An ISA Flouromax-3 luminescence spectrofluorometer (USA) was used to measure photoluminescence experiments in solution (THF).

Cyclovoltammetry (CV)

Electrochemical studies were performed on a Bio-analytical (BAS) Epsilon-100w tri-electrode cell system (USA). Three electrodes include a Pt working electrode, an ancillary Pt electrode, and a silver reference electrode (in a CH_3CN solution of $0.01MAgNO_3$ and 0.10M tetra butyl ammonium hexafluoro-phosphonate, TBA-HFP). Polymer samples were typically dissolved in solvent (typically o-Dichlorobenzene) and then coated onto Pt working electrode. The measurements were performed in 0.10 M TBA-HFP/acetonitrile solution purged with argon gas.

Materials Synthesis

All materials were synthesized following reported procedures [13, 16] except the materials below that were not reported before.

DfA Block copolymer synthesis (Figure **1**)

To a solution of D (50 mg, 0.0058 mmol), fA monomer (53.5 mg, 0.0582 mmol) and 2.0 mL of THF in 50 mL round bottom flask in a glove box was added NaH (1.95 mg, 0.0813 mmol) in 2.0 mL of THF) over 5 minutes. The mixture was continued to stir to 15 more minutes, and was dropped into stirred methanol (50 mL). Dark red polymer solid (95 mg) was collected by filtration and dried at 60 °C in vacuum for two days. Yield: 65 mg.

Bridge Synthesis (Bp, p= 1,6) (Figure **2a**)

B_1 Bridge

To a 250 mL two-neck round bottom flask was added 4-hydroxybenzaldehyde (3 g, 0.0245 mol), dibromomethane (2.03 g, 0.0117 mol), potassium carbonate (5.08 g, 0.0362 mol) and 20 mL acetonitrile and the mixture was refluxed at 90°C for 24 hours. The mixture was cooled to room temperature. After that the crude product was purified by recrystallization (1:1, Hexanes: ethylacetate) to give 3 g of white solid product. Yield: 91%.

B_6 Bridge

To a 250 mL two-neck round bottom flask was added 4-hydroxybenzaldehyde (3 g, 0.0245 mol), 1,6-dibromohexane (2.85 g, 0.0117 mol), potassium carbonate (4.84 g, 0.0350 mol) and 20 mL acetonitrile and the mixture was refluxed at 90°C for 24 hours. The mixture was cooled at room temperature. After that the crude product was purified by crystallization (1:1, Hexanes: Ethylacetate) to give 2.8 g of white solid product. Yield: 87%.

Results and Discussion

Materials Synthesis

The synthesis of DBpfA copolymers shown in Figure **1** follow an earlier reported procedure [16].

The non-conjugated and flexible bridge units **B**p (p=1, 2, 4 and 6) were prepared according to the literature procedure as shown in Figure **2a** [13-14]. The fluorinated terminator (F-terminator) was synthesized based on the literature procedure shown in Figure **2b** [13, 15]. The crystallization and vacuum oven drying methods were used to purify all bridge compounds before use.

Preliminary results of the molecular weight, degree of polymerization (DP), and polydispersity index (PDI) of the donor block D, acceptor block fA, and the DBfA's are listed in Table **1**. Thermal properties of the synthesized polymers are shown in Table **2** and optical electrical properties of D and fA are shown in Table **3**.

Photoluminescence spectra of D, D/fA blend, DfA and DBpfA in THF solution are shown in Figure **3**, where the concentration of D repeat unit are kept at $1x10^{-5}$M in all sample solutions, and only D is being

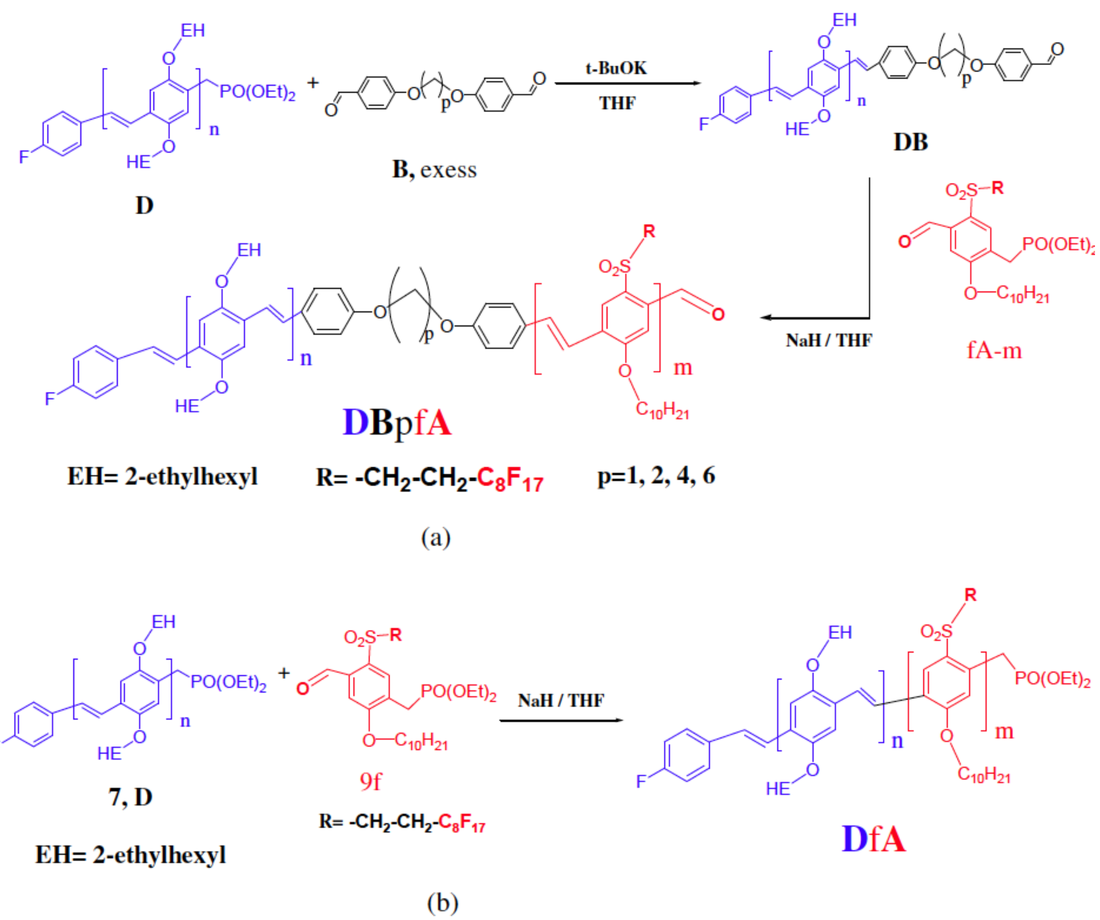

Figure 1: Chemical structures and synthetic schemes of (**a**) **DB**pf**A** and (**b**) **D**f**A** type block copolymer systems.

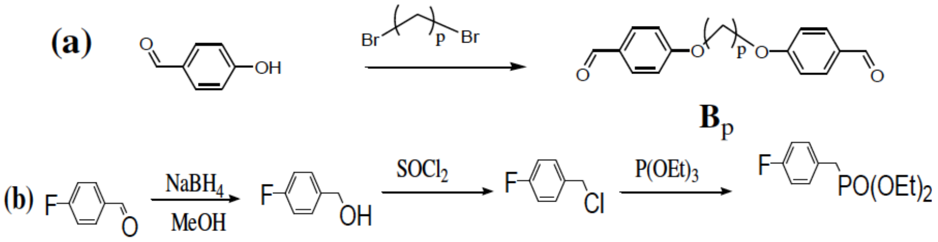

Figure 2: Synthetic Scheme of (**a**) Non- Conjugated Bridge B, and (**b**) Terminator.

Table 1: Molecular Weight, DP and PDI Calculated by GPC

Polymers	M_w(g/mol)	M_n(g/mol)	DP	PDI
D	10218	8877	24	1.15
fA	2938	2585	3	1.14
DfA	12253	10987	24+3	1.12
DB_1fA	12283	10797	24+3	1.13
DB_2fA	13102	11278	24+3	1.16
DB_4fA	13190	11142	24+3	1.18
DB_6fA	17058	14637	24+3	1.17

Table 2: Thermal Properties of Synthesized DB$_1$fA & DfA

Polymer	DSC endothermic peaks onset T (°C)	TGA 5 % drop-onset T (°C)
D	93-245	370
fA	78	290
DB$_1$fA's and DfA	72-230	330-360

Table 3: Optical & Electrical Properties of D & fA

Polymer	$\lambda_{max\ (nm)}$	$\lambda_{onset\ (nm)}$	Optical Eg (eV)	HOMO/LUMO
D	495	574	2.16	-5.82/-3.66
fA	370	464	2.67	-6.10/-3.43

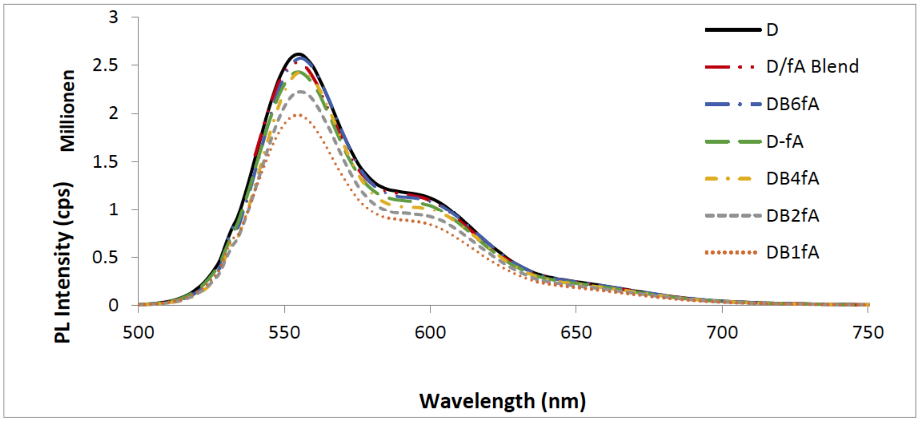

Figure 3: PL Spectra of D, D/fA, DfA, and DBpfAs, where D repeat unit concentrations are 1x10^{-5}M in all solutions (Ex: 530nm).

excited at 530nm and fA is not excited. The data shows that PL of D/fA blend, DfA, and DBpfA quenched up to about 26% as compared to pristine D, with DB$_1$fA consistently quenched strongest than other DBpfAs. Similarly, as shown in Figure **4**, when the acceptor fA block is excited at 370nm, and fA repeat unit concentration is fixed at 1x10^{-}5M, the PL of D/fA blend, DfA, and DBpfAs are quenched up to 88% as compared to pristine fA, again with DB1fA quenched strongest than other DBpfAs.

Stern-Volmer (SV) PL quenching experiment and the SV-Plot is a standard method of determining a PL quenching coefficient between two molecular species in solution. When the fA block repeat units concentration is fixed at 2.8x10^{-}5M, as the concentration D increases, the PL of fA is quenched gradually as shown in Figure **5**. After subtracting the energy transfer (ET) contributions [12], the charge transfer induced SV-Plot is shown in Figure **6**, where a PL quenching coefficient of K_{sv}= 19222 is obtained for the fA/D pair.

In the D PL quenching case, the PL quenching of D in D/fA blend is attributed mainly to the photo induced electron transfer from D block to fA block via collision in THF, while the PL quenching of D in DfA and DBpfAs could be attributed to the photo induced electron transfer from D block to fA block via collision as well as intra- molecularly via the bridge B unit. In the fA PL quenching case, the PL quenching of fA in D/fA blend is attributed mainly to the photo induced electron transfer from D block to fA block via collision in THF, while the PL quenching of fA in DfA and DBpfAs could be attributed to the photo induced electron transfer from D block to fA block via collision as well as intra-molecularly via the bridge B unit. One interesting observation is that the PL quenching is not the strongest for the conjugated block copolymer without bridge (DfA), and this may be explained by at least four stable states of different twist angles (with lowest energy state at a seventeen (17) degree twist angle) between the D and fA conjugated plains as predicted from the First Principle 3-21G calculation method [17].

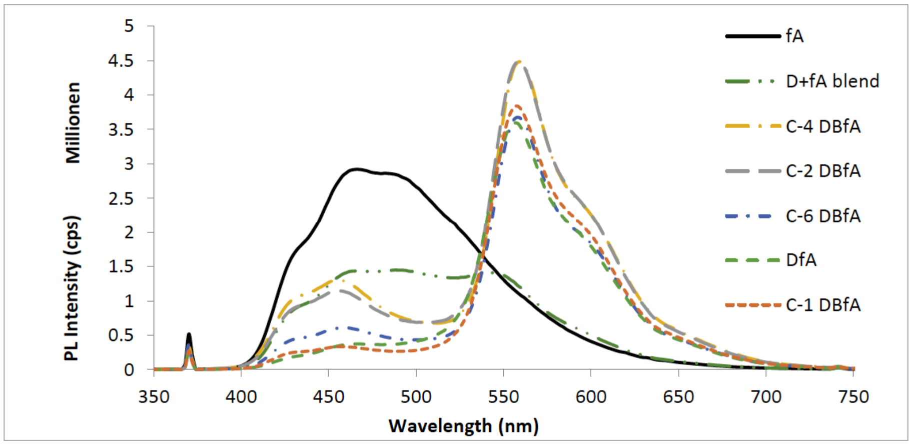

Figure 4: PL Spectra of fA, D/fA, DfA, and DBpfAs, where fA repeat unit concentration 1×10^{-5} M in all solutions (Ex: 370nm).

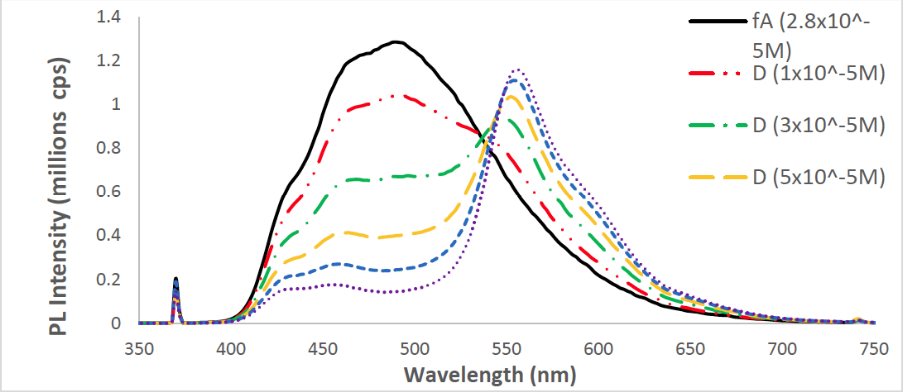

Figure 5: Stern-Volmer PL spectra of fA quenched by different concentrations of D, where fA repeat unit concentration 2.8×10^{-5} M and excitation at 370nm.

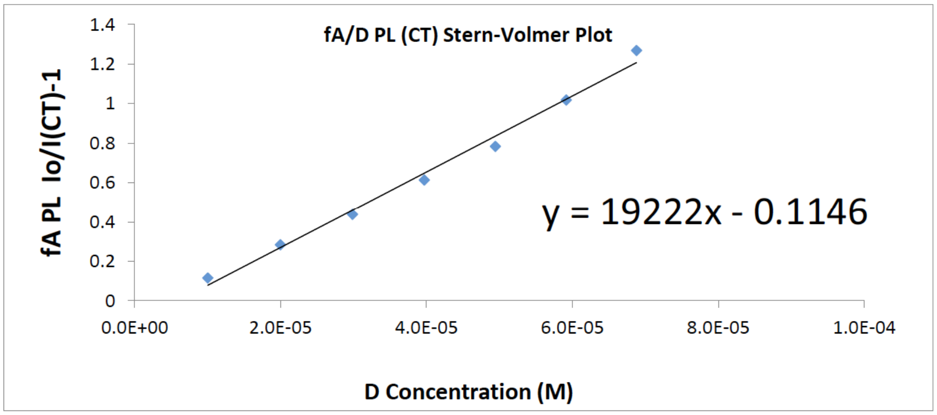

Figure 6: Stern-Volmer plot of fA quenched by different concentrations of D based on PL spectra shown above, where I (CT) represents PL intensity dropped due to charge transfer (CT).

Solar Cell Device Fabrications

Active polymer solutions were prepared by dissolving a mixture of 15mg photovoltaic block polymer samples with 15mg of PCBM (*e.g.* 15 mg of DBpfA **+** 15mg acceptor PC60BM, so total active materials is 30mg) dissolved in one-milliliter *o*-Dichlorobenzene (DCB). Solar cell devices were fabricated in standard five steps [13, 16]: (1) ITO glass substrates (37.5mm x 25mm x 0.4mm ITO slide) were taped in the middle part (yellow and blue parts in Figure **6**) with scotch tape to protect ITO from HCl dissolution, then the taped slides were immerged in 6M HCl for 15-20 minutes to etch away ITO outside the

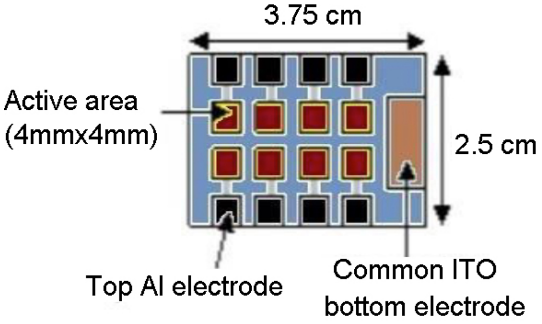

Figure 7: Scheme of eight solar cells fabricated on an ITO slide.

tape area (grey part in Figure **6**). (2) After HCl etching, ITO slides were rinsed with DI water and the scotch tapes was removed immediately. Then the ITO slides were sonicated for five minutes each in soap/DI water, DI water, acetone, and isopropanol, respectively, and then blown dried with compressed nitrogen. (3) Spin coat PEDOT: PSS aqueous solution onto ITO side. The thin film spinning protocol typically included a key step of 5000RPM for 30 seconds, yielding a 30-50 nm thick PEDOT: PSS film after dried at 80°C in the vacuum oven for an hour. Spin coating the photovoltaic active polymer solution on top of dried "ITO/PEDOT: PSS" film via a critical spinning step of 1000RPM for 60 seconds and subsequently dried in a 80°C heated vacuum oven for overnight, typically yielding a film thickness of 150-200 nm. (5) In an inert gas filled glove box, the polymer coated ITO slides were placed in a vacuum deposition jar, and the patterned metal (such as aluminum) electrodes (see Figure **7**) were deposited to a thickness of about 100-150 nm on top of the active polymer layer by thermal evaporation under high vacuum (1×10^{-6} to 1×10^{-7} Torr). After electrode deposition, the positive ITO electrode was exposed by scratching off a 2 mm diameter spot of polymer coating on the orange part of ITO (Figure **7**). The negative electrode will be clipped to one of the eight-cell aluminum electrode on the ITO edge [13, 16].

Optoelectronic Device Studies

The solar cell device efficiency had been studied by AM 1.5G solar simulator with 80-100 mW/cm^2 intensity. A Keithley 237 source-measure unit (SMU) was used to collect the voltage-current data that were processed by computer into J-V curves. A solar cell device had been built which was composed of multiple stack layers (ITO/PEDOT: PSS/Polymer: PC70BM/Al). Cells were made from and DBpfA's as donor polymers and were fabricated into solar cell devices and compared. The short-circuit current density (*Jsc*), open-circuit voltage (*Voc*), fill factor (*FF*), and power conversion efficiencies (PCE) of fabricated cells are listed in Table **4**. A best photo J-V curve (in log scale) among a set of eight cells made of either DBpfA are shown in Figure **8** for all the DBpfA's, where the shorter the bridge length, the better the PCE. However, the no-bridge DfA block copolymer cell does not perform as good as the DB$_1$fA possibly due to the stable state twist angles between D and fA blocks [17]. The absolute efficiencies of the cells reported here are relatively low compared to other literature reported best organic cell values (over 10%) due to, for instance, the PPVs reported here have much higher energy gaps (more than 2.2 eV) compared to popular donor type polymers (such as regio-regular P3HT) that exhibits lower energy gaps (less than 2.0 eV) and better charge transport, and our cell fabrication protocols as well as polymer solid state morphologies have not yet been systematically optimized. However, higher energy gaps and

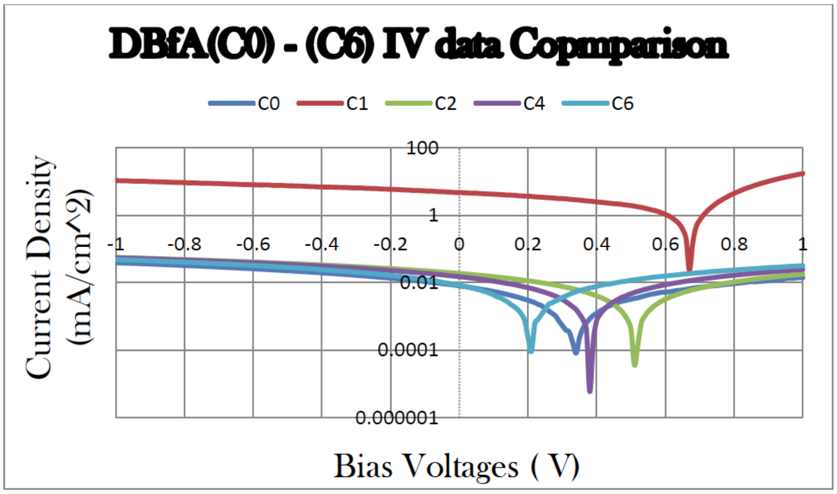

Figure 8: DBpfA (p=0, 1, 2, 4, 6) IV data Comparisons.

Table 4: Solar Cell Performance of DBpfA

Polymer's	Voc	Jsc	FF%	PCE%
DfA (C0)	0.34	0.01	19.85	0.001
DBfA (C1)	0.67	5.89	31.72	1.56
DBfA (C2)	0.51	0.02	25	0.003
DBfA (C4)	0.38	0.02	25	0.002
DBfA (C6)	0.21	0.01	25	0.0007

fluorination of the conjugated polymer may find important applications in certain higher energy radiations or in applications where hydrophobicity is desired [16].

CONCLUSION

A series of DBpfA (p=0, 1, 2, 4 and 6) type of conjugated block copolymer systems have been synthesized where D is a conjugated PPV donor block, fA is a conjugated PPVacceptor block (f represents fluorinated side groups), and B is a non-conjugated bridge unit containing zero, one, two, four and six methylene units. With such series of block copolymers, the optoelectronic properties particularly the photo induced electron transfers from D block to fA block can therefore being studied in a systematic manner. One interesting finding is that the electronic coupling between D and fA block in DfA (without bridge unit) block copolymer is still in weak electronic coupling regime, *i.e.*, stable state twist angles between the two conjugated planes of D and fA are proposed to account for such weak couplings. The PL quenching of D in DfA and DBpfAs in solution are attributed to photo induced exciton dissociation or electron transfer from D to fA via both collision in solution (bi-molecular process) and bridge unit (uni-molecular process). This study provides useful insights for designing and developing potential high efficiency block copolymer based optoelectronic materials and devices such as solar cells or photo detectors.

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