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Effect of branching on the physical and photovoltaic properties of donor–acceptor oligomers based on triphenylamine

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CONTENTS

1. Materials

Tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ and malononitrile were obtained from Sigma–Aldrich (USA) and used without further purification. THF, toluene and pyridine were dried and purified according to the known techniques. 5,5-dimethyl-2-phenyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithien-5-yl]-1,3-dioxane **5**[1] and *N*,*N*-bis(4-bromophenyl)phenylamine **4**[2] were obtained as described. All reactions, unless stated otherwise, were carried out in an inert atmosphere.

2. Characterization

^{1}H NMR spectra were recorded using a Bruker WP-250 SY spectrometer (USA) at working frequency 250.13 MHz, with $CDCl_3$ peak at 7.25 ppm as the internal standard. ^{13}C NMR spectra were recorded utilizing a Bruker Avance II 300 spectrometer (USA) at working frequency 75 MHz. The compounds were taken as 1% and 5% solutions in $CDCl_3$ for 1H and ^{13}C NMR, respectively. The spectra were processed using an ACD/Labs software (Canada).

MALDI mass-spectra were registered using an Autoflex II Bruker apparatus (USA) with resolution FWHM 18000, equipped with a nitrogen laser (wavelength 337 nm) and time-of-flight mass detector operating in reflections mode, the accelerating voltage was 20 kV. Samples were deposited on a polished stainless steel substrate, and mass-spectrum was recorded in the positive ion mode. The final spectrum represented the total of 300 spectra obtained at different points of sample. 2,5-Dihydroxybenzoic acid (99%) and α-cyano-4-hydroxycinnamic acid (99%), both from Acros Organics (USA), were used as matrices.

Elemental analysis of C, N and H was carried out using a CHN automatic analyzer CE 1106 (Italy). The settling titration using $BaCl_2$ was applied to analyze sulfur. Experimental error for elemental analysis was 0.30–0.50%. The Knoevenagel condensation was carried out in a CEM Corporation microwave oven Discovery (USA) using a standard method with the open vessel option at 50 W. Silica gel 60 Merck (Germany) was used for column chromatography. Absorption spectra were recorded with a Shimadzu UV 2501 PC spectrometer (Japan) in 350–1100 nm range at room temperature for 10^{-5} M solutions in THF and for films cast from THF solutions on quartz substrate.

Cyclic voltammetry (CV) measurements were carried out using solid compact layers of the compounds prepared by electrostatic rubbing onto a glassy carbon electrode. Measurements were carried out in CH_3CN–*o*-$C_6H_4Cl_2$ 1 : 4 solution with 0.1 M Bu_4NPF_6 as supporting electrolyte using an IPC-Pro M potentiostat (Russia) at scan rate 200 mV s^{-1} and glassy carbon electrode as a work electrode. Potential values were measured relative to a saturated calomel electrode (SCE). The HOMO and LUMO energy levels were calculated using the first standard formal oxidation and reduction potentials obtained from CV measurements of films, according to the following equations: LUMO = $e(\varphi_{\mathrm{red}} + 4.40)$ and HOMO = $-e(\varphi_{\mathrm{ox}} + 4.40)$ (eV).[3–5]

Thermogravimetric analysis was carried out in dynamic mode in 30–900 °C range using a Mettler Toledo TG50 system (USA) equipped with M3 microbalance, which allowed to measure the sample weight in 0–150 mg range with 1 μg precision, at heating/cooling rate 10 °C min^{-1}. Each compound was investigated in air and in nitrogen flow of 200 ml min^{-1}. DSC scans were obtained using a Mettler Toledo DSC30 system (USA) at 10 °C min^{-1} heating/cooling rate in temperature range +20–290 °C for all compounds in nitrogen flow 50 ml min^{-1}.

Solubility was measured using saturated solutions prepared by stirring of an excess of solid material in *o*-dichlorobenzene. For this purpose, materials were added in small portions to 1 ml of pure solvent. The prepared saturated solutions were filtered through 0.25 mm PTFE syringe filters and the solvent was evaporated *in vacuo*. Afterwards the residue was dried *in vacuo* at 130°C until constant weight, which was used to calculate the exact solubility value.

The samples of organic solar cells were prepared in the following way. The glass substrates coated with patterned indium–tin oxide (ITO) layer were cleaned in ultrasonic bath (in surfactant and isopropanol) and under UV lamp. Then 50 nm layer of poly(ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) polymer complex was deposited on the ITO layer by spin coating at 3000 rpm and after that annealed at 140 °C for 15 min. The active layer was bladed (85 °C, 15 mm s^{-1}) on PEDOT:PSS layer from 24 mg ml^{-1} solution of compound:$PC_{71}BM$ in *o*-dichlorobenzene. The solutions were stirred on a magnetic stirrer at 100 °C for one day before the deposition. Ca and Al electrode layers were formed on the top of the active layer by vapor deposition. For each substrate eight devices were obtained using a shadow mask during the top electrode evaporation, the active area (S) of each device was 3 mm^2.

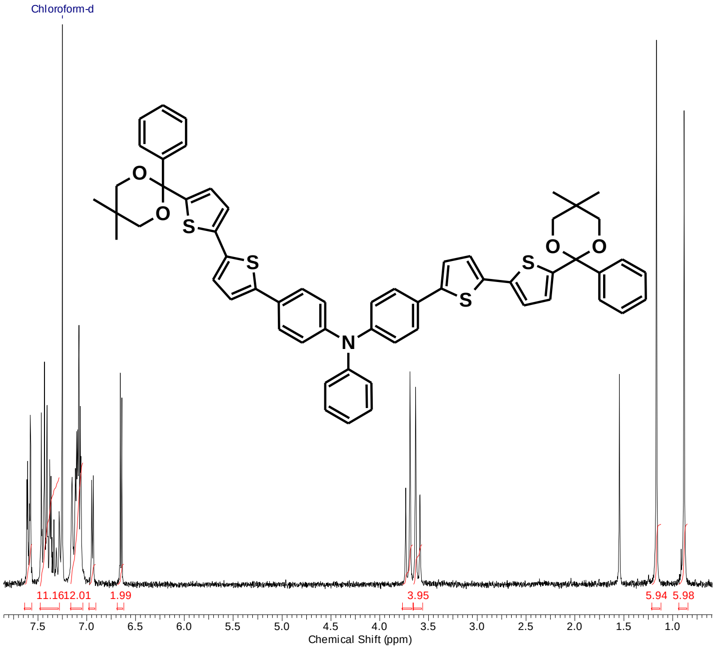
Current–voltage characteristics of the solar cells were measured using a Keithley Instruments SourceMeter 2400 (USA) under the irradiation of a Newport Corporation AM1.5G solar simulator (USA) with 100 mW cm^{-2} intensity in a glove box with an inert atmosphere.

3. Synthesis of compounds 6 and 7

N,N-*Bis{4-[5'-(5,5-dimethyl-2-phenyl-1,3-dioxan-2-yl)-2,2'-bithien-5-yl]phenyl}phenylamine* **6**. Degassed solutions of dibromide **4** (1.26 g, 3.13 mmol) and compound **5** (3.62 g, 7.50 mmol) in toluene–ethanol (120 : 12 ml) and 2 M aq. Na_2CO_3 (5 ml) were added to $Pd(PPh_3)_4$ (217 mg, 0.19 mmol) in an inert atmosphere. The reaction mixture was stirred and refluxed for 12 h, then cooled to room temperature and poured into a mixture of water (100 ml) and toluene (100 ml). The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated and the residue was dried *in vacuo*. The product was purified by column chromatography on silica gel (toluene–hexane, 1 : 1) to give compound **6**. Yield 1.80 g (60%), yellow solid, mp 112–115 ºC. ^1H NMR (250 MHz, $CDCl_3$) δ: 0.90 (s, 6H), 1.17 (s, 6H), 3.61 (d, 4H, *J* 11.0 Hz), 3.71 (d, 4H, *J* 11.1 Hz), 6.67 (d, 2H, *J* 3.8 Hz), 6.95 (d, 2H, *J* 3.7 Hz), 7.04–7.16 (overlapping peaks, 12H), 7.28–7.47 (overlapping peaks, 11H), 7.56–7.64 (overlapping peaks, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.25, 22.70, 30.05, 72.45, 99.59, 122.72, 122.95, 123.55, 124.04, 124.62, 124.83, 126.44, 126.74, 126.87, 128.36, 128.52, 129.02, 129.43, 135.96, 138.10, 140.12, 142.97, 145.95, 146.86, 147.05. MS (MALDI), *m*/*z*: 955.31 $[M]^+$ (calc. for $C_{58}H_{51}NO_4S_4$, *m*/*z*: 955.88).

N,N-*Bis[4-(5'-benzoyl-2,2'-bithien-5-yl)phenyl]phenylamine* **7**. To a solution of compound **6** (1.70 g, 1.78 mmol) in THF (45 ml), 1 M HCl (4.0 ml) was added. Then the reaction mixture was stirred and refluxed for 4 h. The product was gradually formed as a red precipitate. The organic phase was separated with diethyl ether, washed with water and filtered to give pure compound **7**. Yield 1.36 g (98%), red powder, mp 125–127 ºC. ^1H NMR (250 MHz, $CDCl_3$) δ: 7.08–7.21 (overlapping peaks, 11H), 7.28–7.35 (overlapping peaks, 4H), 7.45–7.60 (overlapping peaks, 12H), 7.82–7.90 (overlapping peaks, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 123.35, 123.61, 123.98, 125.22, 126.60, 126.73, 128.28, 128.85, 129.46, 131.88, 134.86, 135.33, 138.37, 141.55, 145.49, 146.16, 146.93, 147.42, 187.23. MS (MALDI), *m*/*z*: 781.83 $[M]^+$ (calc. for $C_{48}H_{31}NO_2S_4$, *m*/*z*: 782.03).

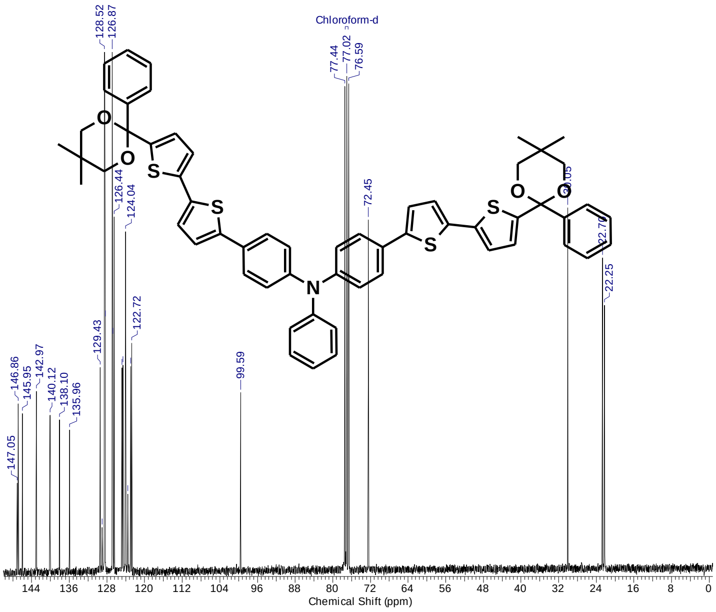
4. ^1H, ^{13}C NMR spectra



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[0.84 .. 0.94]	5.979	1.39233e+7
2	[1.12 .. 1.21]	5.944	1.38429e+7
3	[3.56 .. 3.65]	3.950	9.19898e+6
4	[3.66 .. 3.77]	3.944	9.18459e+6
5	[6.62 .. 6.69]	1.990	4.63375e+6
6	[6.91 .. 6.98]	1.982	4.61487e+6
7	[7.04 .. 7.16]	12.013	2.79776e+7
8	[7.28 .. 7.47]	11.162	2.59949e+7
9	[7.56 .. 7.64]	4.002	9.32069e+6

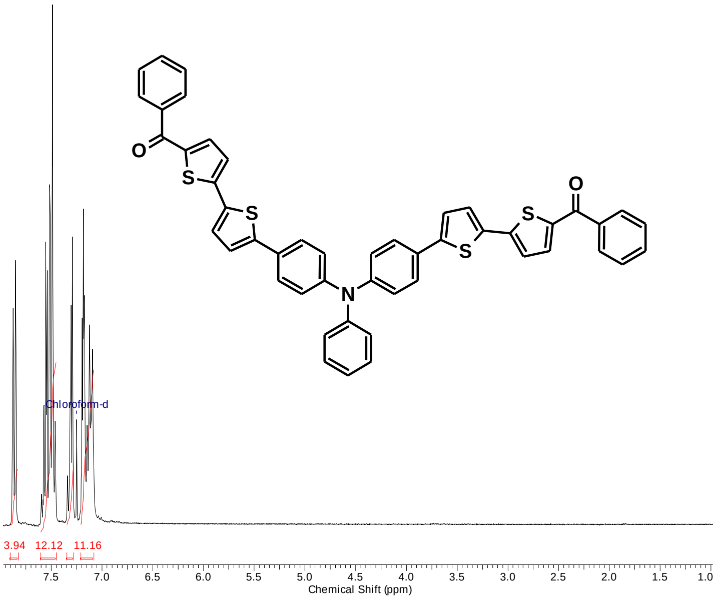
Figure S1 ^1H NMR spectrum of compound **6** in $CDCl_3$.



No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	22.25	1679.4	0.4639	15	126.44	9543.1	0.6155
2	22.70	1713.1	0.5453	16	126.74	9566.0	0.4103
3	30.05	2268.2	0.6315	17	126.87	9575.7	0.9904
4	72.45	5468.7	0.6108	18	128.36	9688.2	0.4399
5	76.59	5781.1	0.8444	19	128.52	9700.4	1.0000
6	77.02	5813.2	0.8573	20	129.02	9738.5	0.0826
7	77.44	5845.0	0.8399	21	129.43	9769.2	0.3572
8	99.59	7516.5	0.3141	22	135.96	10262.1	0.2499
9	122.72	9262.8	0.3990	23	138.10	10423.2	0.2674
10	122.95	9280.2	0.3589	24	140.12	10575.8	0.2749
11	123.55	9325.5	0.1398	25	142.97	10791.4	0.3159
12	124.04	9362.6	0.5904	26	145.95	11016.2	0.2782
13	124.62	9405.7	0.3610	27	146.86	11084.7	0.2949
14	124.83	9421.7	0.3564	28	147.05	11098.8	0.1583

No.	Annotation	(ppm)
1	Chloroform-d	[76.71 .. 77.35]

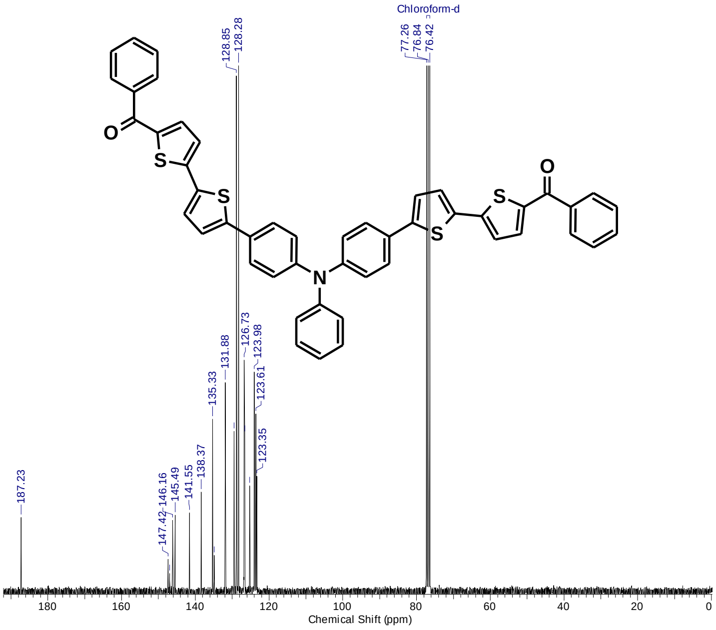
Figure S2 ^{13}C NMR spectrum of compound **6** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[7.08 .. 7.21]	11.157	3.10638e+10
2	[7.28 .. 7.35]	4.058	1.12986e+10
3	[7.45 .. 7.60]	12.120	3.37468e+10
4	[7.82 .. 7.90]	3.940	1.09702e+10

Figure S3 ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

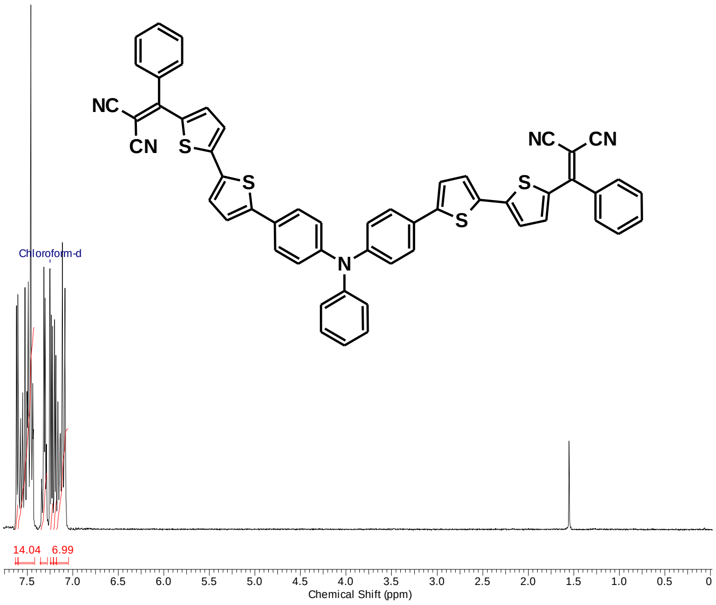


No.	(ppm)	(Hz)	Height
1	76.42	5767.7	0.9998
2	76.84	5799.5	0.9962
3	77.26	5831.6	1.0000
4	123.35	9310.2	0.2027
5	123.61	9329.8	0.3122
6	123.98	9357.5	0.3859
7	125.22	9451.5	0.1863
8	126.60	9555.7	0.2762
9	126.73	9565.6	0.4069
10	128.28	9682.0	0.9382
11	128.85	9725.7	0.9062

No.	(ppm)	(Hz)	Height
12	129.46	9771.3	0.2816
13	131.88	9953.7	0.3674
14	134.86	10178.8	0.0636
15	135.33	10214.4	0.3029
16	138.37	10443.9	0.1750
17	141.55	10683.5	0.1387
18	145.49	10981.2	0.1345
19	146.16	11031.6	0.1251
20	146.93	11089.9	0.0317
21	147.42	11127.2	0.0570
22	187.23	14132.0	0.1307

No.	Annotation	(ppm)
1	Chloroform-d	[76.41 .. 77.26]

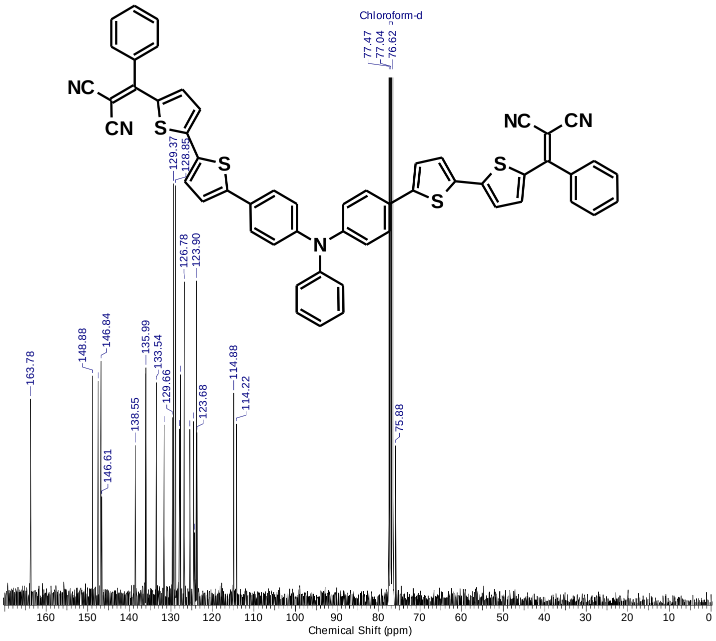
Figure S4 ^{13}C NMR spectrum of compound **7** in $CDCl_3$.



No.	Annotation	(ppm)
1	Chloroform-d	7.25

No.	(ppm)	Value	Absolute Value
1	[7.04 .. 7.18]	6.989	1.51965e+10
2	[7.18 .. 7.21]	2.039	4.43377e+9
3	[7.21 .. 7.24]	2.011	4.37242e+9
4	[7.28 .. 7.35]	4.000	8.69750e+9
5	[7.42 .. 7.60]	14.037	3.05224e+10
6	[7.60 .. 7.63]	2.041	4.43691e+9

Figure S5 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.



No.	(ppm)	(Hz)	Height
1	75.88	5727.5	0.0524
2	76.62	5783.0	0.9780
3	77.04	5814.8	1.0000
4	77.47	5846.9	0.9817
5	114.22	8621.2	0.0594
6	114.88	8670.6	0.0692
7	123.68	9335.5	0.0566
8	123.90	9351.8	0.1048
9	124.33	9383.8	0.0248
10	124.55	9400.7	0.0601
11	125.41	9465.7	0.0576
12	126.78	9569.3	0.1046
13	127.69	9637.6	0.0751
14	127.92	9655.3	0.0578
15	128.85	9725.0	0.1351
16	129.37	9764.8	0.1357
17	129.66	9786.6	0.0615
18	131.61	9933.4	0.0590
19	133.54	10079.1	0.0725
20	135.99	10264.6	0.0772
21	136.10	10272.8	0.0752
22	138.55	10457.5	0.0525
23	146.61	11065.9	0.0363
24	146.84	11083.3	0.0793
25	147.52	11134.2	0.0729
26	148.88	11237.0	0.0746
27	163.78	12361.8	0.0673

No.	Annotation	(ppm)
1	Chloroform-d	[76.67 .. 77.46]

Figure S6 ^{13}C NMR spectrum of compound **2** in $CDCl_3$

5. Thermal, optical and electrochemical properties

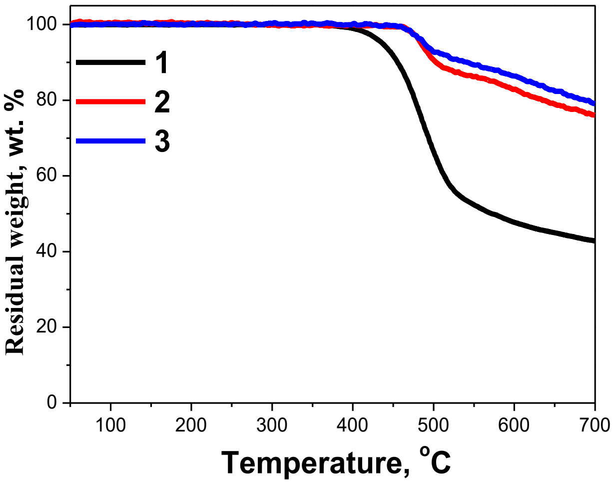


Figure S7 TGA curves for compounds **1**, **2** and **3** under argon.

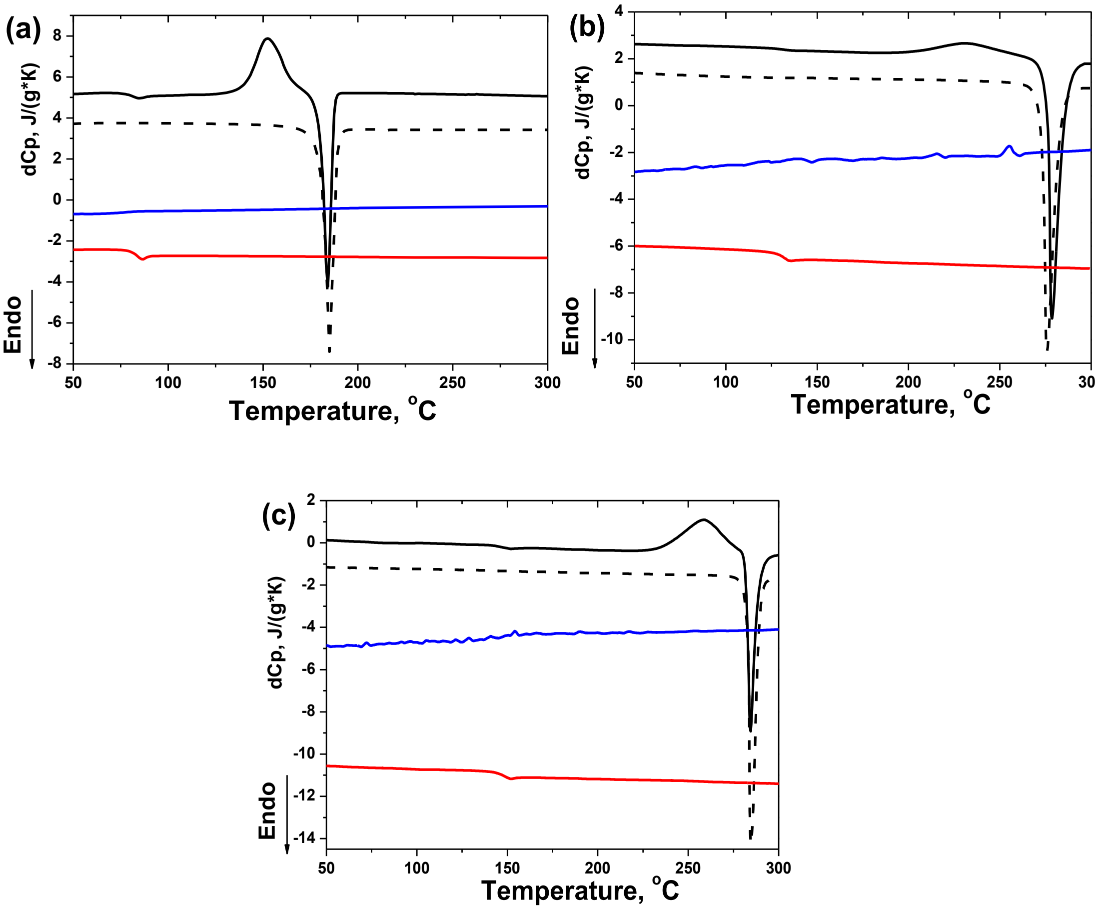


Figure S8 DSC scans of compounds (*a*) **1**, (*b*) **2** and (*c*) **3** at (black) first heating, (blue) cooling, (red) second heating and (black dashed) heating of the preliminary annealed sample at (*a*) 170 ºC, (*b*) 245 ºC and (*c*) 230 °C.

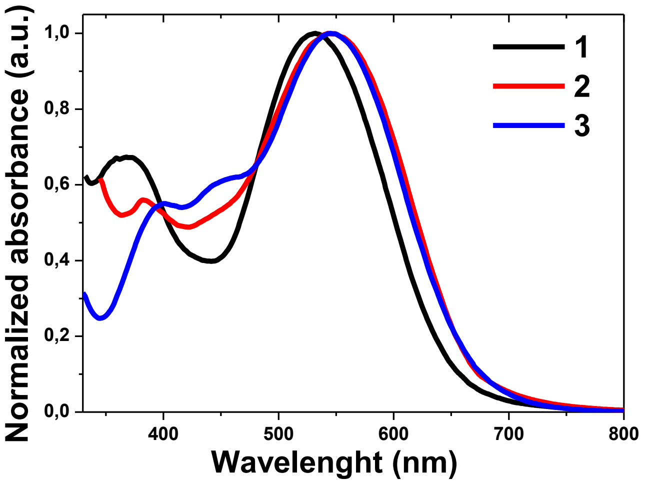


Figure S9. UV-vis absorption spectra of compounds **1**, **2** and **3** in film cast from THF.

Table S1 The first standard formal oxidation and reduction potentials obtained from cyclic voltammetry experiments.

Compound	φ_{ox}/V	φ_{red}/V
1	0.94	-1.02
2	0.94	-0.98
3	0.94	-0.97

6. DFT computer simulations

DFT calculations were performed on the B3LYP/6-31G(d) level using the version 4.0.1 of the ORCA software package.

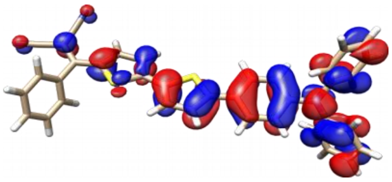
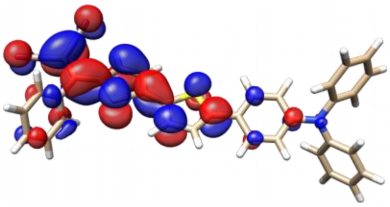
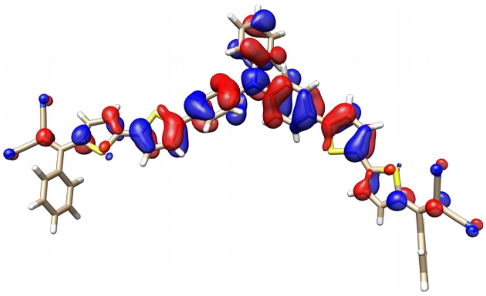
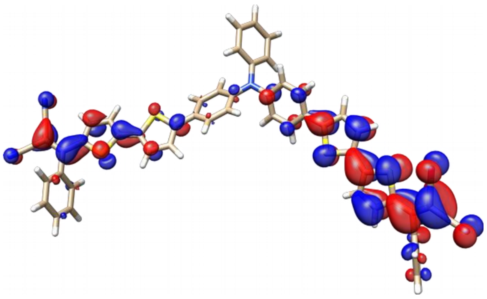
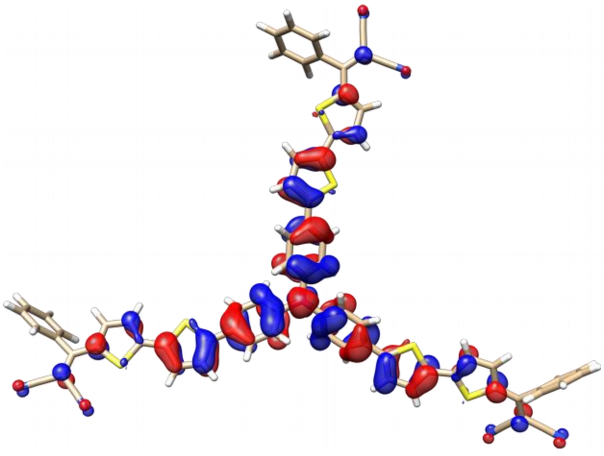
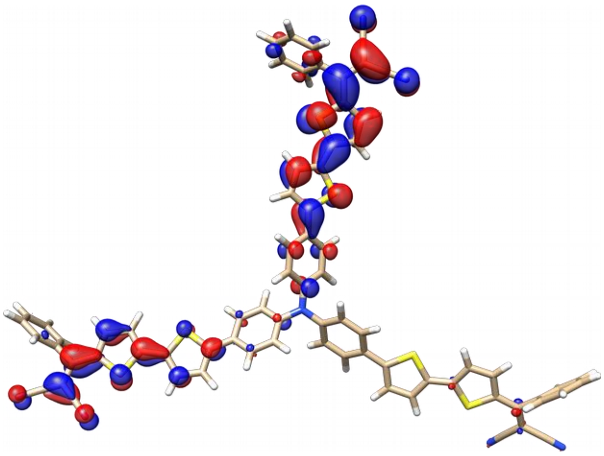
	HOMO	LUMO
1	 -5.03 eV	 -2.71 eV
2	 -5.16 eV	 -2.84 eV
3	 -5.26 eV	 -2.94 eV

Figure S10 HOMO, LUMO and energy gap values of the calculated structures **1**–**3** (isovalue contours given at ±0.002).

7. Photovoltaics properties

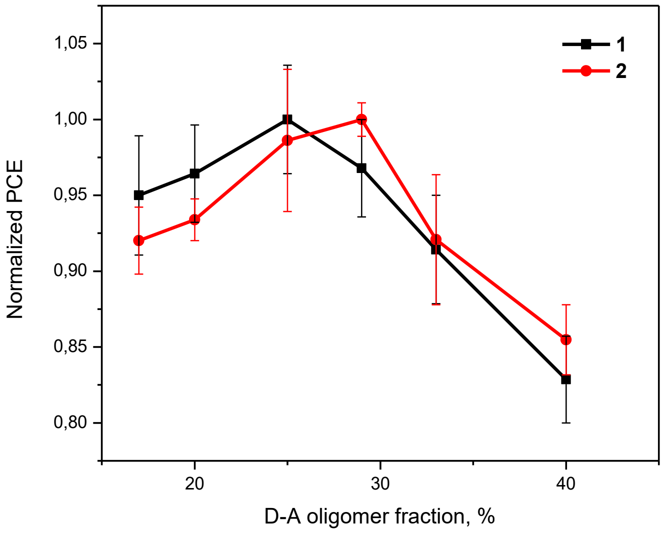


Figure S11 Normalized PCE *vs*. DA compound(**1**, **2**):PC$_{71}$BM mass ratio. The mass ratio for compound **3**:PC$_{71}$BM was optimized previously.[1]

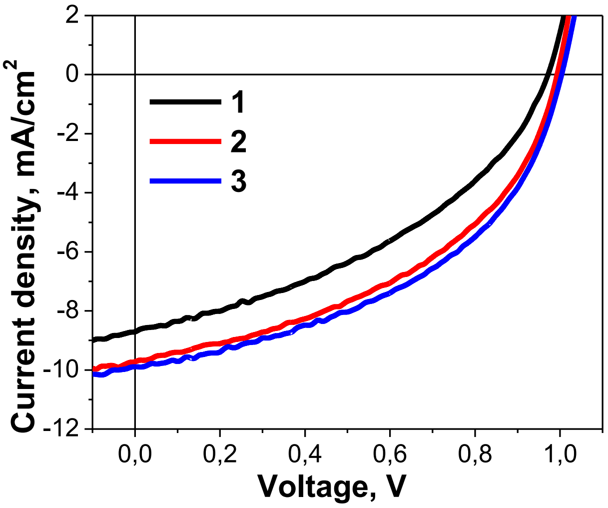


Figure S12 *J*–*V* curves for DA compounds(**1**, **2**, **3**):PC$_{71}$BM organic solar cells.

References

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