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Supporting Information

Ferrocene-diketopyrrolopyrrole based non-fullerene acceptors for bulk heterojunction polymer solar cells

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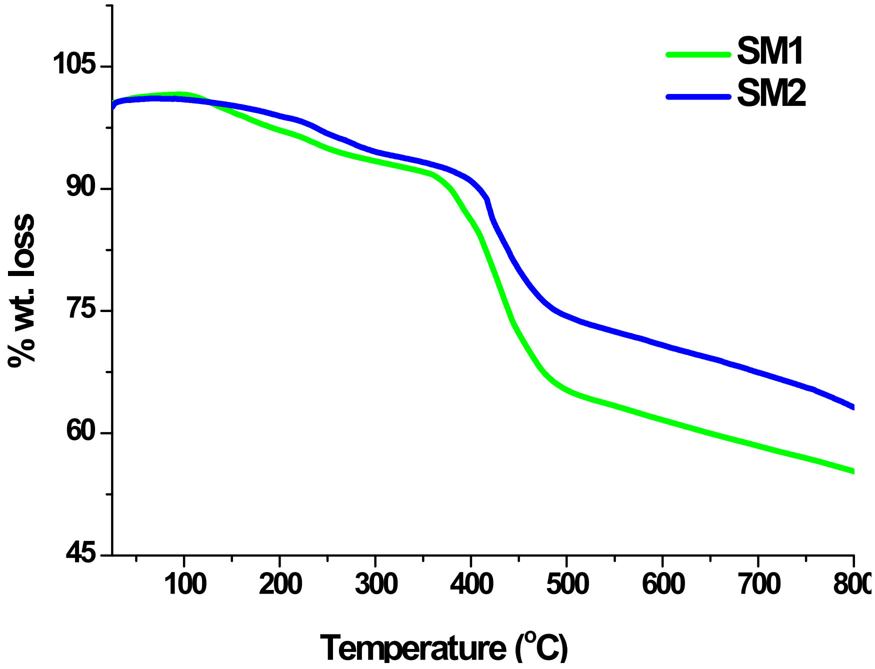


Fig. S1 Thermogravimetric analysis of **SM1** and **SM2** measured at a heating rate of 10 °C/min under nitrogen atmosphere.

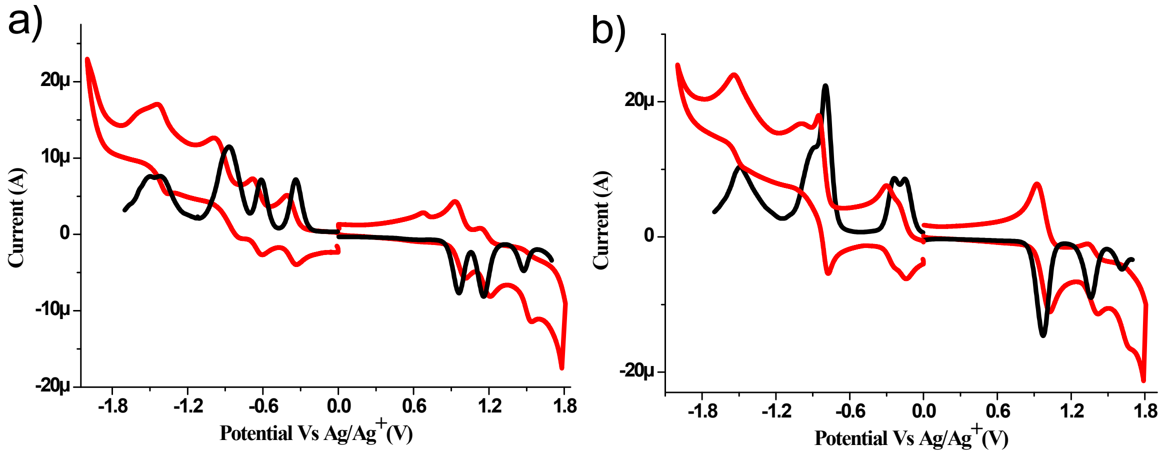


Fig. S2 CV (red line) and DPV (black line) plots of (a) **SM1** and (b) **SM2**.

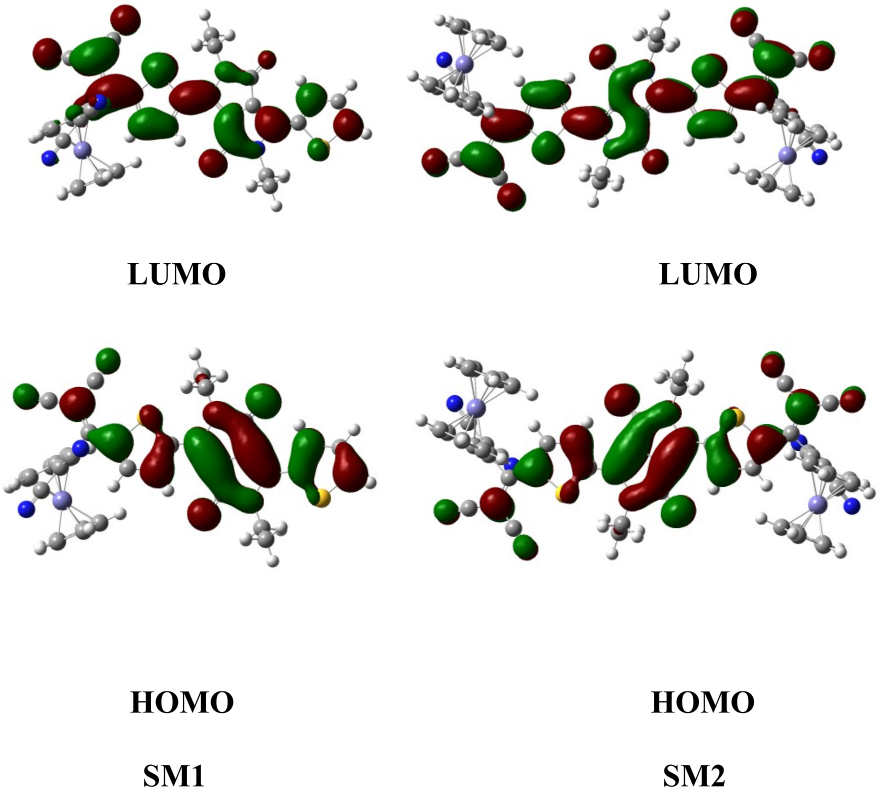


Fig. S3 The frontier molecular orbitals of **SM1** and **SM2** at B3LYP/6-31G(d) level.

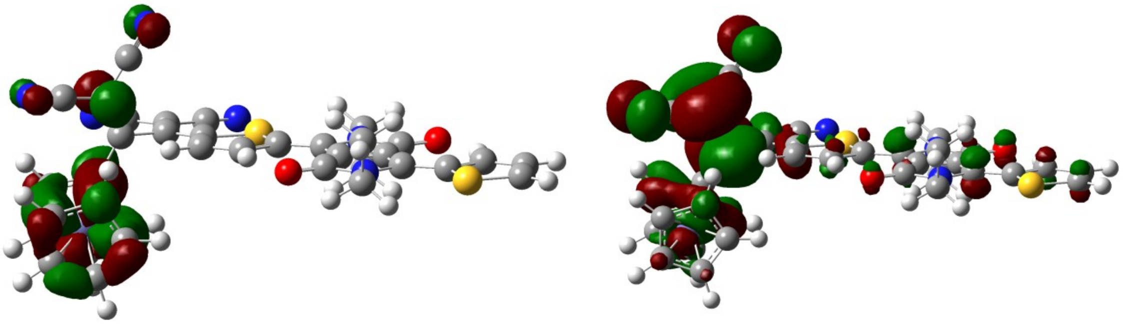


Fig. S4 The frontier molecular orbitals of **SM1** at B3LYP/6-31G(d) level.

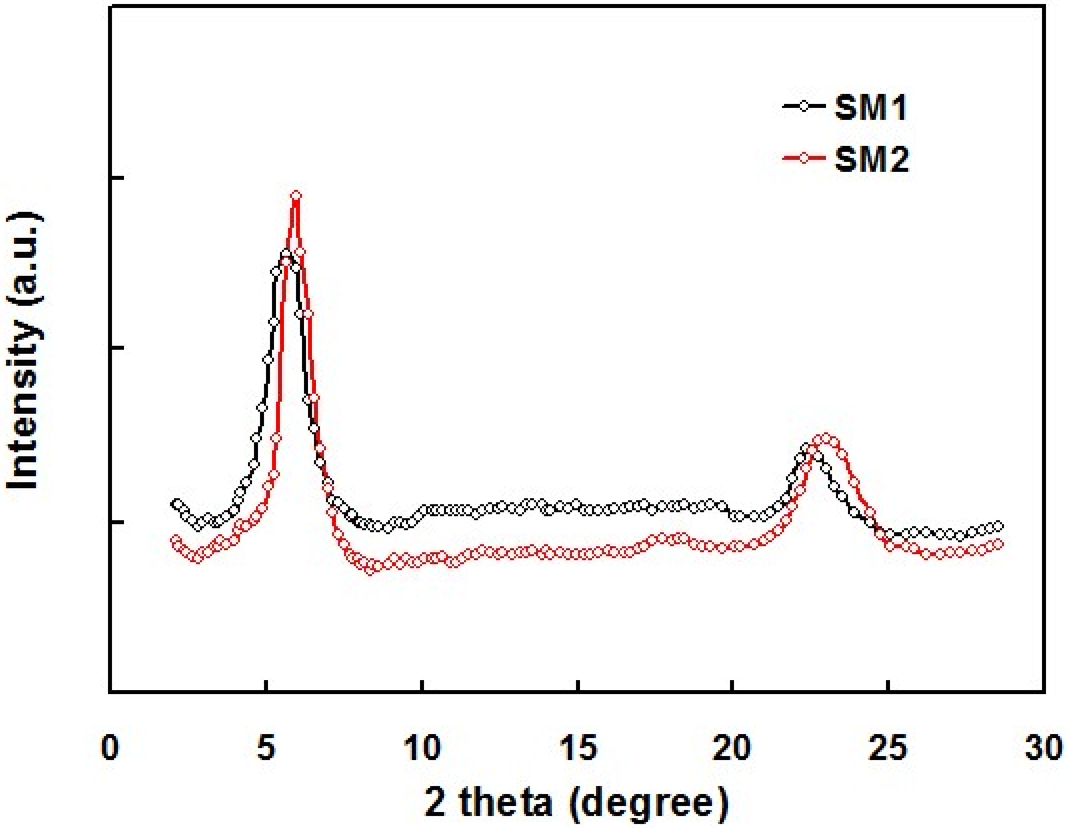


Fig. S5 XRD patterns of the **SM1** and **SM2** thin films.

Table S1. Calculated major electronic transitions for **SM1** and **SM2** in the gas phase.

	Wavelength (nm)	Composition	Assignment	f^a
SM1	672	HOMO→LUMO (0.60)	$\pi-\pi^*$ transition	0.51
SM1	662	HOMO→LUMO (0.37)	$\pi-\pi^*$ transition	0.20
		HOMO-1→LUMO+1 (0.38)	-----	
SM2	735	HOMO→LUMO (0.70)	$\pi-\pi^*$ transition	1.07

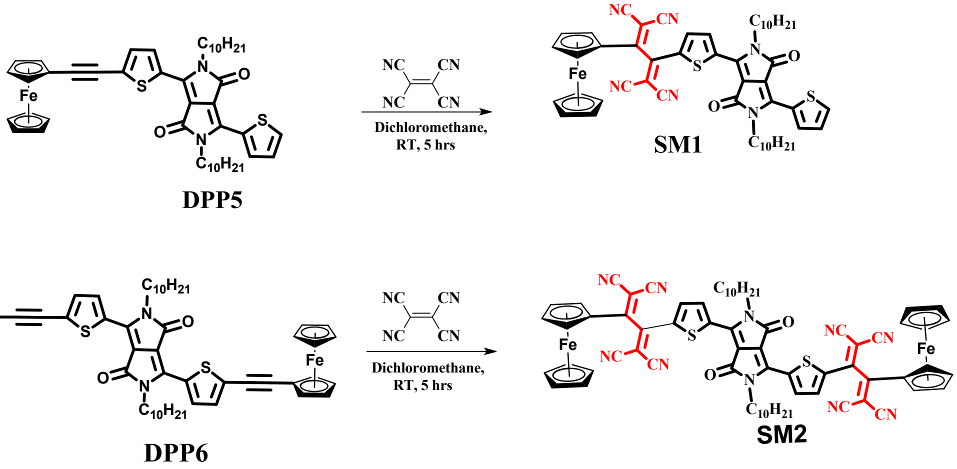
f^a= Oscillation Strength

Table S2 Photovoltaic properties of the devices based on as cast and DIO (3v%) additive **P**:**SM1 (1:2)** and **P**:**SM2 (1:2)** active layers

Active layers	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
P:**SM1** (as cst)	6.23	1.02	0.38	2.41
P:**SM2** (as cast)	7.05	0.91	0.41	2.66
P:**SM1** (DIO additive)	8.81	0.98	0.49	4.23
P:**SM2** (DIO additive)	9.68	0.88	0.52	4.88

Experimental Section:

The UV-visible absorption spectra of DPPs were recorded on UV-visible Spectrophotometer in dichloromethane. The TGA analyses were performed on the thermal analysis system at the heating rate of 10 °C per minute under a nitrogen atmosphere. Cyclic voltammograms (CVs) and differential voltammograms (DPVs) were recorded in dichloromethane solvent using 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte on an electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and saturated Ag/Ag^+ as the reference electrode.



Scheme S1. Synthesis of TCBD based DPPs **SM1** and **SM2**.

Synthesis of SM1:

In 50 ml round bottom flask DPP **5** (0.100 g, 0.13 mmol) and TCNE (0.018 g, 0.14 mmol) were dissolved in dichloromethane (15 ml) under argon atmosphere. The reaction mixture was stirred at room temperature for 5 hours. The solvent was removed under vacuo and the product was purified by silica-column chromatography with hexane : dichloromethane (1:1) as an eluent to yield **SM1** as a dark blue colored solid in 91% yield.

Synthesis of SM2:

In 50 ml round bottom flask DPP **6** (0.100 g, 0.10 mmol) and TCNE (0.026 g, 0.20 mmol) were dissolved in dichloromethane (15 ml) under argon atmosphere. The reaction mixture was stirred at room temperature for 5 hours. The solvent was removed under vacuo and the product was purified by silica-column chromatography with hexane : dichloromethane (2:1) as an eluent to yield 95% **SM2** as a dark green colored solid.

Device fabrication

The PSCs were fabricated with a configuration of ITO/ PEDOT:PSS (40 nm)/**P**:**SM1** or **SM2**/PFN/Al. Firstly, indium tin oxide coated glass substrates were cleaned with detergent powder solution and then ultrasonicated in deionized water, acetone and isopropyl alcohol sequentially for 15 min each and then dried in vacuum oven for 2 hr at 50° C. A thin layer of PEDOT:PSS was deposited through spin-coating on pre-cleaned ITO-coated glass substrate from a PEDOT:PSS aqueous solution (Baytron P VP AI 4083) at 2000 rpm and dried subsequently at 120 °C for 15 min in air. The active layer solution was prepared by mixing P and SM1 or SM2 in different weight ratio from 1:1 to 1:2.5 in THF solution with total concentration of 16 mg/mL and spun cast on the top of PEDOT:PSS film at 1500 rpm for 30s. For solvent additive, different concentration of DIO was added to the host THF solution and then the solution was stirred overnight on a hot plate at 120 °C. The warm solution was spun on the top of PEDOT:PSS film at 1500 rpm for 30 s. After the films were (i) either transferred to vacuum oven immediately for slow vacuum drying at room temperature for 2 hr or (ii) thermally annealed at 110 ^{o}C for 2 min. Then methanol solution of PFN at a concentration of 1.0 mg/ mL was deposited on the top the active layer at 3000 rpm for 30 s to afford a thickness of 15 nm. Finally, top Al electrode was deposited in vacuum onto the cathode buffer layer at a pressure of $\approx 1.0 \times 10^{-5}$ Pa. The active area of the device was 10 mm^2. We have fabricated four devices in one substrate. The current-voltage (J−V) characteristics of the PSCs were measured on a computer controlled Keithley 2450 Source meter. Solar Simulator with a 450 W xenon lamp and an air mass (AM) 1.5 filter was used as the light source. The light intensity was kept constant at 100 mW/cm^2. The IPCE of the devices was measured at illuminating the device through the light source and monochromator and the resulting current was measured using a Keithley electrometer under short circuit condition. All the measurements were done in ambient condition without encapsulating the devices.

TDDFT Data

Calculation method:

B3LYP/6-31+G** for C, H, N, O, S, and Lanl2DZ for Fe with Gaussian 09 [1].

Excitation energies and oscillator strengths:

For SM1

```
Excited State   1:      Singlet-A      1.8076 eV  685.92 nm  f=0.0010
<S**2>=0.000
     171 ->174         0.17131
     171 ->175         0.49707
     171 ->176        -0.10957
     171 ->179         0.35595
     172 ->178         0.24610
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2784.88234257
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:      Singlet-A      1.8456 eV  671.79 nm  f=0.5106
<S**2>=0.000
     171 ->178         0.13341
     172 ->174        -0.10388
     172 ->175        -0.23952
     172 ->179        -0.18922
     173 ->174         0.60375
     173 <-174        -0.10494

 Excited State   3:      Singlet-A      1.8739 eV  661.64 nm  f=0.2008
<S**2>=0.000
     171 ->178        -0.23384
     172 ->174         0.19879
     172 ->175         0.37688
     172 ->179         0.31798
     173 ->174         0.36503

 Excited State   4:      Singlet-A      2.0910 eV  592.93 nm  f=0.0005
<S**2>=0.000
     171 ->178         0.11455
     172 ->174         0.66504
     172 ->175        -0.12685
     172 ->176         0.10087
     172 ->179        -0.11863

 Excited State   5:      Singlet-A      2.1678 eV  571.93 nm  f=0.0013
<S**2>=0.000
     171 ->174         0.67676
     172 ->178        -0.10672

 Excited State   6:      Singlet-A      2.2585 eV  548.97 nm  f=0.0393
<S**2>=0.000
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     173 ->175         0.69450
```

For SM2

```
Excited State   1:      Singlet-A      1.6871 eV  734.88 nm  f=1.0714
<S**2>=0.000
     253 -> 254        0.70456
     253 <- 254       -0.12709
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -3817.95121639
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:      Singlet-A      1.7459 eV  710.13 nm  f=0.0114
<S**2>=0.000
     251 -> 254        0.61586
     251 -> 255        0.17163
     251 -> 256       -0.11147
     251 -> 262        0.10482
     252 -> 254       -0.18876

 Excited State   3:      Singlet-A      1.7507 eV  708.20 nm  f=0.0158
<S**2>=0.000
     251 -> 254        0.18618
     252 -> 254        0.62759
     252 -> 255       -0.15906
     252 -> 256       -0.10477

 Excited State   4:      Singlet-A      1.7620 eV  703.66 nm  f=0.0008
<S**2>=0.000
     249 -> 254        0.39706
     249 -> 255        0.20753
     249 -> 256       -0.29559
     249 -> 257        0.26659
     249 -> 262        0.23177
     249 -> 263        0.13810
     251 -> 260       -0.19076

 Excited State   5:      Singlet-A      1.7706 eV  700.22 nm  f=0.0007
<S**2>=0.000
     250 -> 254        0.39048
     250 -> 255       -0.18462
     250 -> 256       -0.30798
     250 -> 257       -0.27414
     250 -> 262        0.15364
     250 -> 263       -0.23028
     252 -> 261        0.19414

 Excited State   6:      Singlet-A      1.8699 eV  663.06 nm  f=0.0015
<S**2>=0.000
     250 -> 254        0.47629
     250 -> 256        0.15688
     250 -> 257        0.16716
```

```
250 -> 261        -0.13473
250 -> 263         0.13134
252 -> 254        -0.13762
252 -> 256        -0.19937
252 -> 257        -0.19207
252 -> 261        -0.12304
252 -> 262         0.10466
252 -> 263        -0.15704
```

Reference

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. KGaA, Weinheim Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, revision D.01 *Gaussian, Inc.,* Wallingford, CT, USA, 2009.