Supporting Information

Side chain modification on PDI-spirobifluorene based molecular acceptors and its impact on organic solar cell performances

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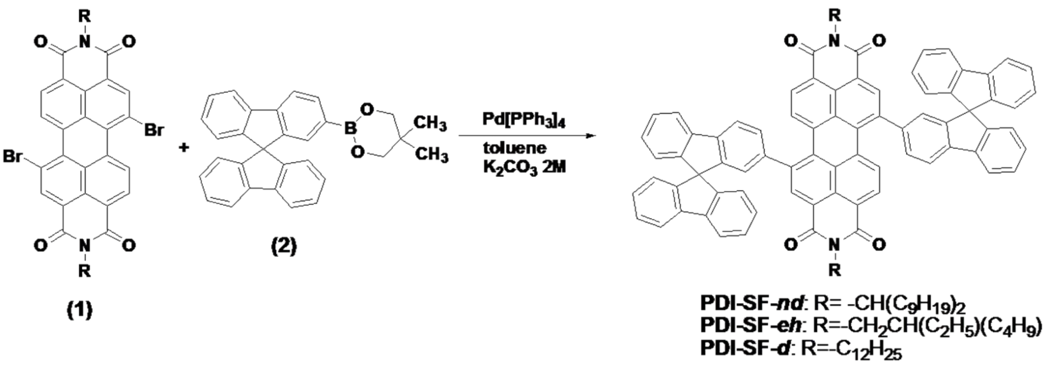


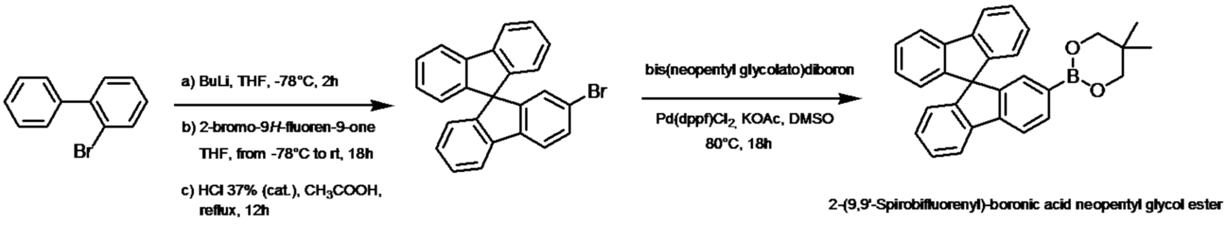
Scheme S1. Synthetic procedures for the preparation of PDI-SF-*alkyl*acceptor molecules.

*General procedure for the preparation of dibromo-N,N'-bis(alkyl)perylene-3,4,9,10-tetracarboxylic acid diimide(**1**)*

Dibromo-N,N'-bis(alkyl)perylene-3,4,9,10-tetracarboxylic acid diimide was obtained as described in literature [1S].A mixture of N,N'-bis(alkyl)perylene-3,4,9,10-tetracarboxylic acid diimide[2S](0.108 mmol), bromine (7.4 mmol) in 2 ml $CH_2Cl_2$was stirred at 60 °C in a closed vial for 4 hours. The reaction mixture was allowed to reach the room temperature and then, after removing the excess of bromine by air bubbling, the solvent was removed under vacuum. The crude product was purified by a silica gel column chromatography, using hexane:$CHCl_3$=6:4 as eluent. The first band was collected to afford dibromo-N,N'-bis(alkyl)perylene-3,4,9,10-tetracarboxylic diimide (as a mixture of 1,7-dibromo and 1,6-dibromo derivative 3:1) as a red solid (yields>90%).

*General procedure for the preparation of 2-(9,9'-spirobifluorenyl)-boronic acid neopentyl glycol ester (**2**)*

2-(9,9'-Spirobifluorenyl)-boronic acid neopentyl glycol ester (**2**) was synthesized by Suzuki-Miyaura cross-coupling reaction from 2-bromo-9,9'-spirobifluorene, which was prepared through a two-step procedure as reported in the literature [3S].



Scheme S2. Synthetic scheme for the preparation of 2-(9,9'-spirobifluorenyl)-boronic acid neopentyl glycol ester

General procedure for the preparation of bis(spirofluorenyl)-N,N'-bis-(alkyl)-perylene-3,4,9,10-bis(dicarboximide)

A mixture of dibromo-N,N'-bis(alkyl)perylene-3,4,9,10-tetracarboxylic diimideandspirofluoreneboronicester (2.04 equivalents) were dissolved in dry toluene (5 ml each 0.25 mmol of dibromo-N,N'-bis(alkyl)perylene-3,4,9,10-tetracarboxylic diimide) and 2M K_2CO_3 solution (1 ml each 4 ml of toluene). Catalytic amounts of $Pd[PPh_3]_4$ were added and the reaction mixture was stirred at 100 °C for 18 hours. Shortly after the addition of the catalyst, the colour of the mixture starts to change. At the end of the reaction time, the solution was cooled to room temperature, extracted with $CHCl_3$, washed with water, extracted and dried over $MgSO_4$anh. concentrated to a smaller volume and dropped into methanol. The precipitate was filtered, and further purified by column chromatography, using hexane/$CHCl_3$ 3:2 as eluent.

Analytical data for the small molecule **PDI-SF-*nd***

Dark violet solid, yield 48 %; ^{1}H NMR (TCE, 400MHz): δ =8.38 (2H, m, pery), 8.04 (2H, m, pery), 7.85 (4H, m, pery and spirofl), 7.60 (6H, m, spirofl), 7.36 (4H, m, spirofl), 7.07 (10H, m, spirofl), 6.62 (8H, m, spirofl), 5.07 (2H, m, -CH-N), 2.08 (4H, m, $-CH_2-$), 1.78 (4H, m, $-CH_2-$), 1.16 (56H, m, $-CH_2-$), 0.77 (12H, t, $-CH_3$); ^{13}C NMR (TCE, 400MHz) δ 172.2 (C=O), 152.7, 142.4, 141.9, 141.0, 137.9, 135.2, 133.2, 59.3, 48.5, 37.2, 32.0, 28.9, 23.1, 15.6, 13.5 ppm; IR (KBr) υ 1698, 1656 cm^{-1}; HR-MS calculated mass 1550.88 and found mass 1550.55.

Analytical data for the small molecule **PDI-SF-*eh***

Dark violet solid, yield 63%; ^{1}H NMR (TCE, 400MHz): δ =8.35 (2H, m, pery), 8.02 (2H, m, pery), 7.83 (4H, m, pery, spirofl), 7.53 (6H, m, spirofl), 7.31 (4H, m, spirofl), 7.03 (10H, m, spirofl), 6.59 (8H, m, spirofl), 3.93 (4H, m, $-CH_2-N$), 1.86 (2H, m, $-CH-CH_2-N-$), 1.23 (16H, m, $-CH_2-$), 0.81 (12H, t, $-CH_3$); ^{13}C NMR (TCE, 400MHz) δ 170.9 (C=O), 153.6, 142.6, 141.3, 141.1, 135.1, 134.2, 58.7, 48.2, 32.7, 20.3, 14.7, 13.8 ppm; IR (KBr) υ 1697, 1656 cm^{-1}; HR-MS calculated mass 1242.53 and found mass 1242.15.

Analytical data for the small molecule **PDI-SF-*d***

Dark violet solid, yield 58%; ^{1}H NMR (TCE, 400MHz): δ =8.29 (2H, m, pery), 8.03 (2H, m, pery), 7.83 (4H, m, pery, spirofl), 7.43 (6H, m, spirofl), 7.31 (4H, m, spirofl), 7.02 (10H, m, spirofl), 6.52 (8H, m, spirofl), 4.04 (4H, m, $-CH_2-N$), 1.65 (4H, m, $-CH_2-$), 1.13 (36H, m, $-CH_2-$), 0.73 (6H, t, $-CH_3$); ^{13}C NMR (TCE, 400MHz) δ 171.3 (C=O), 152.7, 142.3, 141.8, 136.1, 135.8, 134.7, 55.8, 47.3, 31.6, 21.9, 15.8, 14.3, 12.9 ppm; IR (KBr) υ 1697, 1654 cm^{-1}; HR-MS calculated mass 1354.66 and found mass 1354.30.

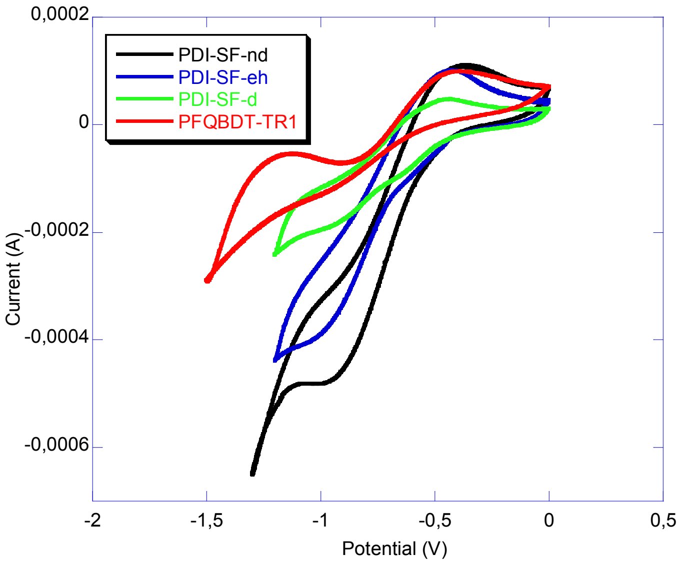


Figure S1. Cyclic voltammetry curves of all materials.

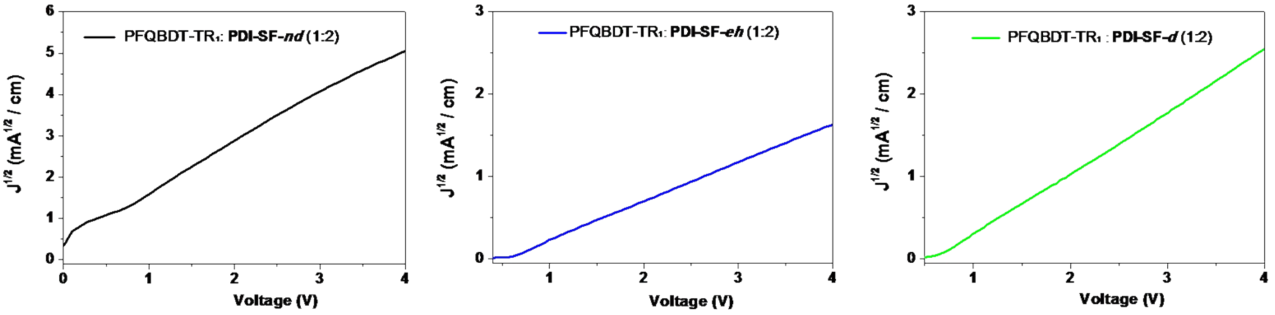


Figure S2. Dark $J^{1/2}$*vs.* V curves of *electron-only devices* based on the best performing BHJ blends.

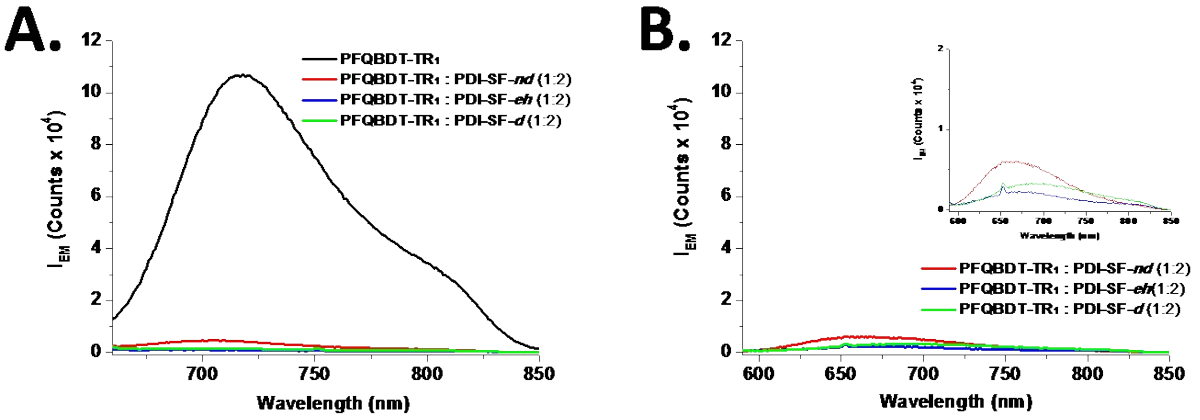


Figure S3. Emission spectra of: A) pristine polymer and optimized blended films (excitation wavelength: 650 nm), and B) optimized blended films (excitation wavelength: 565 nm), deposited on glass substrates.

Table S1. Some representative OPV tests for the performance optimization of PDI-SF based devices

Acceptor	D:A ratio	solvent	additive	annealing	Jsc	Voc	FF	PCE
PDI-SF-*nd*	1:1	ODCB	--	--	1.7	0.79	29	0.4
	1:1	ODCB	3% DIO	--	3.0	0.79	30	0.7
	1:1	ODCB	3% DIO	100°C/10’	3.0	0.80	29	0.7
	1:1	ODCB	3% DIO	140°C/20’	3.9	0.77	33	1.0
	1:2	ODCB	3% DIO	140°C/10’	4.1	0.76	32	1.0
	1:2	ODCB	3% DIO	160°C/10’	4.7	0.79	32	1.2
	1:2	OXY	3% DIO	160°C/10’	5.1	0.76	31	1.2
	1:2 inverted structure	ODCB	3% DIO	140°C/20’	4.2	0.96	35	1.4
	1:2 inverted structure	ODCB	3% DIO	160°C/10’	4.8	0.89	32	1.4
	1:3	ODCB	3% DIO	inhomogeneous films with formation of visible grains/clusters. No PV responses. Poor solubilization of the acceptor				
	1:3	OXY	3% DIO	inhomogeneous films with formation of visible grains/clusters. No PV responses. Poor solubilization of the acceptor				
PDI-SF-*eh*	1:1	**NO PV response, even varying the processing conditions**						
PDI-SF-*eh*	1:3	inhomogeneous films with formation of visible grains/clusters. No PV responses. Poor solubilization of the acceptor						
PDI-SF-*d*	1:1	**NO PV response, even varying the processing conditions**						
PDI-SF-*d*	1:3	inhomogeneous films with formation of visible grains/clusters. No PV responses. Poor solubilization of the acceptor						
$PC_{61}BM$	**1:1**	**ODCB**	**--**	**--**	**10.3**	**0.83**	**53**	**4.5**

References:

[1S] Rajasingh P, Cohen R, Shirman E, Shimon LJW, Rybtchinski B, *J Org Chem* **2007**, 72, 5973.

[2S] Wescott LD, Mattern DL, *J Org Chem* **2003**, 68, 10058.

[3S] Jeon SO, Yook KS, Joo CW, Son HS, Lee JY, *Thin Solid Films* **2010**, 518, 3716-20.