# **Supporting Information**

For

# A stereoregular β-dicyanodistyrylbenzene (β-DCS)-based conjugated polymer for high-performance organic solar cells with small energy loss and high quantum efficiency

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# General:

All reagents were purchased from commercial sources and used as received. Anhydrous toluene was prepared by distillation with sodium and benzophenone. Compound 1<sup>81</sup>, 3<sup>82</sup>, and 5<sup>83</sup> were prepared following previously reported procedures. <sup>1</sup>H-, <sup>13</sup>C-NMR, MALDI-TOF and elemental analysis were measured by using a Bruker Avance-500, SCIEX TOF/TOF 5800 and CE instruments EA1110, respectiv{Kwon, 2014 #427}{Yun, 2012 #428}ely. Gel permeation chromatography (GPC) was performed by using a Waters system and Waters styragel HT4 column eluted with 1,2-dichlororbenzene. UV-Vis absorption spectra and cyclic voltammetry (CV) were recorded by Shimadzu UV-1650PC and Princeton Applied Research Potentiostat/Galvanostat Model 273A. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured by using TA instruments Q50 and DSC-Q1000, respectively, under a nitrogen atmosphere with heating rate of 10°C/min. AFM imaging was performed using Multimode with a Nano Scope V Controller (Bruker) in tapping mode. The 2D-GIXD was measured by using the PLS-II 9A U-SAXS beamline in the Pohang Accelerator Laboratory, Korea. The incidence angle was adjusted to 0.12°

#### **Device Fabrication and Evaluation:**

The patterned indium tin oxide (ITO) glass substrates were cleaned in an ultrasonic bath with acetone, and isopropanol, and then exposed to a UV/O<sub>3</sub> for 20min. PEDOT:PSS (Clavious P VP AI 4083) was spin-coated onto the ITO glass substrate at 5000 rpm for 30 s and the film was subsequently baked at 170 °C for 10min. A chlorobenzene:diphenylether (CB:DPE = 98:2) solution (totally 17.5 mg mL<sup>-1</sup>) of PBDCS:PC<sub>71</sub>BM blend or a chlorobenzene solution (totally 14mg mL<sup>-1</sup>) of PBDCS:ITIC blend was subsequently spin-coated (1400 rpm for PBDCS:PC<sub>71</sub>BM, 1600 rpm for PBDCS:ITIC) on the PEDOT:PSS coated ITO glass to form

active layer (ca. 100 nm for PBDCS:PC<sub>71</sub>BM, ca. 85 nm for PBDCS:ITIC) at room temperature. After drying the resulting films in a N<sub>2</sub> glovebox at room temperature for 30min, PFN (5nm) was spin-coated on the PBDCS:PC<sub>71</sub>BM film, or Ca (5nm) was thermally deposited on PBDCS:ITIC film under a vacuum of  $10^{-6}$  torr. Finally Al (80 nm) was thermally deposited under a vacuum of  $10^{-6}$  torr.

For space-charge-limited currents (SCLC) measurement in this work, we have used Mott-Gurney law and fit the dark current under forward bias. The SCLC mobilities were calculated using the below equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r \mu \frac{V^2}{L^3} \tag{1}$$

In which  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the dielectric constant of the organic semiconductor material (herein  $\varepsilon_r$  was assumed to be 3 that typical value for organic semiconducting material), *V* is effective voltage with the equation of  $V=V_{appl}-V_{bi}-V_r$  ( $V_{appl}$ : applied bias,  $V_{bi}$ : the built in potential due to the difference in electrical contact work function,  $V_r$ : the voltage drop due to contact resistance and series resistance across the electrodes) and L is the thickness of photoactive layer. The hole and electron only devices were fabricated respectively with the structure, ITO/PEDOT:PSS/BHJ layer/V<sub>2</sub>O<sub>5</sub>/Ag and ITO/ZnO/BHJ layer/Ca/Al.

The current density-voltage (J-V) characteristics of the solar cells were measured suing a Keithley 4200 source measurement unit. The solar cell performances were characterized under AM 1.5G condition with an illumination intensity of 100 mW cm<sup>-2</sup>, as generated using an Oriel Sol3A solar simulator (Oriel model 9023A). The measurements were carried out through a shadow mask with well-defined aperture area of 0.04 cm<sup>2</sup> under an ambient atmosphere. The incident photon-to-current efficiency (IPCE) was measured using an Oriel QE/IPCE

Measurement Kit composed of a 300 W xenon lamp, a monochromator (74125), an order sorting filter wheel, a Merlin lock-in amplifier (70104), a calibrated silicon photodiode (70356\_70316NS) and an optical chopper.

### Synthesis:

#### **Compound 2**

(**R=2-hexyldecyl**) According to previous report [1,2], 2-hexyldecy iodide (1.9 g, 5.4 mmol) and K<sub>2</sub>CO<sub>3</sub> (746 mg, 5.4 mmol) were added to solution of the compound 1 (299 mg, 1.8 mmol) in DMF (5 ml). The reaction was stirred at 50°C for 1 day. The resulting mixture was cooled to room temperature. After aqueous work-up, the mixture was dried over anhydrous MgSO<sub>4</sub>, and then the solvent was removed in vacuo. Finally, the crude product was purified by column chromatography (methylene chloride/n-hexane) to afford yellow liquid (808 mg, 73 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.51 (s, 2H, -CHO), 7.43 (s, 2H, Ar-H), 3.97 (d, 4H, -CH2-), 1.82 (m, 2H, -CH-), 1.42-1.25 (m, 48H, -CH2-), 0.86(m, 12H, -CH3); <sup>13</sup>C NMR(400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 189.18, 155.33, 129.24, 111.40, 71.82, 37.82, 31.82, 31.75, 31.36, 29.90, 29.58, 29.49, 29.25, 26.77, 22.60, 14.02; MS (MALDI-TOF, m/z) Calcd for C<sub>40</sub>H<sub>70</sub>O<sub>4</sub>: 614.53, found, 614.5.

#### (R=2-butyloctyl)

The same reaction conditions were used as above. Yield: 70% (351 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 10.51 (s, 2H, -CHO), 7.43 (s, 2H, Ar-H), 3.97 (d, 4H, -CH2-), 1.82 (m, 2H, -CH-), 1.42-1.26 (m, 32H, -CH2-), 0.88(m, 12H, -CH3); <sup>13</sup>C NMR(400 MHz, CDCl<sub>3</sub>, δ): 189.25, 155.34, 129.25, 111.41, 71.84, 37.87, 31.74, 31.37, 31.06, 29.57, 28.98, 26.76, 22.94, 22.59, 14.02; MS (MALDI-TOF, m/z) Calcd for C<sub>32</sub>H<sub>54</sub>O<sub>4</sub>: 502.40, found, 502.6.

# **Compound 4**

(**R=2-hexyldecyl**) According to previous report [1,2], the mixture of compound 2 (614 mg, 1 mmol) and compound 3 (424 mg, 2.1 mmol) were dissolved in tert-butyl alcohol (10 mL) at 50 °C. Potassium tert-butoxide (224 mg, 2 mmol) was added quickly into the mixture. The reaction was stirred at 50°C for 30min. The reaction mixture was diluted in methanol, and then resulting precipitate was filtered. Finally, the crude product was purified by column chromatography (methylene chloride) and recrystallization (ethylacetate/methanol) to afford red solid (637 mg, 65%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.82 (s, 2H, vinyl–H), 7.74 (s, 2H, Ar-H), 7.14 (d, 2H, Ar-H), 7.04 (d, 2H, Ar-H), 3.98 (d, 4H, -OCH<sub>2</sub>-), 1.85 (m, 2H, -CH-), 1.52-1.26(m, 48H, -CH2-), 0.90(m, 12H –CH3); <sup>13</sup>C NMR(400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 151.70, 141.07, 133.20, 131.05, 127.34, 125.40, 116.53, 113.64, 110.63, 105.40, 72.14, 38.07, 31.83, 31.35, 31.32, 29.89, 29.70, 29.17, 26.93, 23.05, 22.68, 14.08; MS (MALDI-TOF, m/z) Calcd for C<sub>52</sub>H<sub>74</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 980.36, found, 981.0.

(**R=2-butyloctyl**) The same reaction conditions were used as above. Yield: 70% (607 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.82 (s, 2H, vinyl–H), 7.75 (s, 2H, Ar-H), 7.14 (d, 2H, Ar-H), 7.05 (d, 2H, Ar-H), 3.98 (d, 4H, -OCH<sub>2</sub>-), 1.85 (m, 2H, -CH-), 1.51-1.26(m, 32H, -CH2-), 0.90(m, 12H –CH3); <sup>13</sup>C NMR(400 MHz, CDCl<sub>3</sub>, δ): 151.68, 141.06, 133.20, 131.04, 127.34, 125.40, 116.53, 113.64, 110.63, 105.39, 72.15, 38.07, 31.84, 31.72, 31.36, 29.75, 29.19, 26.95, 23.10, 22.70, 14.10; MS (MALDI-TOF, m/z) Calcd for C<sub>44</sub>H<sub>58</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: 868.23, found, 868.3.

#### **PBDCS**

(**R=2-hexyldecyl**) A 20ml schlenk tube was charged with compound 4 (90.4mg, 0.1mmol), compound 5 (98.3mg, 0.1mmol),  $Pd_2(dba)_3$  (2mg, 0.0022mmol),  $P(o-tol)_3$  (2.7mg, 0.0088mmol) and anhydrous toluene (4ml), The schlenk tube was degassed with argon for 15min. The reaction was heated to 100°C for 24 hours. The polymer was precipitated into excess methanol, followed

by soxhlet extraction with methanol, acetone, n-hexane and chloroform. The chloroform solution was precipitated into methanol. The polymer was filtered, then dried in vacuo to give product PBDCS as a black solid (130mg, 92%). GPC (1,2-DCB, 90°C): Mn = 90 kDa, PDI = 2.19. <sup>1</sup>H-NMR (400 MHz, 1,1,2,2-tetrachloroethane-d<sub>2</sub>, 120 °C,  $\delta$ ): 7.95 (m, 4H, Ar–H, vinyl–H), 7.76-7.81 (m, 2H, Ar–H), 7.39 (m, 4H, Ar–H), 7.24-7.32 (m, 2H, Ar–H), 7.01 (m, 2H, Ar–H), 4.10 (s, 4H, –O–CH<sub>2</sub>–), 2.98 (m, 4H, –Ar–CH<sub>2</sub>–), 1.96 (m, 2H, –CH–), 1.80 (m, 2H, –CH–), 1.34–1.60 (m, 64H, –CH<sub>2</sub>–), 0.88–1.08 (m, 24H, –CH<sub>3</sub>). Anal. Calcd for C<sub>86</sub>H<sub>116</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>: C, 73.66; H, 8.34; N, 2.00; O, 2.28; S, 13.72. Found: C, 73.93; H, 8.27; N, 2.04; O, 2.22; S, 13.66.

(**R=2-butyloctyl**) The same reaction conditions were used as above. Yield = 90% (116 mg). GPC (chloroform, 90°C): Mn = 60 kDa, PDI = 2.55. <sup>1</sup>H-NMR (400 MHz, 1,1,2,2tetrachloroethane-d<sub>2</sub>, 110 °C, δ): 7.95 (m, 4H, Ar–H, vinyl-H), 7.75-7.81 (m, 2H, Ar–H), 7.39 (m, 4H, Ar–H), 7.24-7.32 (m, 2H, Ar–H), 7.01 (m, 2H, Ar–H) 4.11 (s, 4H, –O–CH<sub>2</sub>–), 2.98 (m, 4H, –Ar–CH<sub>2</sub>–), 1.96 (m, 2H, –CH–), 1.82 (m, 2H, –CH–), 1.31–1.62 (m, 48 –CH<sub>2</sub>–), 0.88–1.08 (m, 24H, –CH<sub>3</sub>). Anal. Calcd for C<sub>78</sub>H<sub>100</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>: C, 72.62; H, 7.81; N, 2.17; O, 2.48; S, 14.91. Found: C, 72.70; H, 7.82; N, 2.24; O, 2.49; S, 14.79.

#### **Rigidity of β-DCS molecules:**

Fig S10 shows the bond length of  $\alpha$ -DCS and  $\beta$ -DCS in crystal. (a) bond is longer than (c) bond, and (d) bond is shorter than (d') bond, which is good agreement with the resonance structure of  $\beta$ -DCS in scheme 1. Fig S11 shows the <sup>1</sup>H-NMR chemical shift differences between  $\alpha$ -DCS and  $\beta$ -DCS in solution. The protons of phenyl ring and alkoxy in  $\beta$ -DCS are located in the downfield compared with those of  $\alpha$ -DCS, which means they are more electron deficient protons. This electron density difference also supports the resonance structure of  $\beta$ -DCS. According to the resonance structure of  $\beta$ -DCS, the electron distribution of the structure between

both cyano groups in  $\beta$ -DCS is well delocalized, which implies structural rigidity of that structure. To verify this, we calculated the rotational energies of  $\alpha$ -DCS and  $\beta$ -DCS by DFT method at the B3LYP/6–31G(d,p) level of theory (Fig S12). The rotational energy of  $\beta$ -DCS was twice as large as that of  $\alpha$ -DCS, which supports the resonance structure and rigidity of  $\beta$ -DCS.

In general, CS molecules have large torsional or conformational changes in solution, leading to very low photoluminescence quantum yield (PLQY) as shown in fig S13. On the other hands, the  $\beta$ -DCS with an alkoxy side chain shows relatively high PLQY (25~30%) in solution, which means that it is hard for  $\beta$ -DCS to rotate or change the conformation in solution. Whereas,  $\beta$ -DCS with an alkyl side chain or without side chain show low PLQY (0.2~1.6%), which means that dialkoxy plays an important role in formation the resonance structures of  $\beta$ -DCS (Fig S13).

In conclusion, dialkoxy- $\beta$ -dicyanodistyrylbenzene ( $\beta$ -DCS) has the unique resonance structures between alkoxy group and cyano group (Scheme 1). The alkoxy group and the cyano group are strong electron donating (push) and electron withdrawing (pull) arising from resonance effect, respectively. As a result, such strong push-pull structure strengthens the resonance structure, thereby rendering more rigid structure than other cyanostyrylbenzene (CS) molecules.



Fig S1. GPC traces of PBDCS under various temperature.



**Fig S2.** <sup>1</sup>H-NMR spectrum of PBDCS under various temperatures.





**Fig S3.** <sup>1</sup>H-NMR spectrum changes of  $\alpha$ -DCS,  $\beta$ -DCS, PBDCS, and CS (CNMBE<sup>S4</sup>) under 365nm UV irradiation.



Fig S4. TGA curve (left) and DSC curve (right) of PBDCS. (5% weight loss: 396.7°C)



**Fig S5.** Optimized geometries of PBDCS calculated using DFT with a basis set of B3LYP/6-31G(d,p).



**Fig S6.** Cyclic voltammograms of thin films of PBDCS and ITIC in acetonitrile–[n-Bu4N]PF6 solutions (0.1 M).



**Fig S7.** *J*–*V* curves of the hole-only device (left) and the electron only device (right).



Fig S8. 2D-GIXD images of PBDCS and ITIC films.



**Fig S9.** Diffraction profiles cut along the  $\sim q_z$  axis of the 2D GIXD images. Fit (green line) fitted to pseudo-Voigt functions.



Fig S10. Crystallographic information<sup>S5</sup> of  $\beta$ -DCS (left) and  $\alpha$ -DCS (right)



Fig S11. <sup>1</sup>H-NMR spectrum of  $\alpha$ -DCS and  $\beta$ -DCS



Fig S12. Torsion potential energies calculated using DFT with a basis set of B3LYP/6-31G(d,p).



Fig S13. Molecular structures of various CS molecules and their PLQYs in solution<sup>S6,S7</sup>.





Fig S14. <sup>1</sup>H-NMR data of PBDCS.

Donor	Acceptor	Hole mobility (cm <sup>2</sup> ·V <sup>-1</sup> sec <sup>-1</sup> )	Electron mobility (cm <sup>2</sup> ·V <sup>-1</sup> sec <sup>-1</sup> )	Mobility balance (electron/hole)
PBDCS	PC71BM	6.48X10 <sup>-4</sup>	9.658X10 <sup>-4</sup>	1.49
PBDCS	ITIC	1.72X10 <sup>-4</sup>	5.137X10 <sup>-5</sup>	0.3

Table S1. SCLC hole mobility of PBDCS:PC<sub>71</sub>BM and PBDCS:ITIC blend.

# References

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