Electronic Supplementary Information

Comparison of Fluorene, Silafluorene and Carbazol as Linkers in Perylene Monoimide Based Non-Fullerene Acceptors

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Detailed synthesis description

Synthesis of **PMI**

In an autoclave, perylene-3,4,9,10-tetracarboxylic dianhydride (4.0 g, 10.2 mmol, 1 equiv.), zinc acetate (1.51 g, 6.86 mmol, 0.67 equiv.) and imidazole (20.4 g) were dispersed in 4.8 ml water. Then 2,6-diisopropylaniline (1.014 ml, 5.38 mmol, 0.53 equiv.) was added and the closed vessel was placed in a muffle furnace at 190 °C for 24 h. After cooling down to room temperature, the reaction mixture was rinsed with water (~ 30 ml) and acidified to a pH of 2 followed by filtration (until completely dry). The filter cake was extracted in chloroform in a Soxhlet extractor for 48 h. The crude product was then purified on SiO_2 (eluent $CHCl_3$) to give the product **2** as a red solid. Yield: 1.03 g (40%). R_f = 0.30-0.36 ($CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) 8.61 (d, *J* = 8.1 Hz, 2H), 8.40-8.35 (m, 4H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 2.78 (sept, *J* = 6.9 Hz, 2H), 1.20 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) 164.1, 145.8, 137.6, 134.4, 132.1, 131.2, 131.1, 130.7, 129.6, 129.3, 128.1, 127.2, 124.2, 123.9, 121.1, 120.3, 29.3, 24.2.

Synthesis of **PMI-Br (2)**

In a two-necked flask 3.72 g (7.72 mmol, 1 equiv.) of *N*-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide were dissolved in 150 ml acetic acid. The reaction mixture was stirred for 30 minutes at room temperature in the dark followed by the addition of iodine (78.4 mg, 0.309 mmol, 0.4 equiv.) and bromine (1.58 ml, 30.9 mmol, 4 equiv.). The mixture was stirred for another 22 h at room temperature and afterwards flushed with N_2 to remove the remaining bromine. The reaction

mixture was then diluted with 100 ml MeOH and stirred for another 30 minutes. Afterwards it was poured in deionized water followed by filtration to obtain the product in quantitative yield. Yield: 4.30 g (>99%). R_f = 0.38- 0.54 (toluene/acetone – 39/1)

^{1}H NMR (500 MHz, $CDCl_3$) 8.66 (t, J = 8.03 Hz, 2H), 8.49 (d, J = 3.82 Hz, 1H), 8.46 (d, J = 4.00 Hz, 2H) 8.41 (d, J = 4.00 Hz, 1H), 8.31 (d, J = 4.10 Hz, 1H), 8.24 (d, J = 4.16 Hz, 1H), 7.91 (d, J = 4.10 Hz, 1H), 7.72 (t, J = 8.00 Hz, 1H), 7.48 (t, J = 7.87 Hz, 1H), 7.34 (d, J = 3.88 Hz, 2H), 2.81-2.72 (hept, 2H), 1.18 (d, J = 3.41 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) 164.0, 145.9, 137.1, 136.9, 133.14, 132.3, 132.2, 131.5, 131.1, 130.6, 130.2, 129.8, 129.7, 129.3, 129.2, 128.5, 126.8, 126.4, 124.6, 124.2, 124.0, 121.6, 120.9, 120.6, 29.3, 24.2.

Synthesis of **PMI-F-PMI (3a)**

In a Schlenk tube, operated under nitrogen, 250 mg (0.45 mmol, 2 equiv.) of 9-bromo-*N*-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide and 112 mg (0.223 mmol, 1 equiv.) of 9,9-dihexylfluorene-2,7-diboronic acid *bis*(1,3-propanediol) ester (CAS Number 250597-29-6) were dissolved in 25 ml toluene followed by the addition of 1 M K_2CO_3 (2.50 ml) and 1 drop of Aliquat 336. Afterwards, $Pd(PPh_3)_4$ (0.022 mmol, 0.1 equiv.) were added and the reaction mixture was heated at 100 °C for 24 h. Upon completion, the reaction mixture was extracted with H_2O, dried over Na_2SO_4 followed by evaporation of the solvent under reduced pressure. The residue was purified by column chromatography (eluent: CH_2Cl_2/CH – 10/1 – 20/1 gradient) and further recrystallized using CH_2Cl_2/hexane to yield the product as a violet solid. Yield: 211 mg (73%). R_f = 0.45-0.53 (CH_2Cl_2)

^{1}H NMR (500 MHz, $CDCl_3$) 8.71-8.66 (m, 4H), 8.57 (d, *J* = 8.0 Hz, 2H), 8.53 (d, *J* = 7.6 Hz, 2H), 8.51-8.47 (m, 4H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.65-7.57 (m, 6H), 7.49 (*t*, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 4H), 2.80 (hept, *J* = 6.8 Hz, 4H), 2.14-2.08 (m, 4H), 1.24-1.13 (m, 36H), 0.95-0.87 (m, 4H), 0.85-0.80 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) 164.2, 151.6, 145.9, 144.0, 140.7, 139.1, 137.9, 137.8, 133.0, 132.3, 132.2, 131.2, 130.77, 129.7, 129.6, 129.2, 128.7, 128.7, 128.5, 127.2, 127.1, 125.0, 124.17, 124.14, 124.12, 123.8, 121.2, 121.1, 120.5, 120.3, 120.2, 55.7, 40.5, 31.7, 29.9, 29.3, 24.2, 22.8, 14.2. MS (MALDI-TOF) calc. for $C_{93}H_{84}N_2O_4H$ 1293.650, found 1293.647.

Synthesis of **PMI-FSi-PMI (3b)**

In a Schlenk tube, operated under nitrogen, 300 mg (0.535 mmol, 2 equiv.) of 9-bromo-*N*-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide and 176.3 mg (0.27 mmol, 1equiv.) of 9,9-dioctyl-9H-9-silafluorene-2,7-bis(boronic acid pinacol ester) (CAS Number 958293-23-7) were dissolved in 30 ml toluene followed by the addition of 1 M K_2CO_3 (3 ml) and 1 drop of Aliquat 336. Afterwards, $Pd(PPh_3)_4$ (0.027 mmol, 0.1 equiv.) was added and the reaction mixture was heated at 100 °C for 24 h. Upon completion, the reaction mixture was extracted with H_2O and dried over Na_2SO_4 followed by evaporation of the solvent under reduced pressure. The residue was purified by column chromatography (eluent: CH_2Cl_2/CH – 1/1 – 4/1 – 10/1 gradient) and further recrystallized using CH_2Cl_2/hexane to yield the product as a violet solid. Yield: 136 mg (37%). R_f = 0.47-0.55 (CH_2Cl_2)

^{1}H NMR (500 MHz, $CDCl_3$) 8.69 (dd, *J* = 8.0, 2.0 Hz, 4H), 8.57 (d, *J* = 8.0, 2H), 8.55 (d, *J* = 7.6 Hz, 2H), 8.53-8.49 (m, 4H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.88-7.84 (m, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.71-7.69 (m, 2H), 7.65 (t, *J* = 8.9 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.35

(d, *J* = 7.8 Hz, 4H), 2.79 (hept, *J* = 6.8 Hz, 4H), 1.54-1.46 (m, 4H), 1.37-1.30 (m, 4H), 1.29-1.17 (m, 40H), 1.11-1.05 (m, 4H), 0.85-0.80 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) 164.2, 147.8, 145.9, 143.7, 139.0, 138.9, 137.9, 137.7, 135.1, 133.0, 132.3, 132.4, 132.2, 131.2, 130.8, 129.67, 129.6, 128.7, 128.4, 127.2, 127.2, 124.2, 123.8, 121.3, 121.2, 121.1, 120.5, 120.3, 33.5, 32.0, 29.4, 29.3, 24.3, 24.2, 22.8, 14.2, 12.5. MS (MALDI-TOF) calc. for $C_{96}H_{92}N_2O_4SiH$ 1365.6904, found 1365.6947.

Synthesis of **PMI-FN-PMI (3c)**

In a Schlenk tube, operated under nitrogen, 300 mg (0.535 mmol, 2 equiv.) of 9-bromo-*N*-(2,6-diisopropylphenyl)-perylene-3,4-dicarboximide and 176 mg (0.27 mmol, 1 equiv.) of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (CAS Number 958261-51-3) were dissolved in 30 ml toluene followed by the addition of 1 M aqueous K_2CO_3 (3 ml) and 1 drop of Aliquat 336. Afterwards, $Pd(PPh_3)_4$ (0.027 mmol, 0.1 equiv.) was added and the reaction mixture was heated at 100 °C for 24 h. Upon completion, the reaction mixture was extracted with H_2O and dried over Na_2SO_4 followed by evaporation of the solvent under reduced pressure. The residue was purified by column chromatography (eluent: CH_2Cl_2/CH – 1/1 – 4/1 – 10/1 gradient) and further recrystallized using CH_2Cl_2/hexane to yield the product as a violet solid. Yield: 205 mg (56%). R_f = 0.47-0.55 (CH_2Cl_2)

^{1}H NMR (500 MHz, $CDCl_3$) 8.69 (t, J = 7.6 Hz, 4H), 8.62-8.55 (m, 2H), 8.56-8.49 (m, 6H), 8.39-8.31 (m, 2H), 8.22-8.14 (m, 2H) 7.83-7.76 (m, 3H), 7.67-7.60 (m, 3H), 7.53-7.46 (m, 4H), 7.35 (d, *J* = 7.8 Hz, 4H), 4.68 (hept, *J* = 5.0 Hz, 1H), 2.80 (hept, *J* = 6.8 Hz, 4H), 2.40-2.30 (m, 2H), 2.00-1.90 (m, 2H), 1.34-1.11 (m, 48H), 0.83-0.78 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) 164.2, 145.9, 144.6, 142.8, 139.43, 139.39, 137.9, 137.8, 137.3, 133.2, 132.3, 132.2, 131.3, 130.8, 129.9, 129.7,

129.6, 128.9, 128.7, 128.6, 127.2, 127.1, 124.2, 124.1, 123.7, 123.5, 122.1, 121.5, 121.2, 121.0, 120.8, 120.5, 120.2, 113.5, 110.8, 56.9, 34.0, 31.9, 29.6, 29.5, 29.4, 29.3, 27.1, 24.2, 22.8, 14.2. MS (MALDI-TOF) calc. for $C_{97}H_{93}N_3O_4H$ 1364.7200, found 1364.7173.

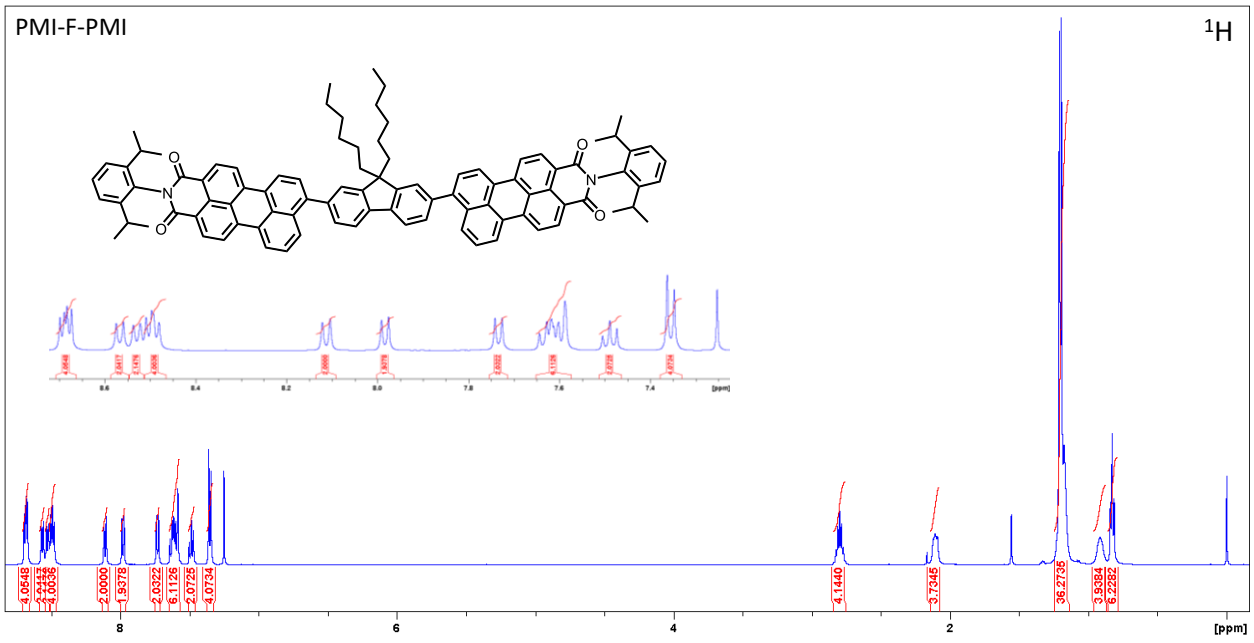

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **PMI-F-PMI** (**3a**) with an inset of the aromatic region, referenced to TMS.

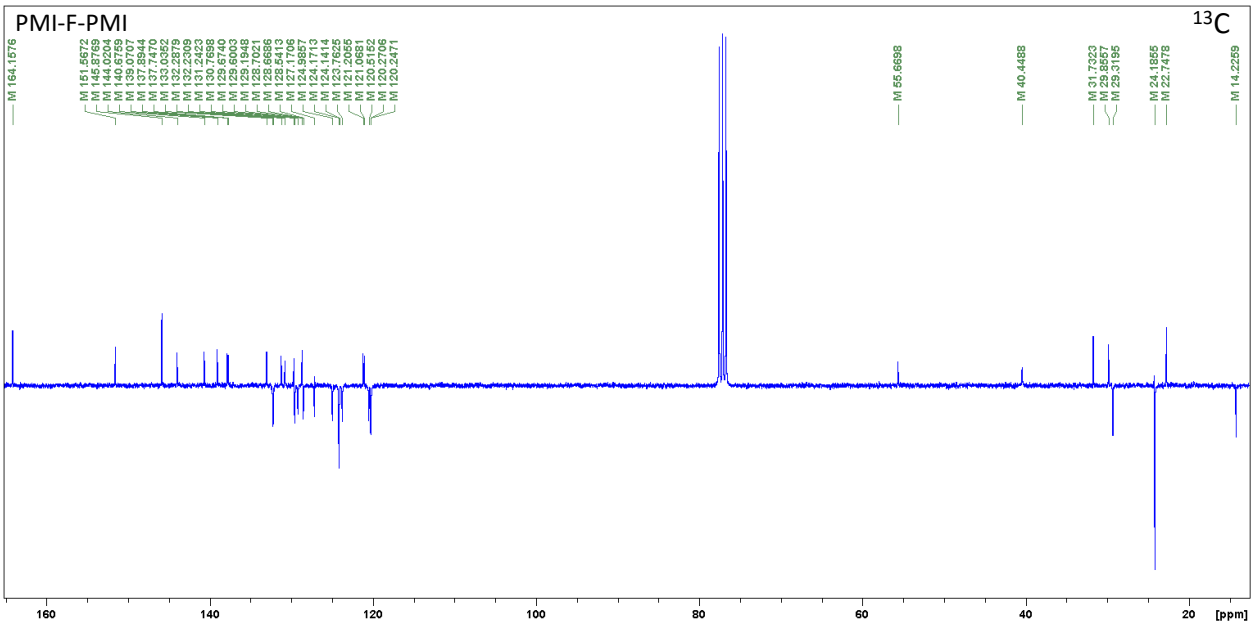

Figure S2. ^{13}C APT NMR (75 MHz, $CDCl_3$) spectrum of **PMI-F-PMI** (**3a**), referenced to $CDCl_3$.

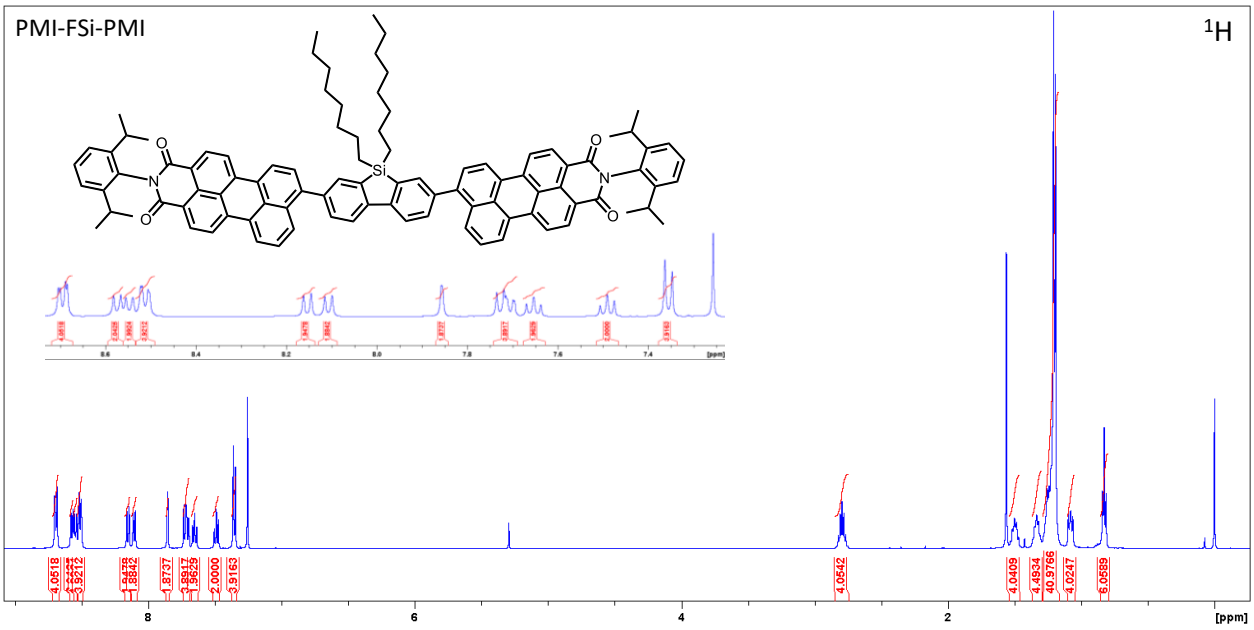

Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) of **PMI-FSi-PMI** (**3b**) with an inset of the aromatic region, referenced to TMS.

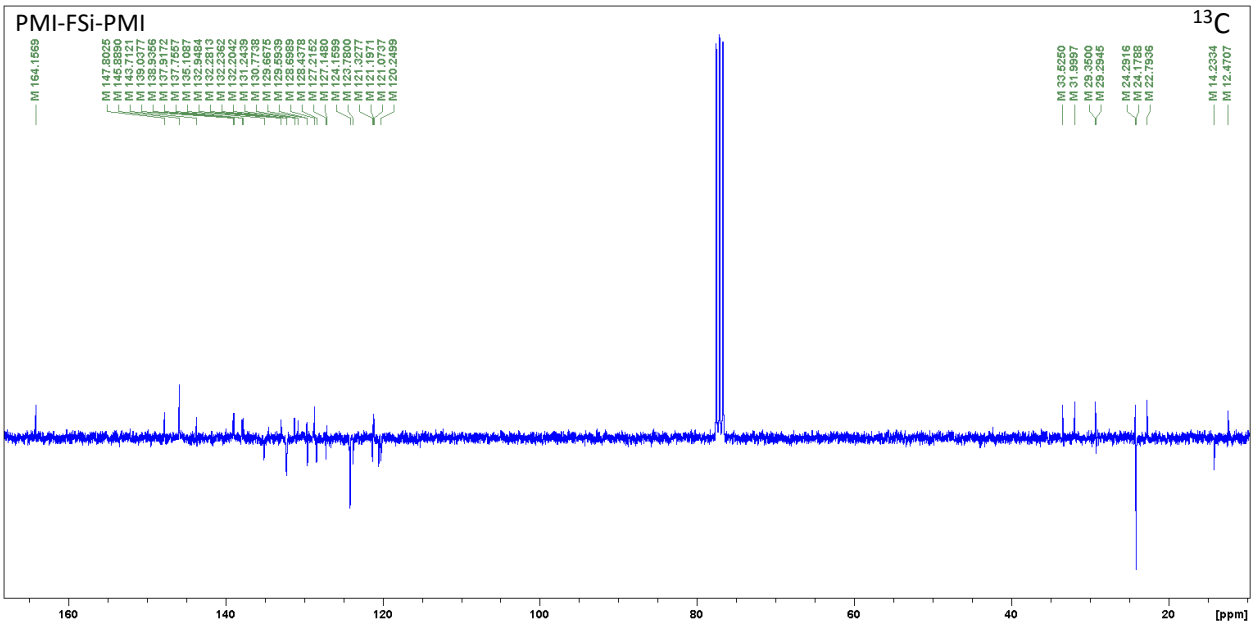

Figure S4. ^{13}C APT NMR spectrum (75 MHz, $CDCl_3$) of **PMI-FSi-PMI** (**3b**), referenced to $CDCl_3$.

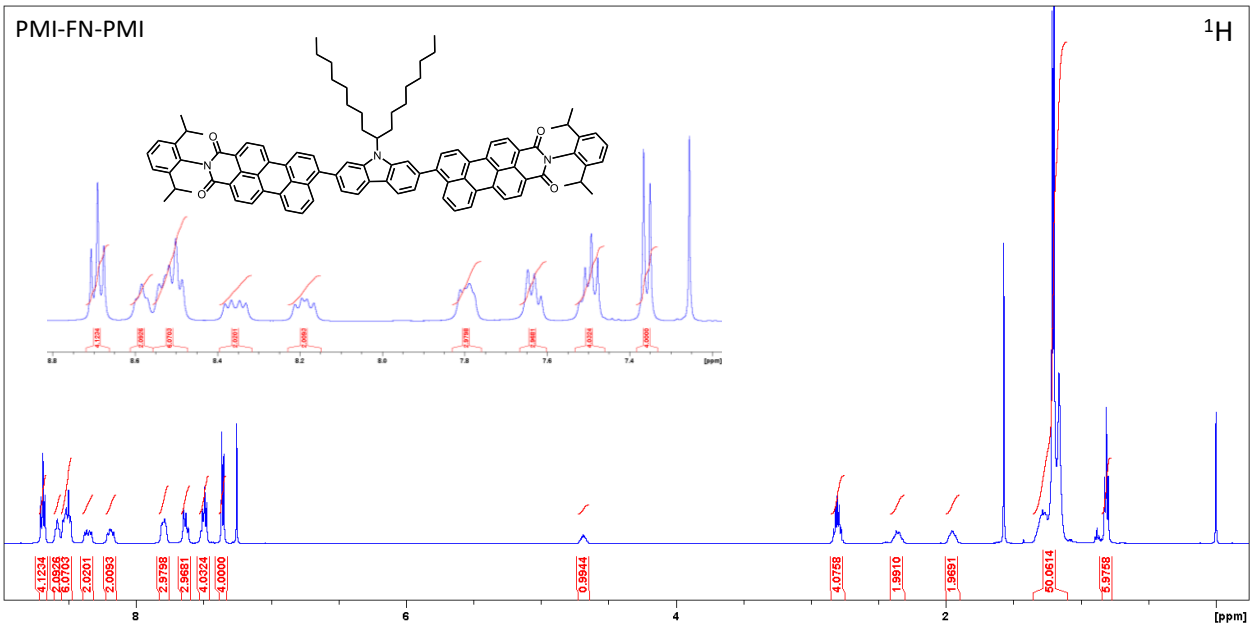

Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **PMI-FN-PMI** (**3c**) with an inset of the aromatic region, referenced to TMS.

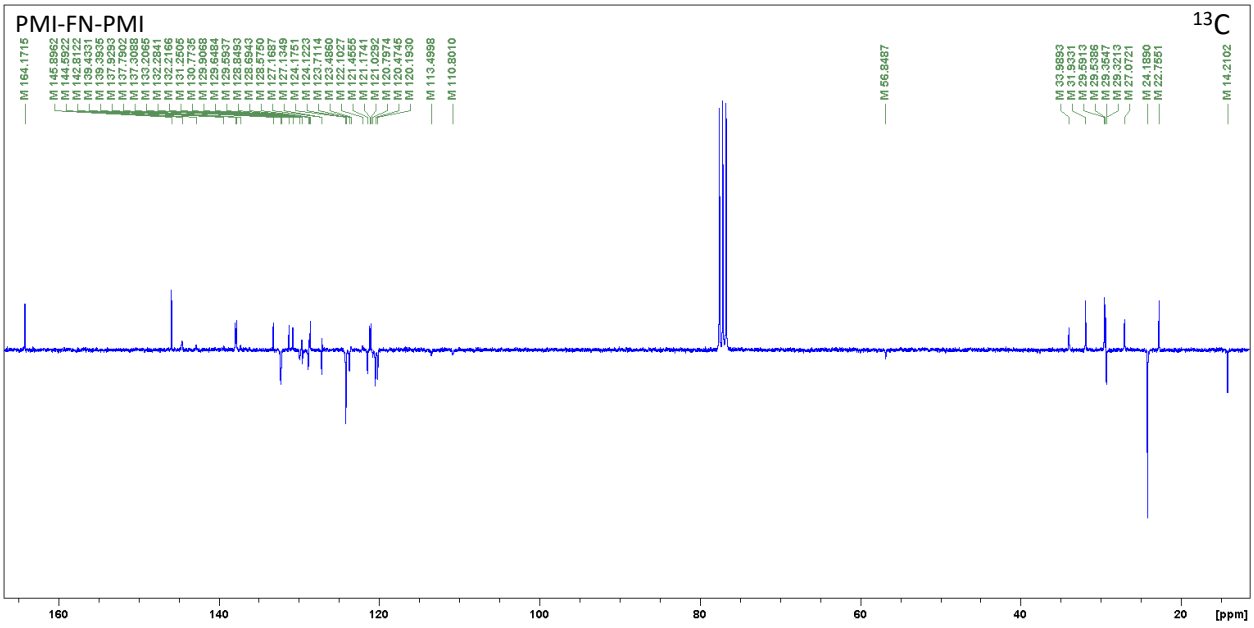

Figure S6. ^{13}C APT NMR spectrum (75 MHz, $CDCl_3$) of **PMI-FN-PMI** (**3c**), referenced to $CDCl_3$.

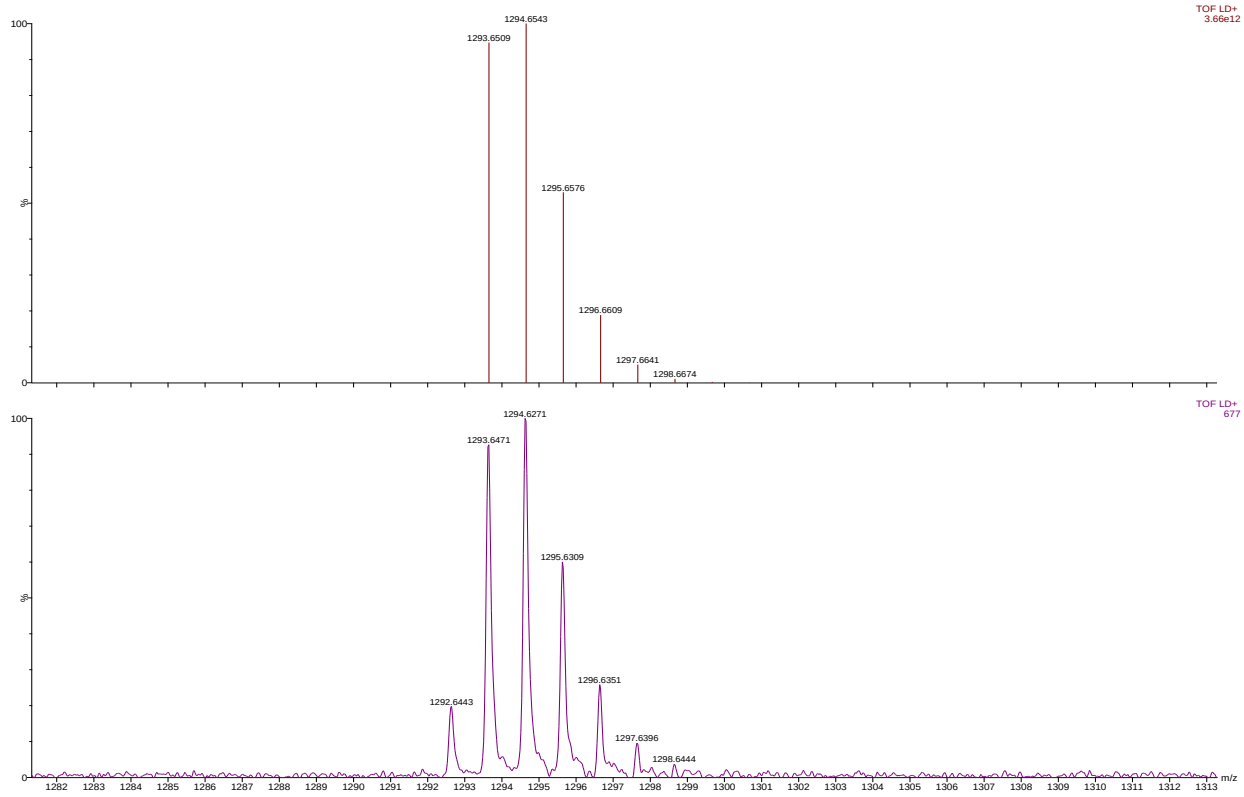

Figure S7. HRMS (MALDI-TOF, Dithranol matrix) of **PMI-F-PMI** (**3a**), upper – simulated, lower - found.

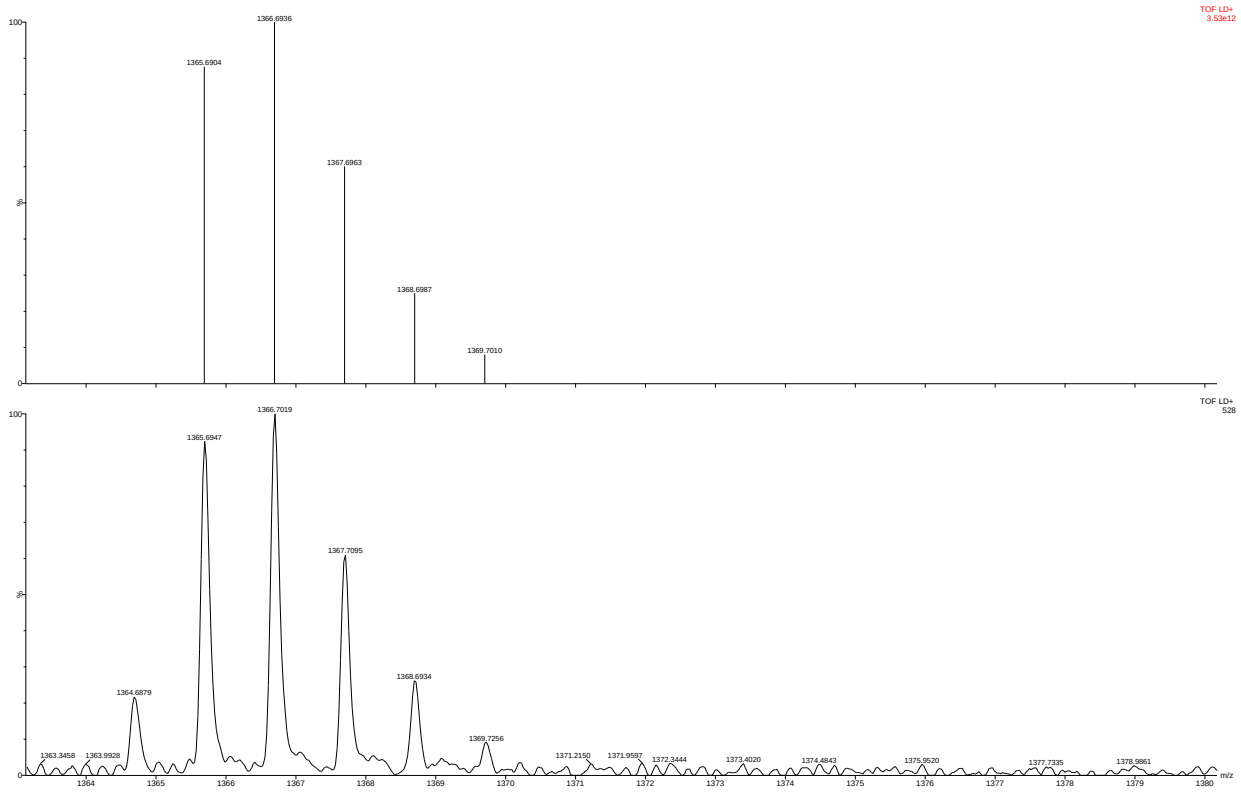

Figure S8. HRMS (MALDI-TOF, Dithranol matrix) of **PMI-FSi-PMI** (**3b**), upper – simulated, lower - found.

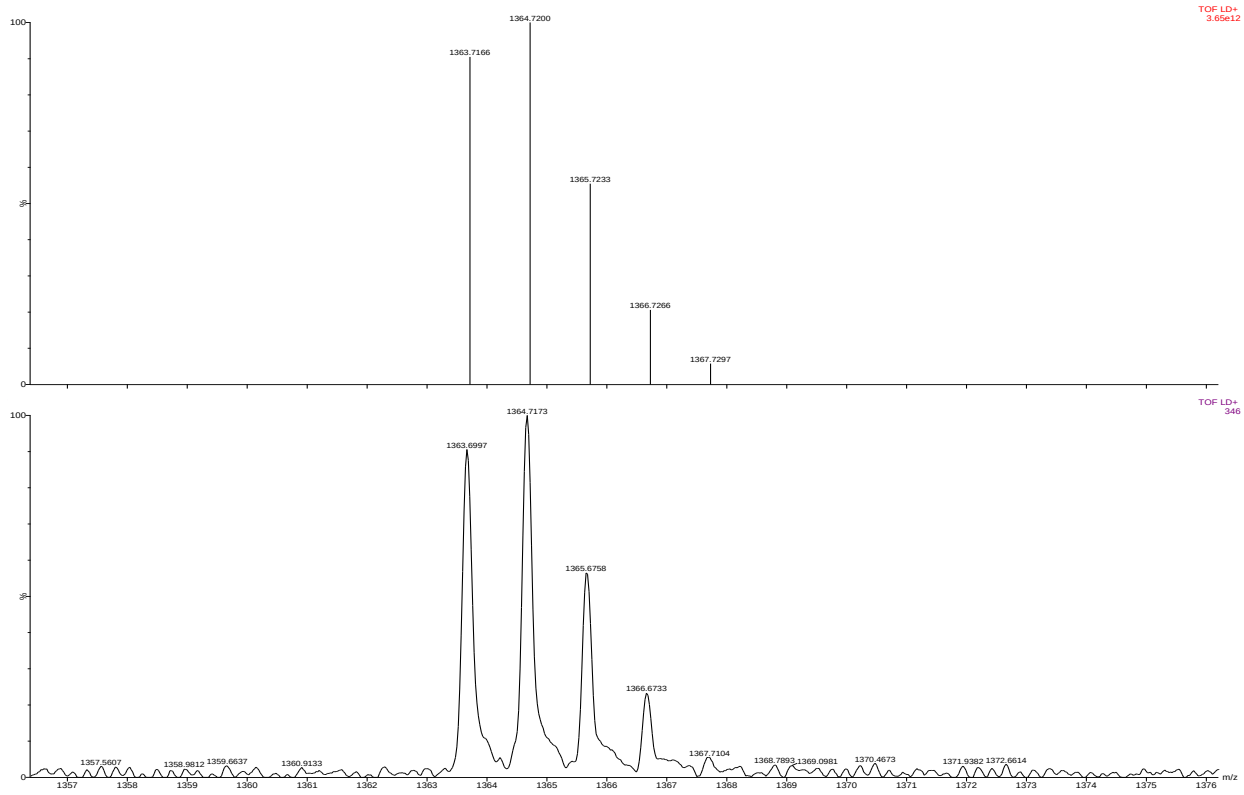

Figure S9. HRMS (MALDI-TOF, DCTB matrix) of **PMI-FN-PMI** (**3c**), upper – simulated, lower - found.

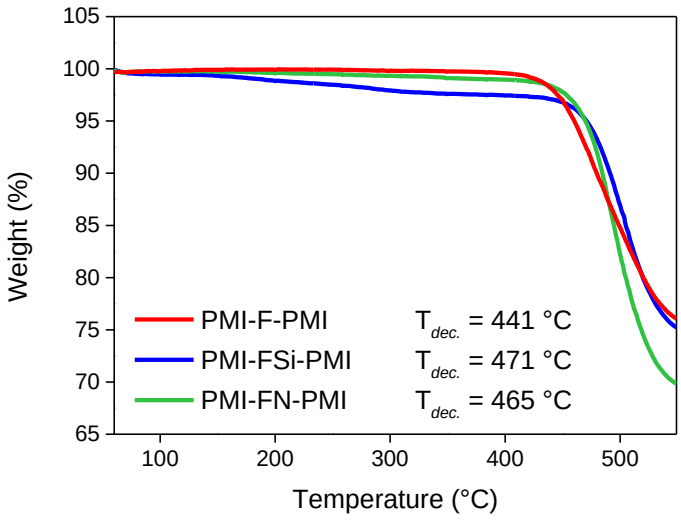

Figure S10. TGA measurements with the respective decomposition temperatures of: red - **PMI-F-PMI** (**3a**), blue - **PMI-FSi-PMI** (**3b**) and green - **PMI-FN-PMI** (**3c**).

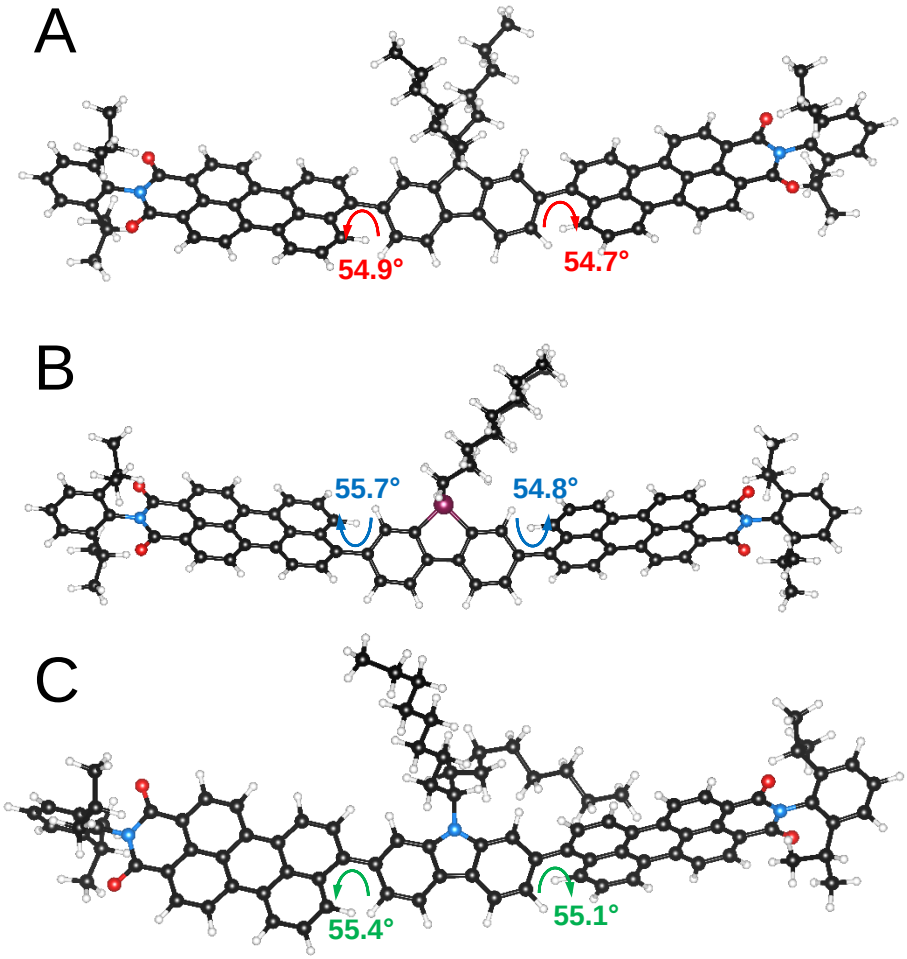

Figure S11. Computed (B3LYP/6-31G*) optimal geometries and the dihedral angles of: A - **PMI-F-PMI** (**3a**); B - **PMI-FSi-PMI** (**3b**); C - **PMI-FN-PMI** (**3c**).

Table S1 Cartesian coordinates for the DFT (B3LYP/6-31G*) optimized structures of **PMI-F-PMI** (**3a**), **PMI-FSi-PMI** (**3b**) and **PMI-FN-PMI** (**3c**).

PMI-F-PMI (3a)				PMI-Si-PMI (3b)				PMI-FN-PMI (3c)			
C	18.39259	0.87382	-0.43067	C	-12.65472	-0.18179	1.12317	C	-12.48076	-1.32043	-0.23179
C	17.80821	-0.00341	-1.33929	C	-11.98346	-0.71083	2.21286	C	-12.09903	-2.65041	-0.16699
C	16.44534	-0.31448	-1.26972	C	-10.60433	-0.5338	2.35414	C	-10.75132	-3.00919	-0.25847
C	15.68734	0.29078	-0.25229	C	-9.8494	0.17518	1.41652	C	-9.74051	-2.05654	-0.41239
C	16.25169	1.18024	0.67861	C	-10.51857	0.71326	0.27221	C	-10.11296	-0.67772	-0.49418
C	17.61905	1.45764	0.56796	C	-11.93206	0.53473	0.13886	C	-11.4941	-0.3183	-0.39446
C	15.43476	1.83275	1.78782	C	-9.80402	1.42483	-0.74282	C	-9.13361	0.35015	-0.67135
C	15.91772	1.37701	3.17817	C	-10.5221	1.9369	-1.82685	C	-9.56451	1.67905	-0.71387
C	15.42995	3.36771	1.65824	C	-11.90423	1.76648	-1.94492	C	-10.91434	2.02268	-0.60069
C	15.83712	-1.28174	-2.27839	C	-12.61455	1.07145	-0.97976	C	-11.88149	1.0424	-0.44926
C	15.93044	-0.72969	-3.71351	C	-8.39909	0.38383	1.56661	C	-8.31627	-2.42273	-0.49206
C	16.46708	-2.68293	-2.16234	C	-7.67057	1.06035	0.53302	C	-7.33461	-1.40209	-0.71849
N	14.2703	-0.01204	-0.16001	C	-8.34808	1.5866	-0.61403	C	-7.71833	-0.02511	-0.80662
C	13.88682	-1.09666	0.65283	C	-7.71331	-0.05129	2.69692	C	-7.89302	-3.74075	-0.34624
C	12.43656	-1.38086	0.73536	C	-6.33427	0.15609	2.84476	C	-6.53636	-4.08886	-0.41611
C	11.49486	-0.59508	0.02741	C	-5.61329	0.77983	1.85101	C	-5.58212	-3.12659	-0.66047
C	11.94315	0.48025	-0.77767	C	-6.24707	1.22749	0.66293	C	-5.94852	-1.76752	-0.84161
C	13.38317	0.80287	-0.89063	C	-5.50553	1.87702	-0.38117	C	-4.96237	-0.7567	-1.10243
C	10.09746	-0.88673	0.12461	C	-6.20478	2.38661	-1.46455	C	-5.37706	0.56453	-1.1656
C	9.16315	-0.08746	-0.60728	C	-7.59352	2.24989	-1.57656	C	-6.72212	0.92318	-1.01603
C	9.65434	0.96261	-1.38779	C	-14.11664	-0.38189	1.00537	C	-13.91493	-0.97151	-0.12276
C	11.02037	1.24518	-1.47196	C	-14.07666	0.90328	-1.1367	C	-13.30353	1.43703	-0.34036
C	11.99566	-2.43499	1.51793	N	-14.73977	0.18122	-0.12513	N	-14.24619	0.39002	-0.26143
C	10.63199	-2.72361	1.62077	O	-14.76844	-1.00113	1.83603	O	-14.78408	-1.812	0.06871
C	9.66371	-1.97158	0.95026	O	-14.69639	1.35903	-2.08813	O	-13.66406	2.60569	-0.32871
C	8.22356	-2.25874	1.06424	C	-16.17487	0.0039	-0.2595	C	-15.64631	0.76274	-0.13814
C	7.28475	-1.48351	0.30634	C	-4.02591	2.01914	-0.35539	C	-3.52321	-1.06965	-1.31674
C	7.72894	-0.39996	-0.51815	C	-17.0328	0.95534	0.31965	C	-16.4579	0.85131	-1.28722
C	5.88123	-1.78888	0.39212	C	-18.41132	0.76171	0.17612	C	-17.79311	1.23478	-1.09867
C	4.93651	-1.0342	-0.38294	C	-18.91479	-0.33503	-0.51755	C	-18.30693	1.51281	0.16346
C	5.40871	0.02137	-1.14752	C	-18.04257	-1.26127	-1.08114	C	-17.48346	1.41302	1.27839
C	6.77163	0.33445	-1.21081	C	-16.65569	-1.11234	-0.96442	C	-16.14104	1.03918	1.15093
C	7.74448	-3.26257	1.90112	C	-16.51481	2.16577	1.08669	C	-16.04447	0.51792	-2.72541
C	6.37271	-3.52833	2.01952	C	-16.93959	3.48381	0.41137	C	-14.70662	1.0996	-3.21827
C	5.45807	-2.81033	1.28203	C	-16.94079	2.11616	2.56624	C	-16.13077	-0.99831	-3.00091
C	3.48105	-1.3399	-0.40565	C	-15.72763	-2.14392	-1.59506	C	-15.27571	0.94337	2.4035
C	3.00797	-2.6262	-0.72818	C	-15.93514	-3.53942	-0.97666	C	-15.14243	2.3106	3.10111
C	1.64292	-2.89732	-0.79009	C	-15.87622	-2.16904	-3.12797	C	-15.79917	-0.14179	3.36391
C	0.73218	-1.8694	-0.53822	C	-3.43568	3.27806	-0.55911	C	-3.12031	-1.99181	-2.31269

C	1.18287	-0.56692	-0.24205	C	-2.05162	3.43383	-0.58951	C	-1.77693	-2.24376	-2.55709
C	2.54769	-0.31206	-0.16242	C	-1.21464	2.32541	-0.41763	C	-0.80348	-1.57634	-1.80498
C	-0.72994	-1.87768	-0.50682	C	-1.78796	1.04241	-0.21877	C	-1.20249	-0.64577	-0.80899
C	-1.18174	-0.58142	-0.18655	C	-3.17526	0.90803	-0.19188	C	-2.55539	-0.3901	-0.56478
C	-9E-5	0.37894	0.01132	C	0.26987	2.36057	-0.42428	C	0.63774	-1.59904	-1.79416
C	-1.63993	-2.90846	-0.74966	C	0.9068	1.10574	-0.23451	C	1.05616	-0.67897	-0.7937
C	-3.00524	-2.64082	-0.67795	Si	-0.4086	-0.23449	-0.01811	N	-0.06946	-0.11032	-0.19665
C	-3.47909	-1.34908	-0.37931	C	1.05018	3.5095	-0.59647	C	1.5953	-2.30313	-2.53283
C	-2.5467	-0.31856	-0.14519	C	2.44098	3.42131	-0.5839	C	2.94436	-2.08547	-2.28766
C	-4.93397	-1.03882	-0.38681	C	3.09288	2.18978	-0.40682	C	3.36832	-1.16163	-1.30288
C	0.10748	0.92452	1.46961	C	2.2997	1.03926	-0.23005	C	2.41696	-0.46005	-0.54985
C	-0.10986	1.50969	-1.05943	C	4.57676	2.1311	-0.33279	C	4.81391	-0.96815	-1.00642
C	0.97994	2.59041	-1.08232	C	5.36056	1.23911	-1.14021	C	5.77778	-0.63347	-2.01718
C	0.70701	3.65933	-2.1509	C	6.78529	1.16913	-0.95417	C	7.17074	-0.52946	-1.67263
C	1.79002	4.74336	-2.22389	C	7.42004	2.02164	0.00571	C	7.58305	-0.70447	-0.31239
C	1.51926	5.8068	-3.29597	C	6.62518	2.90825	0.7257	C	6.60822	-0.98723	0.63906
C	2.60788	6.8823	-3.36908	C	5.23546	2.95748	0.5636	C	5.25698	-1.12184	0.29812
C	-0.98433	1.88689	1.95745	C	4.76408	0.44748	-2.15603	C	5.38266	-0.35845	-3.35232
C	-0.71605	2.3912	3.38346	C	5.5243	-0.40684	-2.92314	C	6.3159	-0.04236	-4.31432
C	-1.79366	3.35149	3.90287	C	6.90679	-0.51019	-2.71065	C	7.6796	0.00624	-3.99079
C	-1.53053	3.85455	5.32822	C	7.55677	0.25704	-1.74795	C	8.13071	-0.23281	-2.69584
C	-2.60951	4.81532	5.83812	C	9.01136	0.15951	-1.53545	C	9.56244	-0.17889	-2.35539
C	-5.89316	-1.7713	0.39115	C	9.63637	1.01384	-0.57272	C	9.96227	-0.33236	-0.99044
C	-7.29398	-1.46319	0.27636	C	8.87619	1.94792	0.20044	C	9.00395	-0.57591	0.04378
C	-7.72122	-0.40017	-0.583	C	11.05155	0.93135	-0.3765	C	11.34957	-0.24229	-0.65241
C	-6.75057	0.31344	-1.27887	C	11.68949	1.77421	0.56578	C	11.76262	-0.36908	0.69619
C	-5.38984	-0.00155	-1.18547	C	10.93467	2.67371	1.30009	C	10.81557	-0.58492	1.68385
C	-5.48727	-2.77336	1.31065	C	9.55124	2.75544	1.12008	C	9.4601	-0.68906	1.35992
C	-6.4158	-3.46983	2.05142	C	9.81208	-0.74271	-2.2408	C	10.55421	0.01777	-3.31993
C	-7.78454	-3.20056	1.90734	C	11.19312	-0.82083	-2.03999	C	11.90879	0.09221	-2.98355
C	-8.24712	-2.21504	1.03992	C	11.82039	0.00508	-1.12226	C	12.31584	-0.02763	-1.66507
C	-9.68413	-1.92375	0.89889	C	13.28512	-0.09978	-0.93535	C	13.75657	0.06579	-1.34022
C	-10.10106	-0.86091	0.03666	C	13.15237	1.7105	0.78194	C	13.19135	-0.27289	1.07059
C	-9.15277	-0.08639	-0.70381	N	13.86255	0.76944	0.01063	N	14.10474	-0.06033	0.01914
C	-11.49559	-0.56644	-0.08914	O	13.73419	2.42842	1.58401	O	13.58066	-0.37082	2.22647
C	-11.92743	0.48674	-0.93166	O	13.97662	-0.8922	-1.56163	O	14.61686	0.24506	-2.1915
C	-10.99145	1.22699	-1.63494	C	15.29903	0.69144	0.20545	C	15.51217	0.03657	0.36233
C	-9.62804	0.94176	-1.52242	C	16.13382	1.50731	-0.5772	C	16.28033	-1.13958	0.41309
C	-10.66532	-2.65106	1.57782	C	17.51509	1.41327	-0.37129	C	17.63341	-1.01954	0.75027
C	-12.02606	-2.35958	1.4473	C	18.04313	0.54184	0.57645	C	18.19914	0.22224	1.02315
C	-12.45095	-1.32725	0.6277	C	17.19289	-0.25394	1.33846	C	17.41599	1.37104	0.96334
C	-13.89859	-1.03952	0.51592	C	15.80454	-0.19613	1.17037	C	16.05756	1.3036	0.63318

N	-14.26535	0.02328	-0.33274	C	14.90146	-1.08263	2.02008	C	15.22931	2.58169	0.57309
C	-13.36412	0.81244	-1.07414	C	15.15788	-2.57585	1.73998	C	15.18454	3.29	1.94033
C	-15.67944	0.33084	-0.45195	C	15.03472	-0.74903	3.51823	C	15.72926	3.52009	-0.54194
C	-16.25211	1.2435	0.45106	C	15.58886	2.46964	-1.62642	C	15.6921	-2.51545	0.12252
C	-17.6164	1.52474	0.31515	C	15.9326	3.93113	-1.281	C	16.38491	-3.18412	-1.07972
C	-18.37883	0.9224	-0.68106	C	16.06855	2.08746	-3.03975	C	15.72692	-3.41261	1.37475
C	-17.78634	0.02239	-1.5617	C	-0.42629	-1.00553	1.71952	C	-0.09522	0.89233	0.88236
C	-16.42621	-0.2937	-1.46603	C	0.87895	-1.6639	2.20863	C	0.5172	0.35071	2.19006
C	-15.80867	-1.28565	-2.44454	C	0.78387	-2.20353	3.64361	C	0.49845	2.2386	0.40892
C	-16.4527	-2.67903	-2.31325	C	2.08163	-2.85553	4.13816	C	0.16671	3.4276	1.32273
C	-15.87163	-0.76028	-3.8913	C	1.9906	-3.39545	5.57156	C	0.67406	4.76486	0.76541
C	-15.44715	1.91666	1.55658	C	3.2866	-4.05396	6.06175	C	0.34707	5.96393	1.6648
C	-15.43182	3.44823	1.39235	C	-0.42457	-1.51657	-1.42113	C	0.8521	7.30159	1.1079
C	-15.95129	1.49487	2.95006	C	0.84054	-2.3792	-1.59661	C	0.52265	8.49688	2.01314
O	13.80291	1.72489	-1.57659	C	0.75477	-3.34389	-2.78854	C	0.95079	9.86392	1.45394
O	14.7252	-1.75626	1.25215	C	2.01143	-4.20545	-2.96813	C	2.46685	10.05118	1.31973
O	-13.76962	1.71594	-1.79258	C	1.92828	-5.17302	-4.15582	C	-0.17853	-0.90331	2.73642
O	-14.74855	-1.67803	1.12166	C	3.18179	-6.04046	-4.32861	C	0.44425	-1.40143	4.04895
H	19.45297	1.10254	-0.5007	C	3.10139	-7.00685	-5.51727	C	-0.27538	-2.60381	4.68264
H	18.41902	-0.45565	-2.11589	C	4.35509	-7.87264	-5.67885	C	-0.22093	-3.89748	3.85746
H	18.08316	2.14046	1.27439	C	3.19691	-4.59597	7.49427	C	-0.88326	-5.09046	4.55895
H	14.39695	1.50138	1.68513	C	4.49701	-5.2467	7.97774	C	-0.84437	-6.38458	3.73586
H	15.28693	1.81006	3.96403	H	-12.55142	-1.26368	2.9539	C	-1.50924	-7.57067	4.44177
H	15.87733	0.28614	3.26353	H	-10.12708	-0.97172	3.22263	H	-12.86802	-3.40584	-0.04386
H	16.95025	1.6935	3.36763	H	-10.01291	2.48561	-2.61021	H	-10.50616	-4.06341	-0.21026
H	14.78954	3.81392	2.42875	H	-12.44377	2.1724	-2.79437	H	-8.84781	2.48213	-0.83768
H	15.05345	3.67373	0.67654	H	-8.24333	-0.54604	3.50217	H	-11.22871	3.06058	-0.63428
H	16.43596	3.78616	1.78026	H	-5.83861	-0.17298	3.75368	H	-8.6124	-4.52855	-0.1561
H	14.77345	-1.3899	-2.04558	H	-4.55131	0.95199	1.98006	H	-6.24181	-5.12432	-0.27102
H	15.43535	-1.4092	-4.41789	H	-5.6581	2.87792	-2.26427	H	-4.53463	-3.40022	-0.70136
H	15.4497	0.25155	-3.78376	H	-8.06986	2.66403	-2.4576	H	-4.6447	1.33946	-1.37198
H	16.97306	-0.62016	-4.03491	H	-19.09872	1.47975	0.61538	H	-6.97394	1.97464	-1.09214
H	15.97819	-3.38071	-2.85298	H	-19.9889	-0.46775	-0.61891	H	-18.44024	1.31393	-1.96898
H	16.36134	-3.0727	-1.14453	H	-18.44318	-2.11441	-1.62208	H	-19.34649	1.80985	0.27549
H	17.53536	-2.6652	-2.40862	H	-15.42111	2.13549	1.06778	H	-17.88447	1.63165	2.26414
H	8.97405	1.58758	-1.95397	H	-16.50592	4.34182	0.93934	H	-16.81762	0.98753	-3.34785
H	11.38176	2.06548	-2.08332	H	-16.60219	3.5129	-0.63003	H	-14.67942	1.06167	-4.31381
H	12.7313	-3.02996	2.04904	H	-18.02923	3.60675	0.41732	H	-14.58004	2.14132	-2.90881
H	10.34015	-3.56216	2.24157	H	-16.50825	2.96016	3.11734	H	-13.84652	0.52832	-2.85706
H	4.70743	0.59997	-1.74175	H	-16.60258	1.18664	3.03572	H	-15.91535	-1.20263	-4.05711
H	7.06809	1.16531	-1.8404	H	-18.03071	2.17266	2.67328	H	-17.13273	-1.38009	-2.77684
H	8.43088	-3.85136	2.49812	H	-14.6962	-1.84819	-1.3782	H	-15.42307	-1.56343	-2.38851

H	6.03503	-4.30159	2.70364	H	-15.22081	-4.25591	-1.40034	H	-14.26823	0.64096	2.10407
H	4.39884	-3.01004	1.3914	H	-15.792	-3.50859	0.10861	H	-14.46863	2.23504	3.96322
H	3.72173	-3.41495	-0.94687	H	-16.9441	-3.92052	-1.17386	H	-14.73974	3.05892	2.41099
H	1.29932	-3.89893	-1.03546	H	-15.15872	-2.87053	-3.5708	H	-16.11054	2.67218	3.46748
H	2.91714	0.67101	0.11223	H	-15.69559	-1.17565	-3.55162	H	-15.13312	-0.23834	4.23002
H	-1.29581	-3.90635	-1.00899	H	-16.88152	-2.48744	-3.42877	H	-15.85332	-1.11204	2.85951
H	-3.71843	-3.43205	-0.88957	H	-4.07533	4.14847	-0.67819	H	-16.79988	0.10116	3.74046
H	-2.91696	0.67825	0.07329	H	-1.63581	4.42626	-0.7409	H	-3.87818	-2.48725	-2.91126
H	1.07999	1.42474	1.56796	H	-3.62414	-0.07421	-0.06195	H	-1.48642	-2.94631	-3.33379
H	0.14781	0.0605	2.14587	H	0.58462	4.47996	-0.74557	H	-2.87605	0.30584	0.20319
H	-0.15171	1.0287	-2.04561	H	3.03606	4.31897	-0.72942	H	1.28726	-3.0212	-3.2883
H	-1.08269	2.00115	-0.92705	H	2.79787	0.08665	-0.06723	H	3.68978	-2.64741	-2.84147
H	1.05814	3.07788	-0.10096	H	7.06989	3.57546	1.45464	H	2.75412	0.25631	0.18907
H	1.957	2.13301	-1.28165	H	4.65642	3.63661	1.18272	H	6.88233	-1.13398	1.67739
H	0.61366	3.173	-3.13314	H	3.69984	0.53742	-2.33813	H	4.54214	-1.386	1.0719
H	-0.26676	4.13152	-1.95307	H	5.05724	-1.00114	-3.70344	H	4.32971	-0.38264	-3.60616
H	1.88363	5.2331	-1.24304	H	7.46803	-1.19561	-3.3346	H	5.99914	0.17654	-5.33006
H	2.76444	4.27142	-2.42069	H	11.44037	3.31068	2.01836	H	8.38201	0.25702	-4.77701
H	1.42257	5.3162	-4.27498	H	9.00576	3.47209	1.7223	H	11.15034	-0.6753	2.71196
H	0.54778	6.28143	-3.09738	H	9.37018	-1.41417	-2.96718	H	8.75938	-0.86197	2.16805
H	2.38509	7.62518	-4.14328	H	11.7966	-1.5284	-2.59896	H	10.28792	0.11231	-4.3659
H	2.70471	7.41472	-2.41484	H	18.18512	2.03125	-0.96259	H	12.66351	0.2467	-3.7476
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H	-1.96082	1.38774	1.93787	H	17.6123	-0.93153	2.0772	H	19.25216	0.29479	1.28296
H	-1.06141	2.75113	1.28347	H	13.86382	-0.87876	1.73809	H	17.86492	2.33718	1.17728
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H	-0.63756	1.53038	4.06365	H	15.02534	-2.79861	0.67621	H	14.53446	4.17205	1.89301
H	-2.77318	2.85147	3.87067	H	16.17572	-2.86941	2.02289	H	14.79862	2.61769	2.71382
H	-1.87121	4.21359	3.22348	H	14.3397	-1.3578	4.10937	H	16.1798	3.62791	2.25241
H	-0.55115	4.35283	5.36112	H	14.81138	0.30713	3.70198	H	15.08742	4.40675	-0.61287
H	-1.45571	2.99341	6.00739	H	16.04772	-0.94952	3.8865	H	15.72194	3.00915	-1.51026
H	-2.39295	5.15609	6.85694	H	14.4974	2.39006	-1.62668	H	16.75212	3.86462	-0.34836
H	-3.59532	4.33429	5.85031	H	15.48297	4.61287	-2.01314	H	14.64003	-2.3845	-0.14884
H	-2.6836	5.70354	5.1986	H	15.55565	4.19375	-0.28707	H	15.90522	-4.14264	-1.31217
H	-7.03406	1.12883	-1.93412	H	17.01541	4.10278	-1.28889	H	16.32658	-2.54503	-1.96704
H	-4.67697	0.55983	-1.78235	H	15.61878	2.7499	-3.78926	H	17.44347	-3.38415	-0.87591
H	-4.43052	-2.9752	1.43924	H	15.79015	1.05577	-3.27845	H	15.24881	-4.37789	1.16814
H	-6.09178	-4.22868	2.75793	H	17.15784	2.17345	-3.13122	H	15.19946	-2.93566	2.20726
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H	-11.34036	2.03033	-2.27537	H	-0.70946	-0.20465	2.4177	H	-1.15816	1.06671	1.07775
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H	-15.36948	-1.45678	-4.57377
H	-15.3819	0.21572	-3.97113
H	-16.90752	-0.6489	-4.23329
H	-14.40991	1.57759	1.47553
H	-14.8005	3.90849	2.1621
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H	-1.29758	-2.17122	-1.2754
H	-0.62189	-0.96679	-2.35268
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H	1.02849	-2.96063	-0.68343
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H	4.781	-6.09007	7.33608

H	1.58696	2.15664	0.29955
H	0.10393	2.43914	-0.59563
H	-0.9231	3.48501	1.46485
H	0.59698	3.27198	2.32117
H	1.7626	4.70676	0.6184
H	0.24172	4.92934	-0.23248
H	-0.74156	6.02	1.81398
H	0.78126	5.79891	2.66213
H	1.93788	7.2367	0.95339
H	0.41218	7.46973	0.11322
H	-0.56177	8.5139	2.19361
H	0.99146	8.34625	2.99738
H	0.55273	10.64978	2.10986
H	0.47565	10.01766	0.47425
H	2.70823	11.0607	0.9679
H	2.90628	9.34294	0.60831
H	2.96929	9.907	2.28463
H	-1.24417	-0.68472	2.90281
H	-0.14179	-1.6963	1.98039
H	1.4988	-1.66167	3.87271
H	0.45301	-0.57501	4.77409
H	0.16876	-2.79589	5.66955
H	-1.32615	-2.33754	4.87111
H	-0.70659	-3.74228	2.88421
H	0.82937	-4.14253	3.63802
H	-0.39177	-5.26249	5.52828
H	-1.92961	-4.84071	4.79063
H	-1.33601	-6.21188	2.76779
H	0.20072	-6.63514	3.50444
H	-1.46585	-8.47783	3.82823
H	-1.01621	-7.791	5.39665
H	-2.56504	-7.36353	4.65613

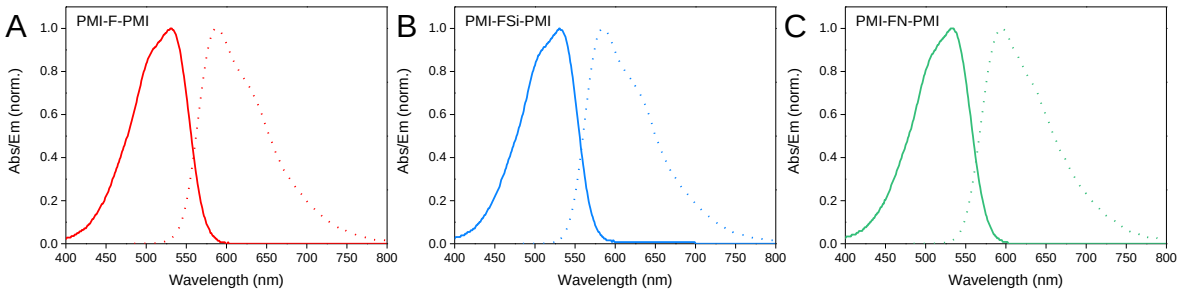

Figure S12. Normalized absorption and fluorescence spectra (dashed lines) in $CHCl_3$ solution of: A - **PMI-F-PMI** (**3a**); B - **PMI-FSi-PMI** (**3b**); C - **PMI-FN-PMI** (**3c**).

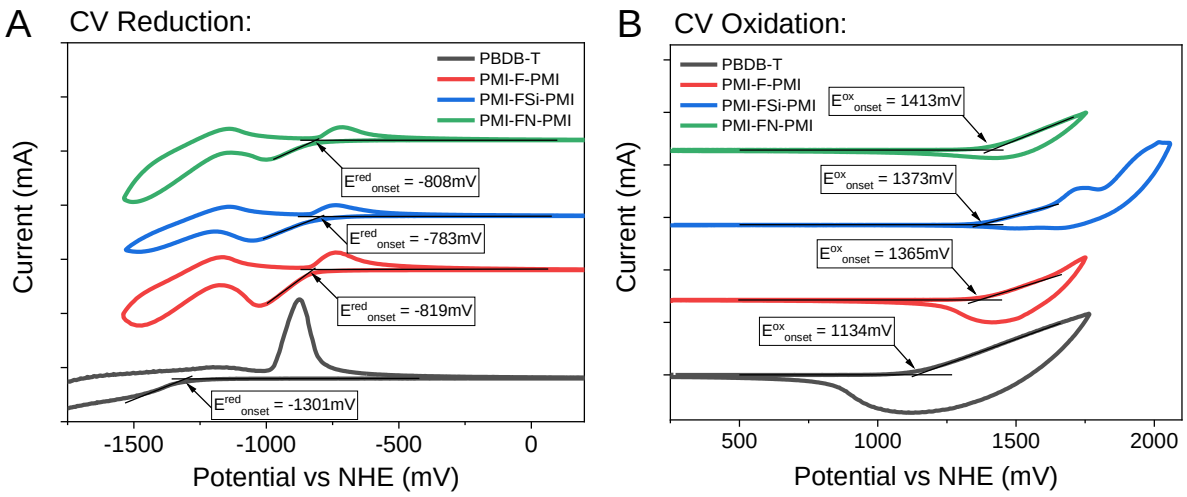

Figure S13. Cyclic voltammetry measurements. Oxidation and reduction were measured separately and with a scan speed of 50 mV/s. Each measurement was calibrated with a Fc/Fc^+ redox couple and the presented data is plotted against NHE.

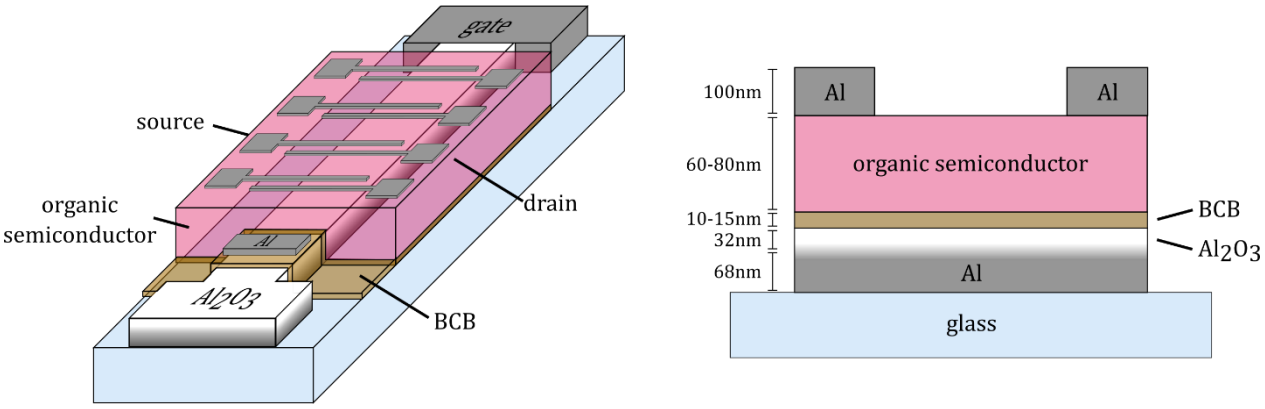

Figure S14. OFET device structure in bottom-gate, top-contact geometry.

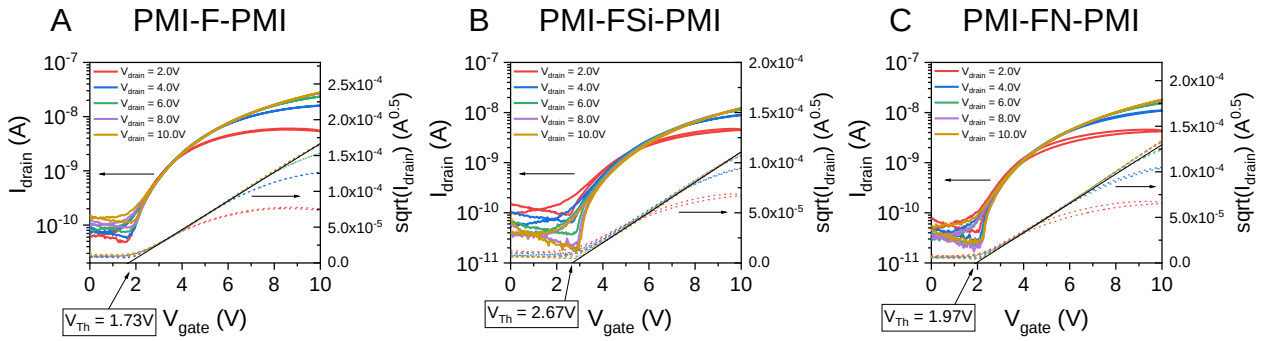

Figure S15. OFET transfer characteristic of: A **PMI-F-PMI** (**3a**), B **PMI-FSi-PMI** (**3b**) and C **PMI-FN-PMI** (**3c**). V_{gate} is swept from 0 to 10 V with constant V_{drain}. After each sweep V_{drain} is increased by 2 V. The solid curves indicate the drain current on a logarithmic scale (left y-axis), while the dashed curves represent the square root of the drain current (right y-axis). The straight black line indicates the linear fit of $\sqrt{I_{drain}}$. The intersection of the black line with the x-axis allows to read out the values of the threshold voltage V_{Th}.

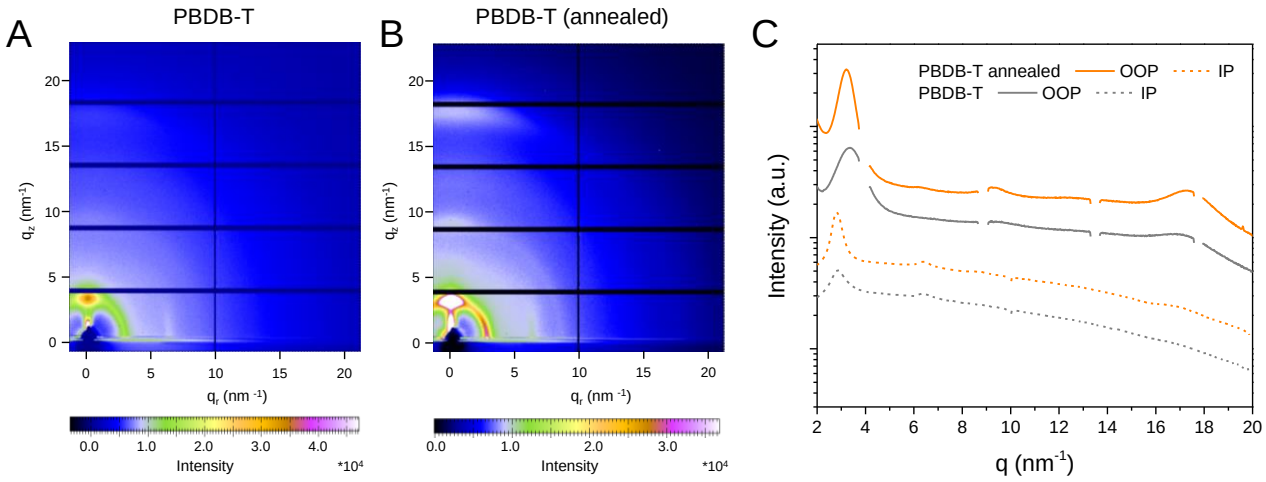

Figure S16. 2D GIWAXS patterns of (A) the donor PBDB-T w/o annealing and (B) w. annealing and (C) the corresponding 1D-line cuts in the out-of-plane (OOP) and in-plane (IP) direction. The scattering profiles are shifted vertically for better visibility.

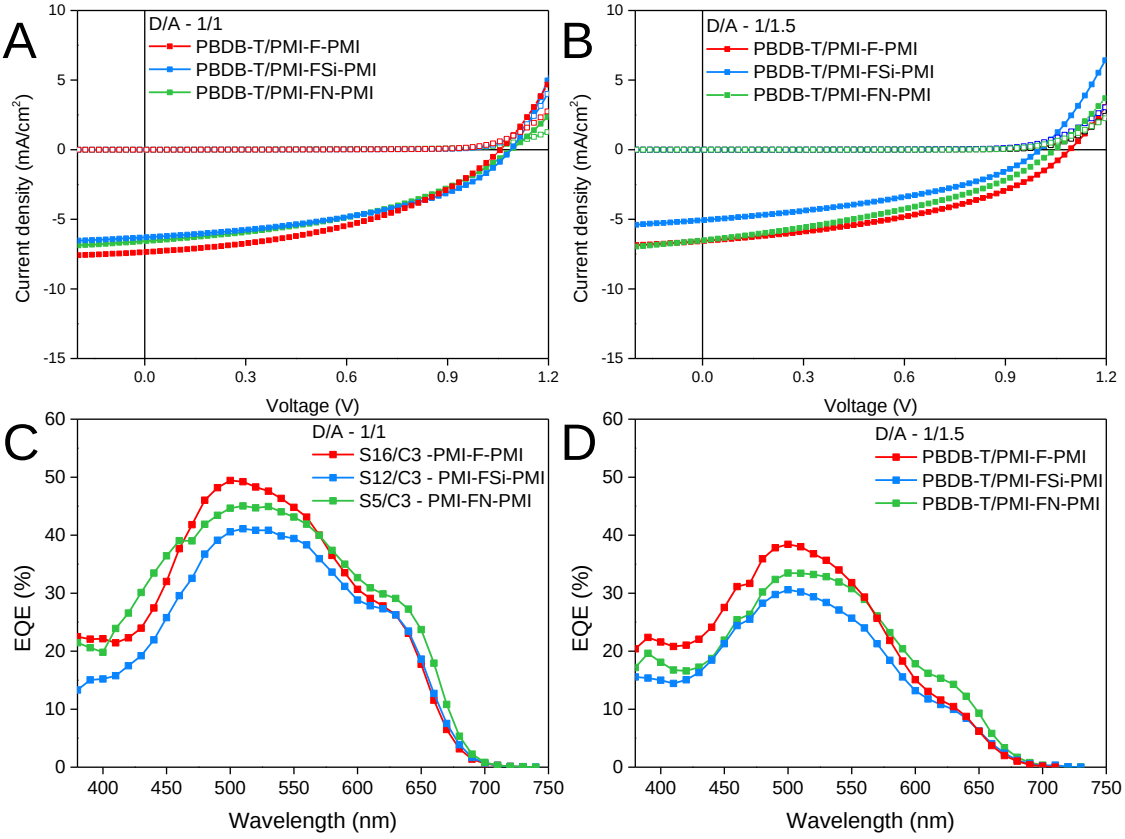

Figure S17. J-V curves (under illumination - solid symbols and under dark conditions - hollow symbols; notice that the hollow curves overlay) and EQE spectra of the best solar cells with a D/A ratio of 1/1 (A, C) and 1/1.5 (B, D) for: red - **PMI-F-PMI** (**3a**); blue - **PMI-FSi-PMI** (**3b**); green - **PMI-FN-PMI** (**3c**).

Table S2 Solar cell characteristics for the best solar cells based on **PMI-F-PMI** (**3a**), **PMI-FSi-PMI** (**3b**) and **PMI-FN-PMI** (**3c**), fabricated with a D/A ratio of 1/1 (top) and 1/1.5 (bottom) w/o annealing the absorber layer

D/A ratio – 1/1					
Acceptor	**Thickness (nm)**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
PMI-F-PMI	125	1.06	7.34	43.3	3.34
PMI-FSi-PMI	94	1.10	6.29	44.9	3.08
PMI-FN-PMI	124	1.10	6.56	42.2	3.02
D/A ratio – 1/1.5					
Acceptor	**Thickness (nm)**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
PMI-F-PMI	121	1.10	6.55	42.2	3.02
PMI-FSi-PMI	110	0.99	5.06	41.1	2.06
PMI-FN-PMI	120	1.06	6.50	37.8	2.58

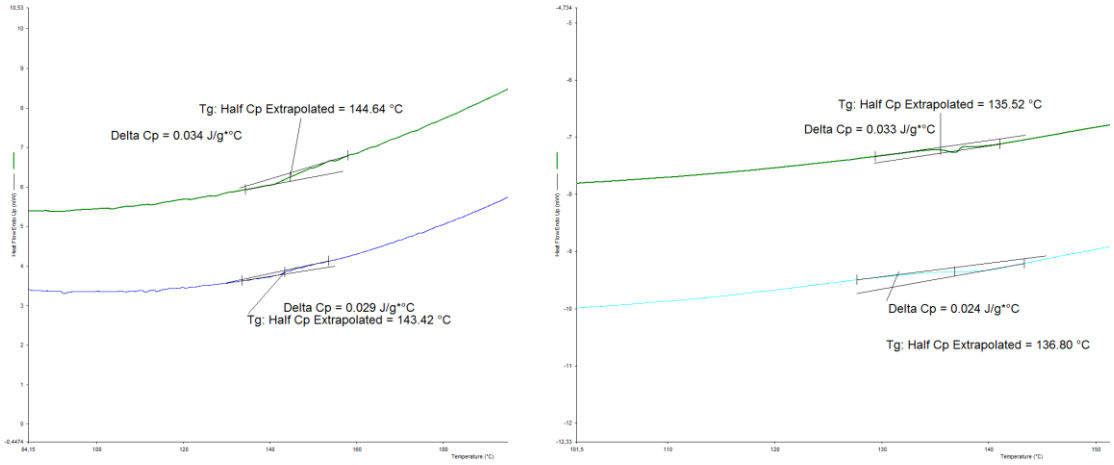

Figure 18. DSC measurements of PBDB-T: heating runs (left), cooling runs (right) (measured with a heating (cooling) rate of 20 K/min (bottom curves) and with 40 K/min (top curves).

Table S3 Characteristic solar cell parameters of the 15 best solar cells with PBDB-T – **PMI-F-PMI** (**3a**), **PMI-FSi-PMI** (**3b**) and **PMI-FN-PMI** (**3c**) absorber layers (D/A – 1 /0.66) without and with annealing

D/A – 1/0.66					
Acceptor	**Annealing**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
PMI-F-PMI					
	-	1.10	7.04	45.4	3.48
	-	1.08	7.08	45.4	3.44
	-	1.04	6.81	46.0	3.23
	-	1.10	6.40	45.5	3.17
	-	1.08	6.57	44.6	3.14
	-	1.10	6.41	44.8	3.13
	-	1.04	6.43	46.6	3.09
	-	1.04	6.45	46.1	3.07
	-	1.08	6.79	42.0	3.06
	-	1.04	6.15	47.1	2.99
	-	1.04	6.60	43.3	2.95
	-	1.08	6.46	42.2	2.93
	-	1.04	6.17	45.8	2.92
	-	1.04	6.32	44.5	2.90
	-	1.06	6.50	41.9	2.88
PMI-F-PMI					
	135 °C	1.10	8.94	52.9	5.16
	135 °C	1.10	8.35	52.6	4.8
	135 °C	1.10	8.24	53.3	4.79
	135 °C	1.12	7.96	52.4	4.64
	135 °C	1.10	8.61	49.0	4.60
	135 °C	1.10	8.09	49.2	4.35
	135 °C	1.12	7.92	49.2	4.33
	135 °C	1.12	7.98	48.6	4.31
	135 °C	0.97	9.11	46.4	4.10
	135 °C	1.14	7.95	45.2	4.07
	135 °C	1.14	8.11	44.2	4.06
	135 °C	1.08	8.06	46.9	4.05
	135 °C	1.12	7.73	46.8	4.02
	135 °C	1.12	7.50	47.6	3.97
	135 °C	1.10	7.47	48.0	3.91

D/A – 1/0.66					
Acceptor	**Annealing**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
PMI-FSi-PMI					
	-	1.08	6.58	43.4	3.06
	-	1.04	6.28	44.8	2.90
	-	0.97	6.56	43.6	2.78
	-	1.10	6.02	41.9	2.75
	-	1.10	6.51	38.6	2.75
	-	1.02	6.22	43.0	2.72
	-	1.06	6.13	41.6	2.68
	-	1.12	5.95	40.6	2.67
	-	0.99	5.97	44.8	2.66
	-	1.10	5.74	42.4	2.64
	-	1.10	5.74	42.1	2.62
	-	0.97	6.27	42.5	2.59
	-	1.08	5.88	40.2	2.53
	-	0.99	5.88	43.5	2.54
	-	1.10	5.42	42.4	2.49
PMI-FSi-PMI					
	150 °C	1.14	8.55	53.4	5.16
	150 °C	1.10	8.41	54.9	5.05
	150 °C	1.10	8.21	54.8	4.92
	150 °C	1.10	8.05	54.7	4.82
	150 °C	1.14	8.09	51.9	4.75
	150 °C	1.14	7.87	53.3	4.74
	150 °C	1.12	8.01	52.9	4.72
	150 °C	1.10	7.90	54.1	4.67
	150 °C	1.14	8.21	50.0	4.65
	150 °C	1.12	7.88	53.0	4.62
	150 °C	1.14	7.76	52.7	4.61
	150 °C	1.10	7.46	55.4	4.52
	150 °C	1.12	7.52	53.3	4.43
	150 °C	1.14	7.33	50.7	4.19
	150 °C	1.14	7.02	52.3	4.15

D/A – 1/0.66					
Acceptor	**Annealing**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
PMI-FN-PMI					
	-	1.08	8.17	39.6	3.46
	-	1.08	7.86	39.4	3.32
	-	1.08	7.55	39.7	3.21
	-	1.08	7.42	39.2	3.11
	-	1.08	7.20	39.7	3.06
	-	1.08	7.21	38.9	3.00
	-	1.08	7.20	38.7	2.98
	-	1.04	7.17	39.5	2.92
	-	1.08	6.86	38.8	2.85
	-	1.08	6.74	39.1	2.82
	-	1.06	5.87	45.7	2.82
	-	1.04	5.79	45.7	2.72
	-	1.06	5.71	45.2	2.71
	-	1.06	6.70	38.4	2.71
	-	1.06	5.80	44.5	2.71
PMI-FN-PMI					
	150 °C	1.06	10.18	48.0	5.16
	150 °C	1.14	10.07	45.2	5.14
	150 °C	1.16	9.48	43.2	4.72
	150 °C	1.12	9.56	43.9	4.66
	150 °C	1.04	9.37	47.7	4.63
	150 °C	1.14	9.37	42.9	4.55
	150 °C	1.08	9.03	45.2	4.41
	150 °C	1.04	8.69	48.3	4.34
	150 °C	1.14	8.17	46.2	4.29
	150 °C	1.16	8.92	41.9	4.29
	150 °C	1.12	9.44	39.8	4.17
	150 °C	1.12	9.01	41.3	4.13
	150 °C	1.14	8.20	43.8	4.09
	150 °C	1.10	8.53	43.6	4.08
	150 °C	1.16	8.46	41.4	4.05

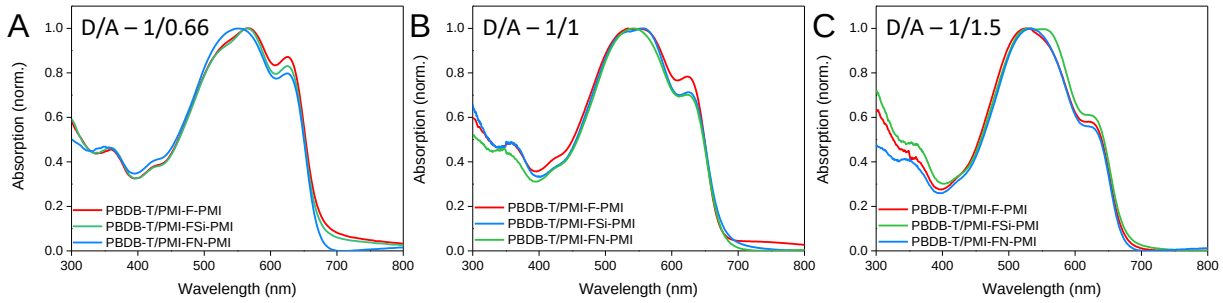

Figure S19. Optical absorption spectra of blend films (PBDB-T/acceptor) in different D/A ratios of 1/0.66 (A) 1/1 (B) and 1/1.5 (C).

Table S4 Comparison between the current densities (mA/cm^2) of solar cells based on **PMI-F-PMI** (**3a**), **PMI-FSi-PMI** (**3b**) and **PMI-FN-PMI** (**3c**) in a D/A ratio of 1/0.66 (w/o and w. annealing), 1/1 and 1/1.5 (w/o annealing) from prior EQE- , from EQE- and post EQE measurements

D/A – 1/0.66			
	PMI-F-PMI (w/o annealing)	**PMI-FSi-PMI (w/o annealing)**	**PMI-FN-PMI (w/o annealing)**
J_{SC} (integrated)	6.37 mA/cm^2	6.46 mA/cm^2	6.88 mA/cm^2
J_{SC} (before EQE)	7.27 mA/cm^2	6.79 mA/cm^2	7.97 mA/cm^2
J_{SC} (after EQE)	6.66 mA/cm^2	6.94 mA/cm^2	7.44 mA/cm^2
	PMI-F-PMI (annealed)	**PMI-FSi-PMI (annealed)**	**PMI-FN-PMI (annealed)**
J_{SC} (integrated)	6.98 mA/cm^2	7.40 mA/cm^2	10.02 mA/cm^2
J_{SC} (before EQE)	8.83 mA/cm^2	8.13 mA/cm^2	10.18 mA/cm^2
J_{SC} (after EQE)	5.81 mA/cm^2	7.64 mA/cm^2	9.33 mA/cm^2
D/A – 1/1			
	PMI-F-PMI	**PMI-FSi-PMI**	**PMI-FN-PMI**
J_{SC} (integrated)	6.50 mA/cm^2	5.19 mA/cm^2	6.08 mA/cm^2
J_{SC} (before EQE)	7.02 mA/cm^2	6.05 mA/cm^2	6.08 mA/cm^2
J_{SC} (after EQE)	6.31 mA/cm^2	5.85 mA/cm^2	5.35 mA/cm^2
D/A – 1/1.5			
	PMI-F-PMI	**PMI-FSi-PMI**	**PMI-FN-PMI**
J_{SC} (integrated)	4.03 mA/cm^2	3.27 mA/cm^2	3.85 mA/cm^2
J_{SC} (before EQE)	6.45 mA/cm^2	4.99 mA/cm^2	6.51 mA/cm^2
J_{SC} (after EQE)	3.01 mA/cm^2	3.02 mA/cm^2	4.40 mA/cm^2