Electronic Supplementary Information

Impact of structure and homo-coupling of the central donor unit of small molecule organic semiconductors on solar cell performance

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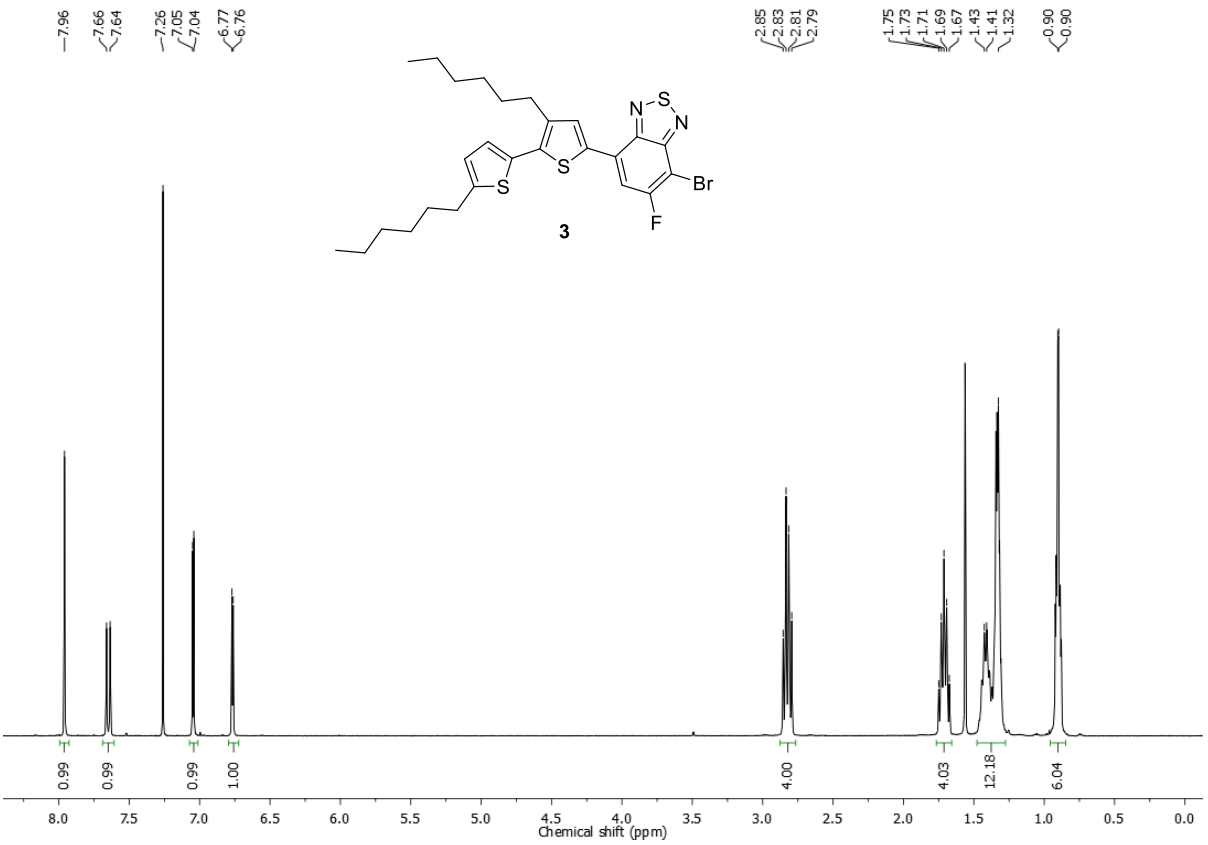
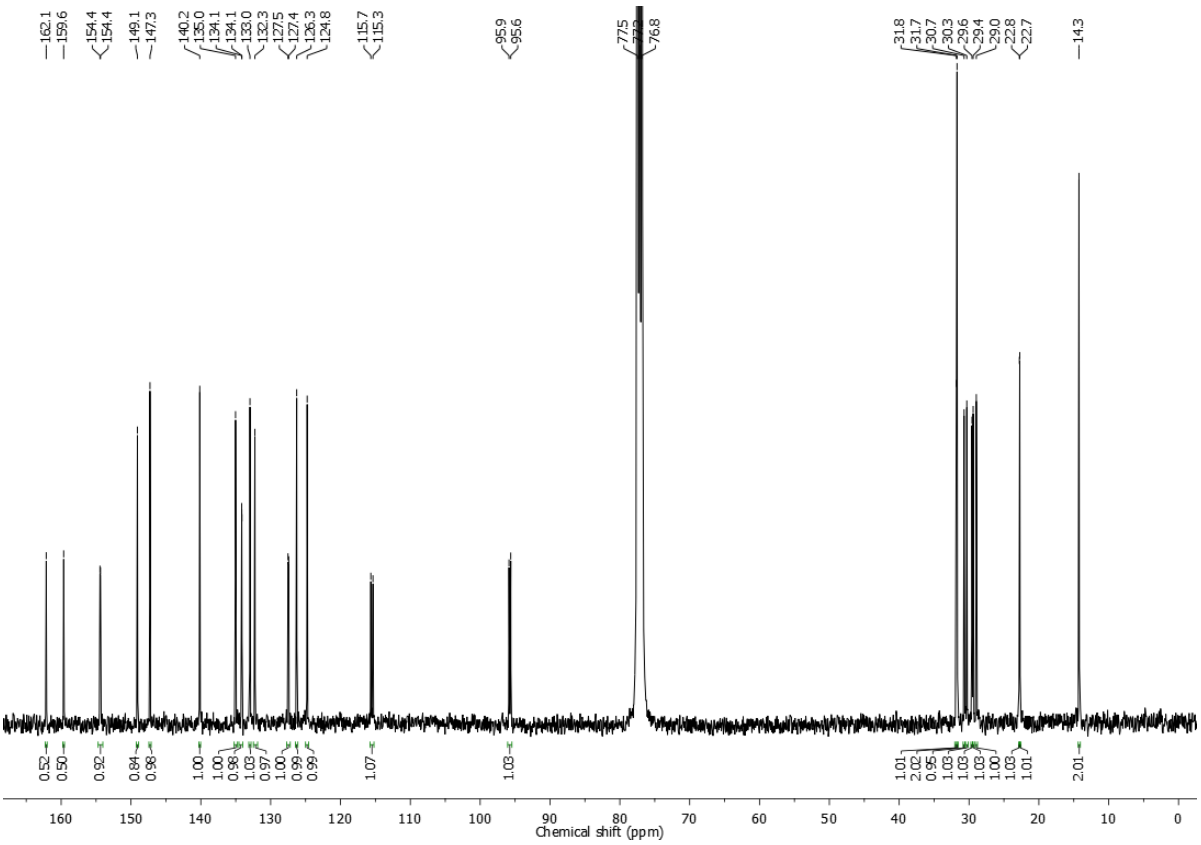
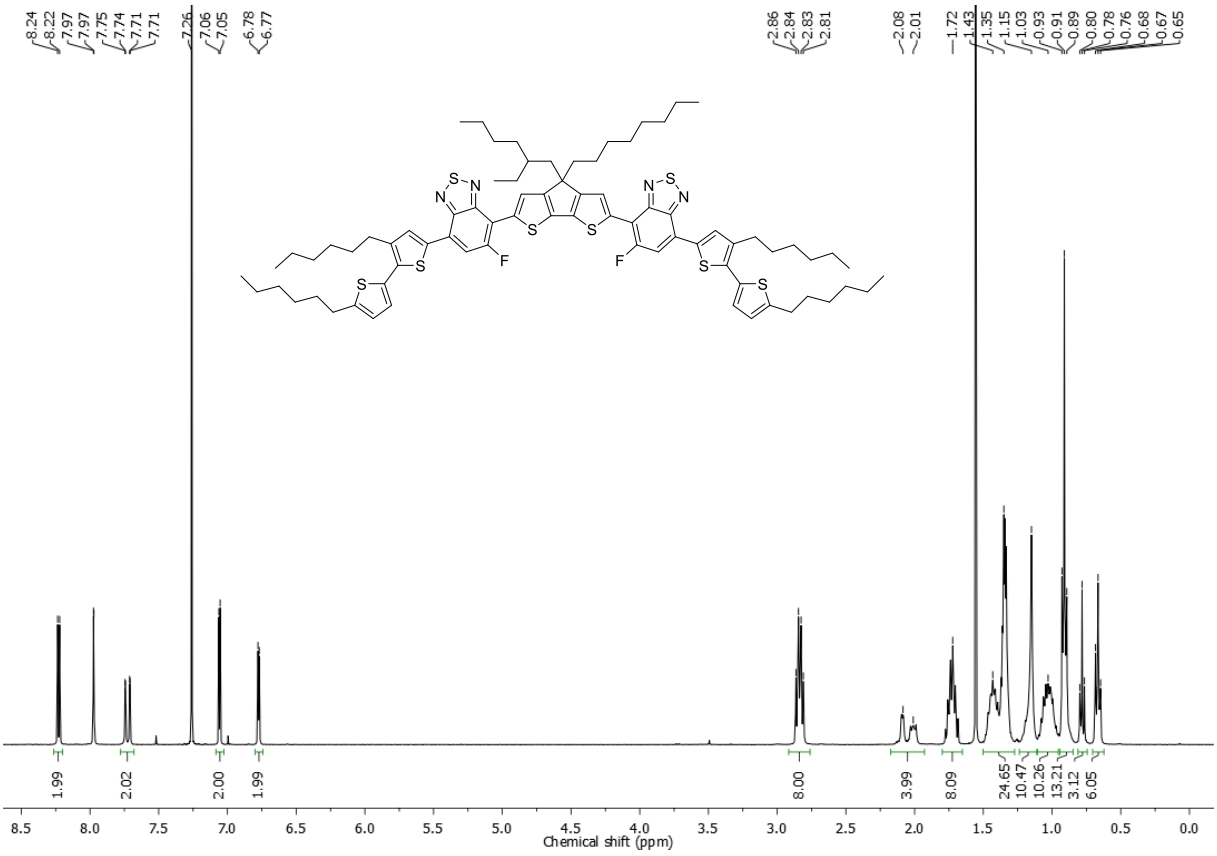
1. ^{1}H and ^{13}C NMR spectra

4-Bromo-7-(3,5'-dihexyl-[2,2'-bithiophen]-5-yl)-5-fluorobenzo[*c*][1,2,5]thiadiazole (3) (in $CDCl_3$)

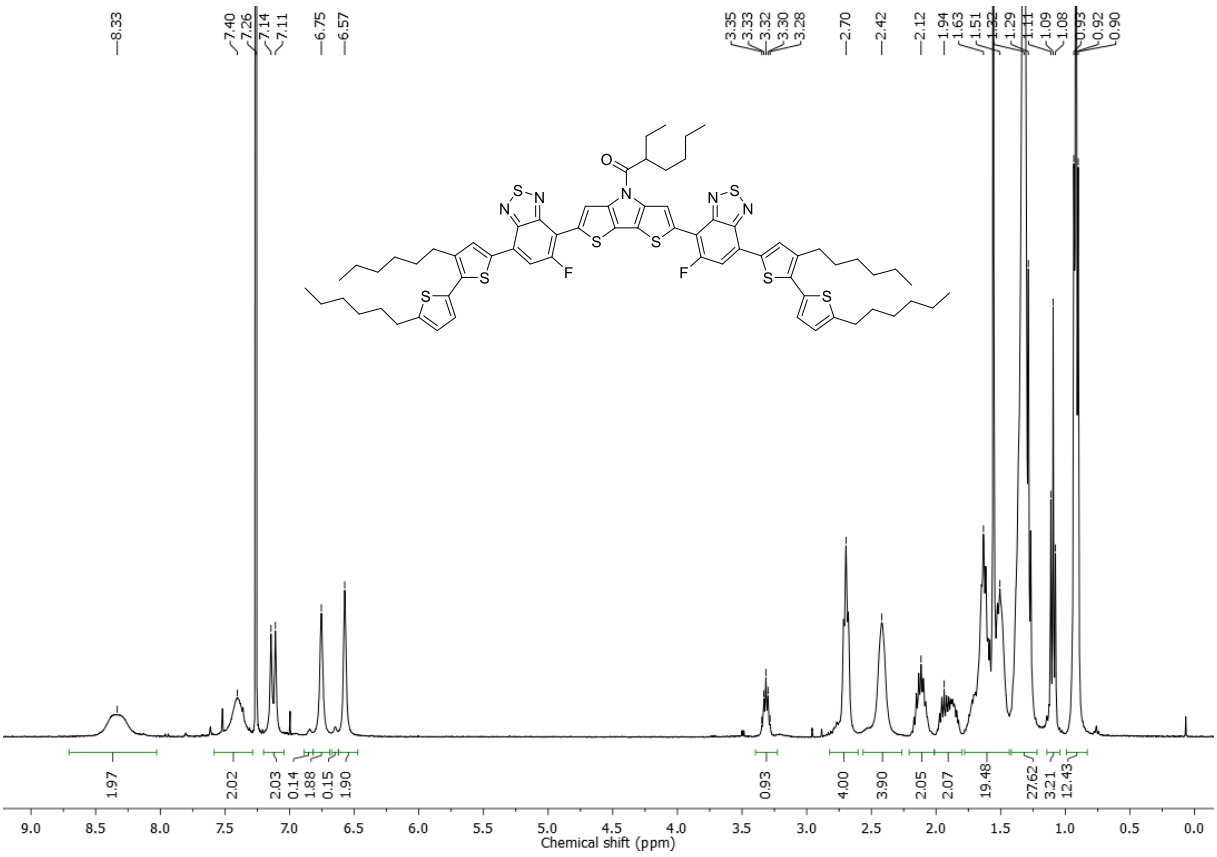




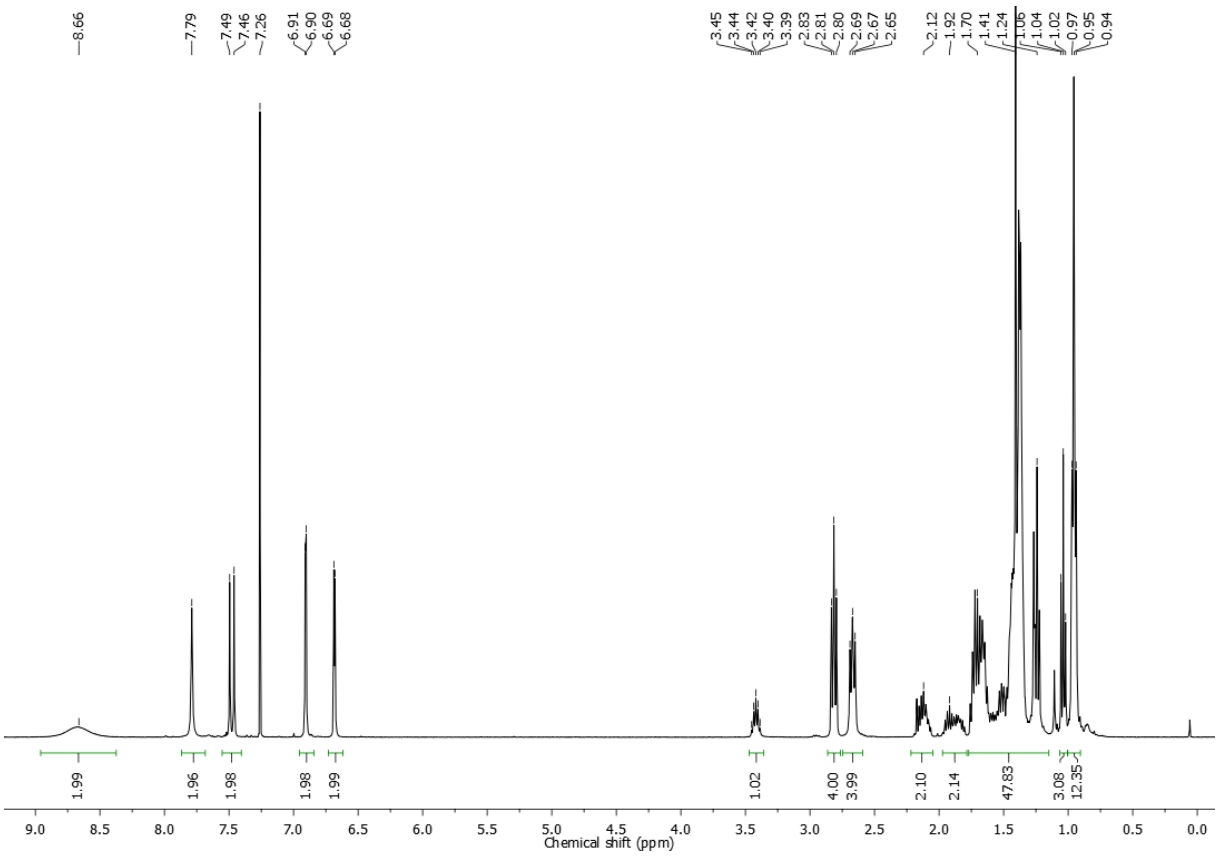
CPDT(FBTTh$_2$)$_2$ (in $CDCl_3$)



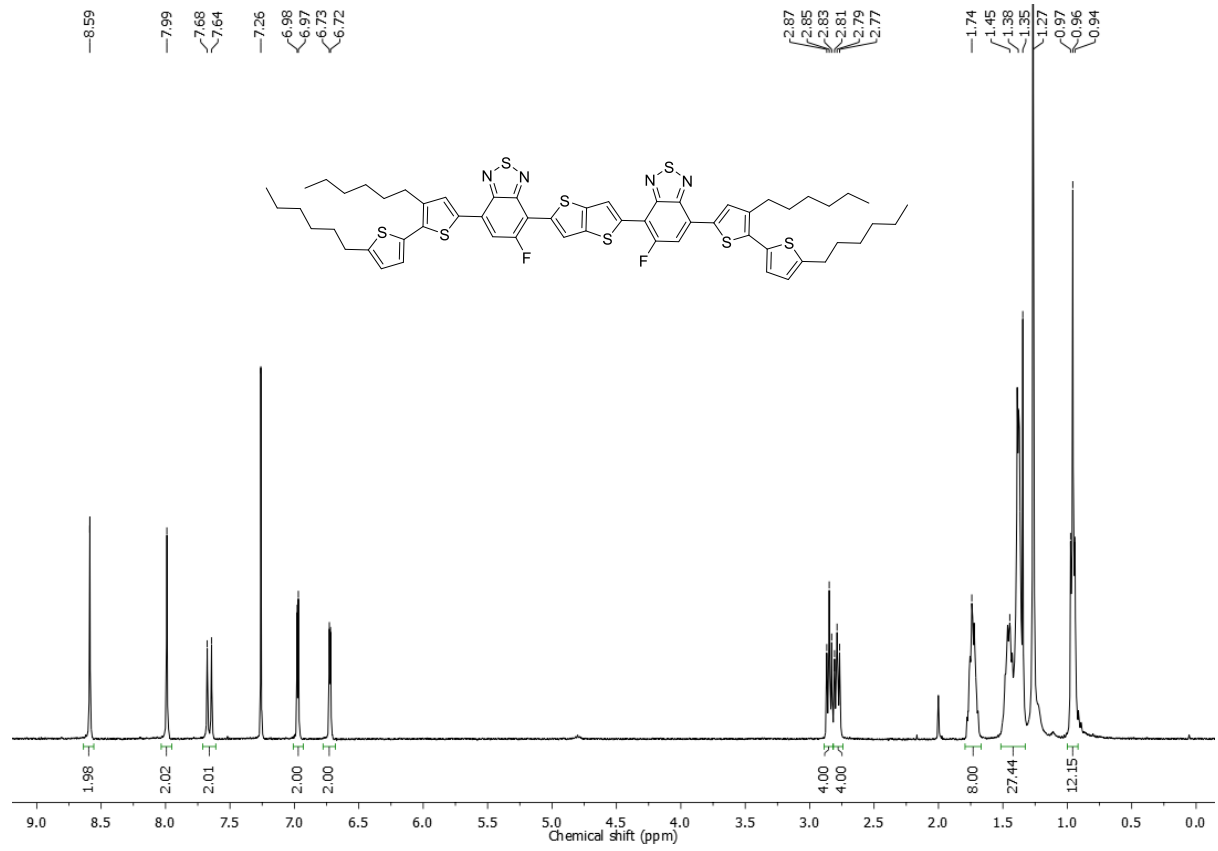
DTP(FBTTh$_2$)$_2$ (in $CDCl_3$)



DTP(FBTTh$_2$)$_2$-pure (in CS_2:$CDCl_3$ 3:1)

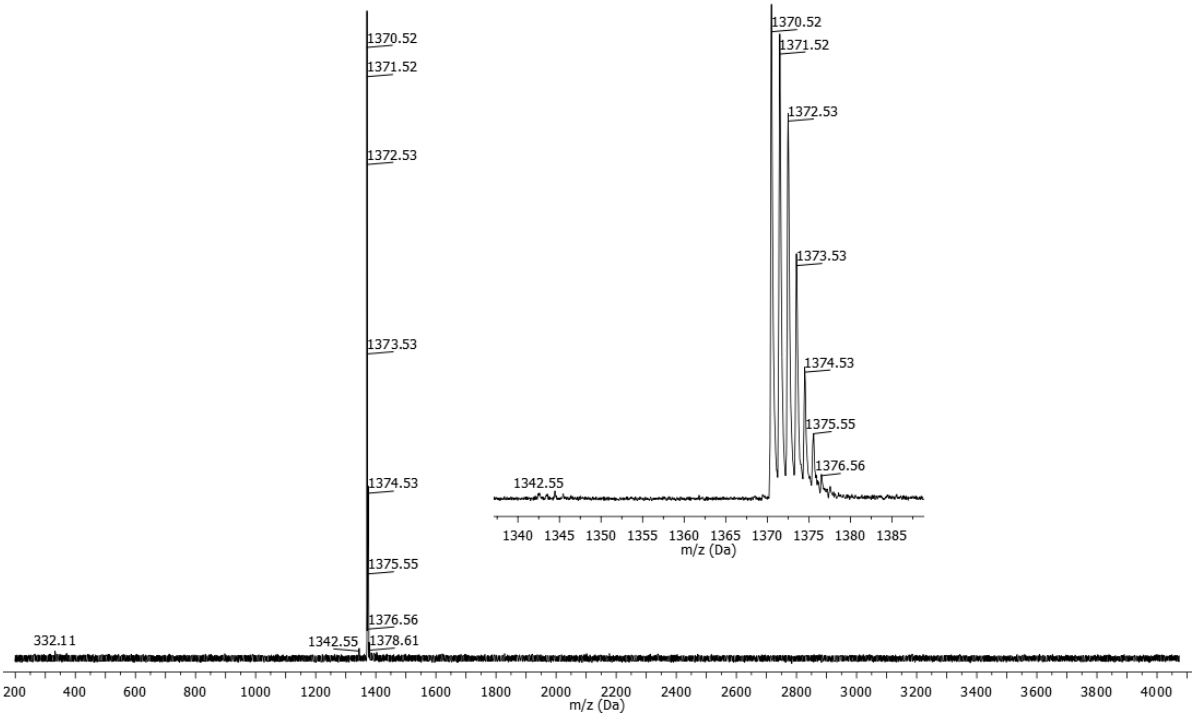


TT(FBTTh$_2$)$_2$ (in CS_2:$CDCl_3$ 3:1)

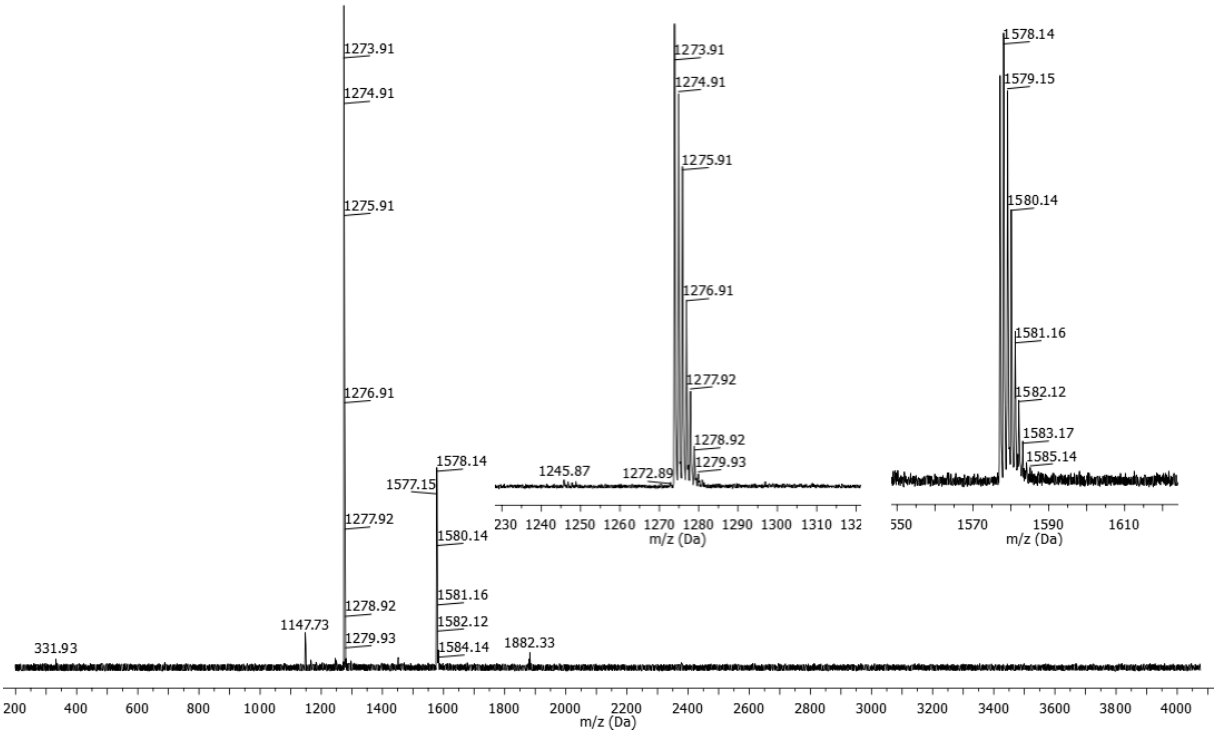


2. MALDI-TOF mass spectra

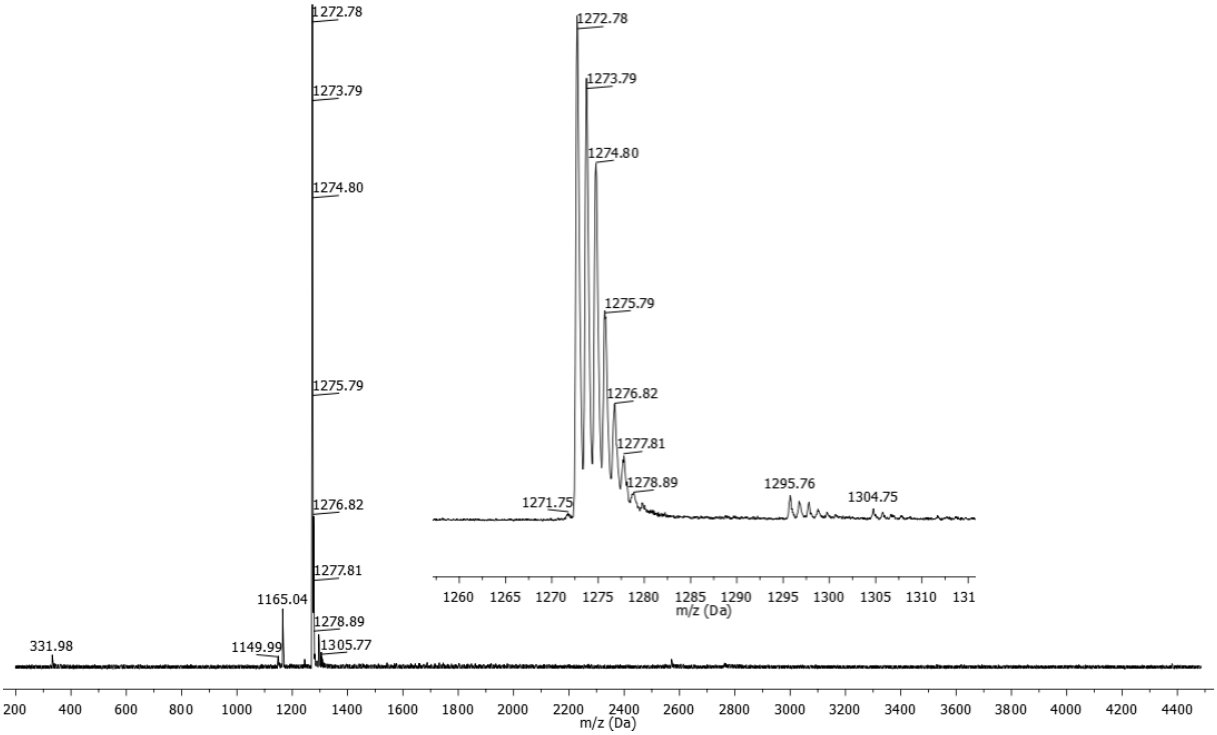
CPDT(FBTTh$_2$)$_2$



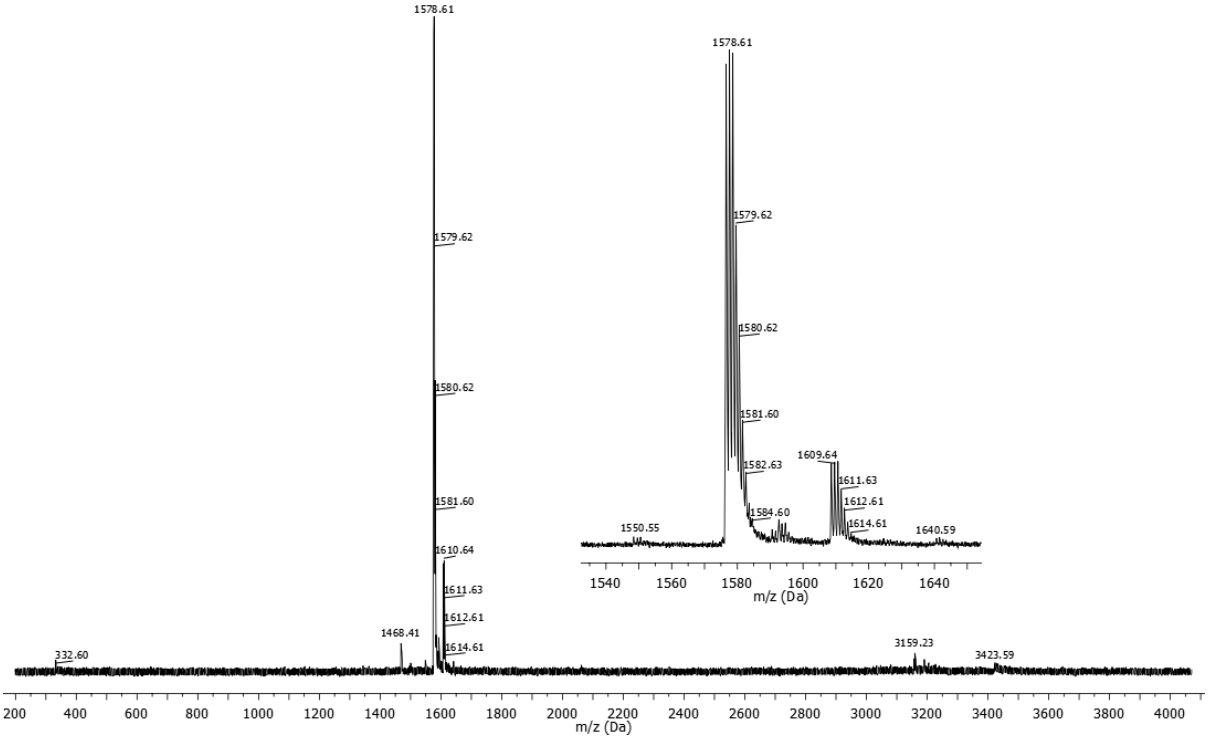
DTP(FBTTh$_2$)$_2$



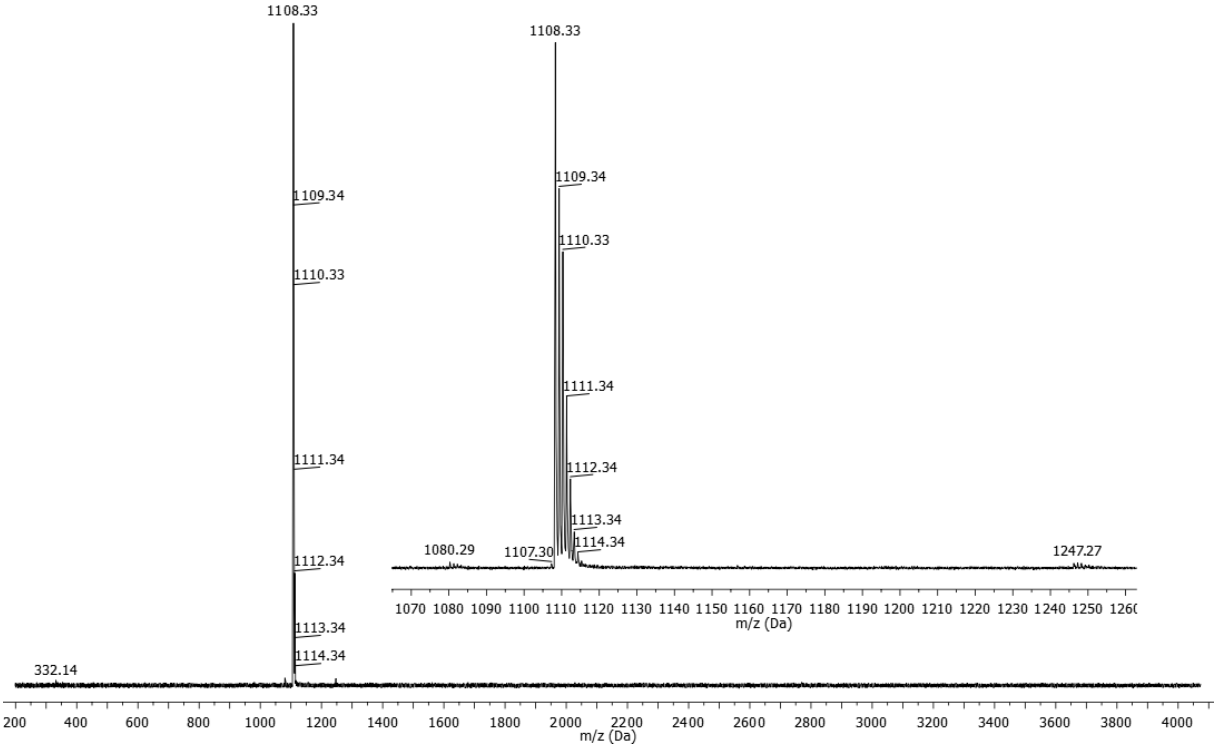
DTP(FBTTh$_2$)$_2$-pure



DTP(FBTTh$_2$)$_2$-homo



TT(FBTTh$_2$)$_2$


1108.33
1109.34
1110.33
1111.34
1112.34
1113.34
1114.34
332.14
200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400 3600 3800 4000
m/z (Da)
1108.33
1109.34
1110.33
1111.34
1112.34
1113.34
1114.34
1080.29
1107.30
1247.27
1070 1080 1090 1100 1110 1120 1130 1140 1150 1160 1170 1180 1190 1200 1210 1220 1230 1240 1250
m/z (Da)

3. Cyclic voltammograms

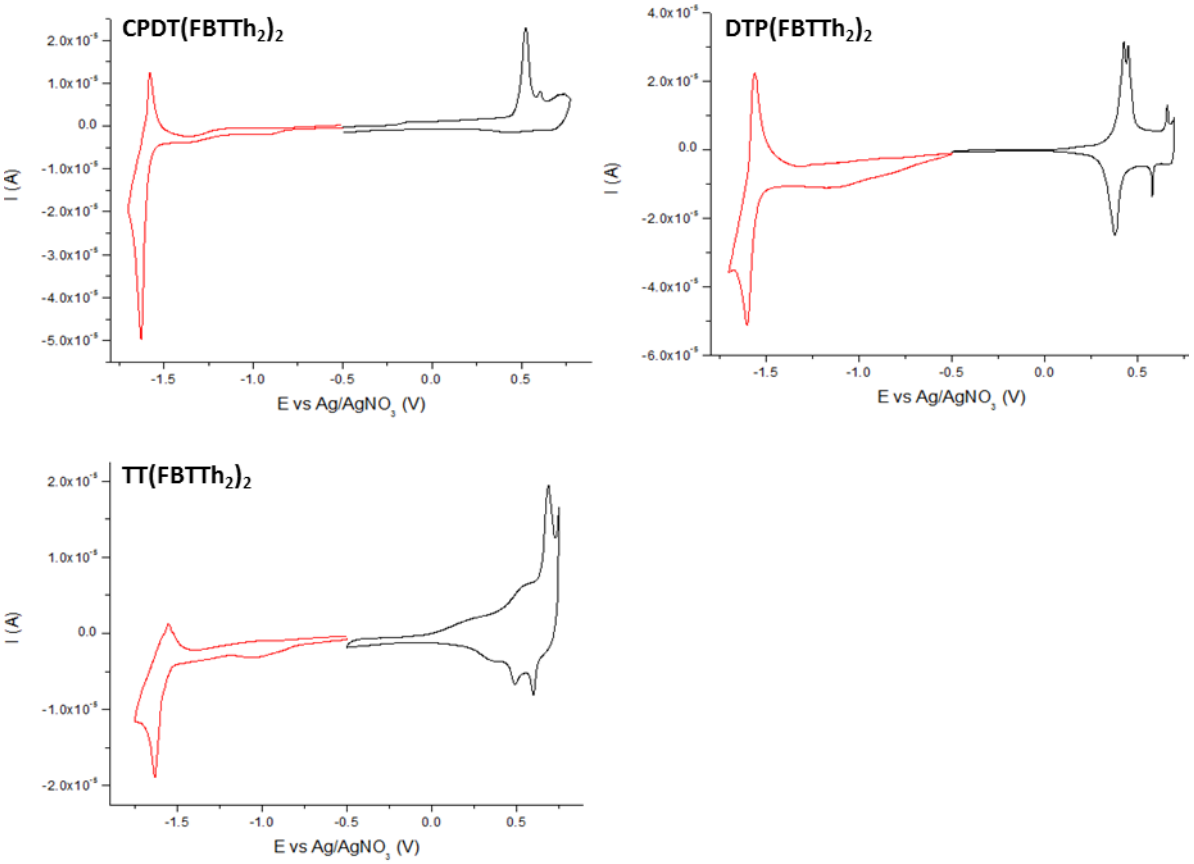


Figure S1: Cyclic voltammograms of the three small molecules in film (**CPDT(FBTTh$_2$)$_2$**: E_{ox}^{onset} = 0.47 V, E_{red}^{onset} = −1.56 V; **DTP(FBTTh$_2$)$_2$**: E_{ox}^{onset} = 0.38 V, E_{red}^{onset} = −1.54 V; **TT(FBTTh$_2$)$_2$**: E_{ox}^{onset} = 0.67 V, E_{red}^{onset} = −1.58 V).

4. Solar cell optimization tables

Table S1: Optimization of the solar cell devices based on **CPDT(FBTTh$_2$)$_2$**.

Acceptor	Ratio	Solvent[a]	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE[b] (%)
$PC_{61}BM$	1:2	CF	4.79	0.81	30	1.17 (1.22)
$PC_{61}BM$	1:2	CF	4.88	0.86	30	1.28 (1.33)[c]
$PC_{61}BM$	1:3	CF	5.12	0.79	32	1.29 (1.33)
$PC_{61}BM$	1:3	CF	5.47	0.84	32	1.40 (1.46)[c]
$PC_{71}BM$	1:2	CB	8.44	0.85	38	2.77 (3.00)
$PC_{71}BM$	1:3	CB	8.39	0.85	40	2.83 (3.10)
$PC_{71}BM$	1:2	oDCB	7.74	0.83	41	2.61 (2.74)
$PC_{71}BM$	1:3	oDCB	7.63	0.82	39	2.46 (2.53)
$PC_{71}BM$	1:3	CB + 0.1% DIO	8.02	0.83	36	2.38 (2.58)
$PC_{71}BM$	1:3	CB + 0.3% DIO	7.90	0.83	37	2.42 (2.52)
$PC_{71}BM$	1:3	CB + 0.1% CN	8.40	0.84	39	2.72 (2.93)
$PC_{71}BM$	1:3	CB + 0.3% CN	8.31	0.83	38	2.64 (2.70)

[a] CF = chloroform, CB = chlorobenzene, oDCB = *ortho*-dichlorobenzene, DIO = 1,8-diiodooctane, CN = 1-chloronaphthalene. [b] Averaged over at least 3 devices. The best device performance is shown in parentheses. [c] Post-annealed at 100 °C.

Table S2: Optimization of the solar cell devices based on **DTP(FBTTh$_2$)$_2$**.

Acceptor	Ratio	Solvent[a]	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE[b] (%)
$PC_{61}BM$	1:2	CF	3.96	0.45	42	0.75 (0.80)
$PC_{61}BM$	1:3	CF	2.72	0.43	45	0.52 (0.53)
$PC_{71}BM$	1:1	CB	5.52	0.59	33	1.08 (1.11)
$PC_{71}BM$	1:2	CB	6.75	0.50	40	1.34 (1.37)

[a] CF = chloroform, CB = chlorobenzene. [b] Averaged over at least 3 devices. The best device performance is shown in parentheses.

Table S3: Optimization of the solar cell devices based on **TT(FBTTh$_2$)$_2$**.

Acceptor	Ratio	Solvent[a]	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE[b] (%)
$PC_{61}BM$	1:1	TCE[c]	4.36	0.80	36	1.26 (1.32)
$PC_{61}BM$	1:2	TCE[c]	5.28	0.71	38	1.42 (1.74)
$PC_{61}BM$	1:2	CB[d]	6.25	0.77	33	1.60 (1.68)
$PC_{61}BM$	1:3	CB[d]	4.45	0.76	34	1.14 (1.37)
$PC_{61}BM$	1:2	CB + 0.1% CN[d]	5.35	0.76	32	1.28 (1.60)
$PC_{61}BM$	1:2	CB + 0.3% CN[d]	5.53	0.69	31	1.16 (1.56)
$PC_{71}BM$	1:2	CB[d]	8.75	0.72	32	1.97 (2.19)
$PC_{71}BM$	1:2	CB + 0.2% DIO[d]	9.13	0.79	36	2.63 (2.96)
$PC_{71}BM$	1:2	oDCB[d]	8.11	0.65	34	1.79 (2.22)

[a] TCE = 1,1,2,2-tetrachloroethane, CB = chlorobenzene, oDCB = *ortho*-dichlorobenzene, CN = 1-chloronaphthalene, DIO = 1,8-diiodooctane. [b] Averaged over at least 3 devices. The best device performance is shown in parentheses. [c] Processed at 85 °C. [d] Processed at 95 °C.

5. EQE spectra

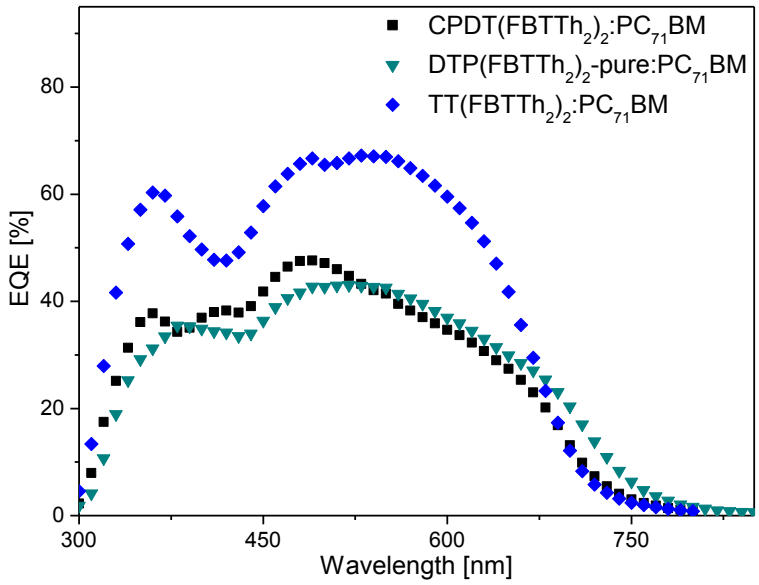


Figure S2: EQE spectra of the optimal devices prepared from the three small molecules.

6. FET mobility measurements

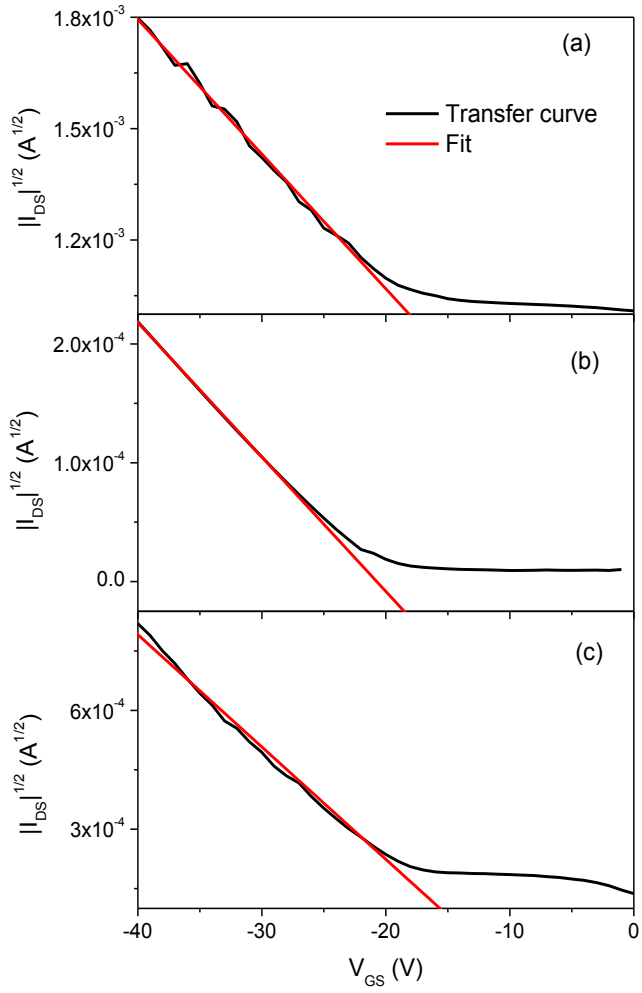


Figure S3: FET transfer characteristics for **CPDT(FBTTh$_2$)$_2$** (a), **DTP(FBTTh$_2$)$_2$-pure** (b), and **TT(FBTTh$_2$)$_2$** (c). The lines used to fit the mobilities in the saturation regime (V_{DS} = −40 V) are shown in red.

7. Purification of DTP(FBTTh$_2$)$_2$ via prep-SEC

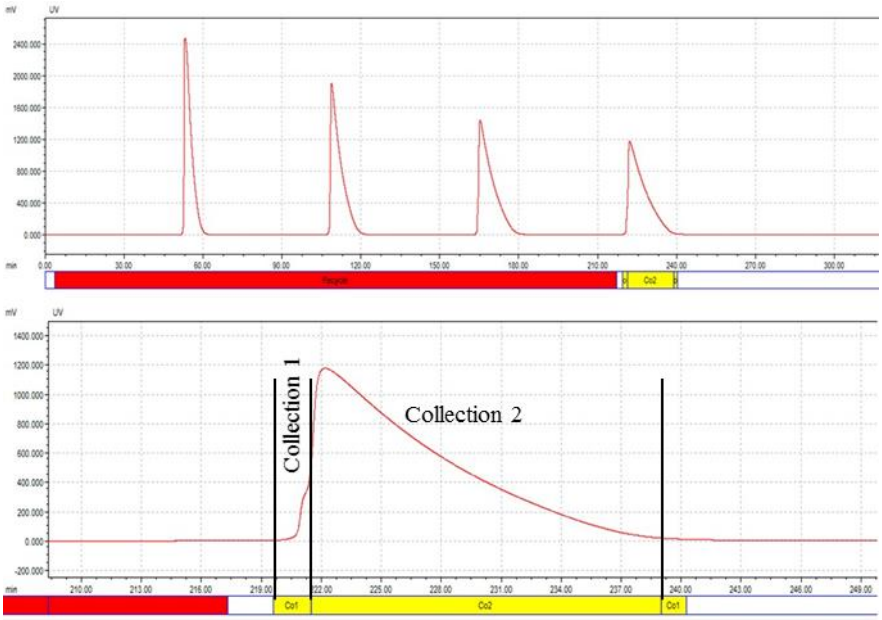


Figure S4: Prep-SEC trace for the purification of **DTP(FBTTh$_2$)$_2$**. **DTP(FBTTh$_2$)$_2$-homo** can be separated as the first collection.

8. UV-Vis absorption spectra for the impure and purified DTP(FBTTh$_2$)$_2$ samples

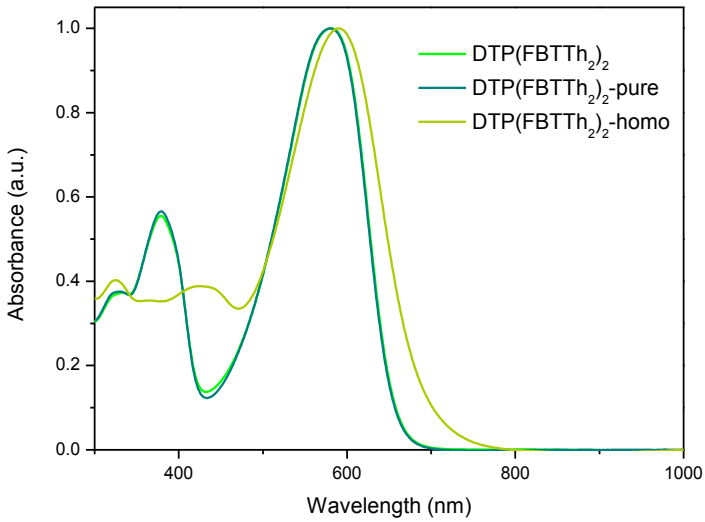


Figure S5: UV-Vis absorption spectra (normalized) for **DTP(FBTTh$_2$)$_2$**, **DTP(FBTTh$_2$)$_2$-pure** and **DTP(FBTTh$_2$)$_2$-homo** in $CHCl_3$.

9. FTPS fitting parameters

Table S4: Fitting parameters for the obtained FTPS signals according to equation 1.

Blend	E_{CT} (eV)	λ (eV)	f (eV²)	V_{oc} (V)	E_{CT}-qV_{oc} (eV)
CPDT(FBTTh$_2$)$_2$:PC$_{71}$BM	1.43	0.25	4.3E-1	0.85	0.58
TT(FBTTh$_2$)$_2$:PC$_{71}$BM	1.33	0.24	1.6E-1	0.79	0.54
DTP(FBTTh$_2$)$_2$:PC$_{71}$BM	1.20	0.30	1.5E-1	0.50	0.70
DTP(FBTTh$_2$)$_2$-pure:PC$_{71}$BM	1.22	0.25	2.1E-1	0.67	0.55