Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplementary Information for:

Thieno[3,4-*b*]thiophene linker enables a low-bandgap fluorene-cored molecular acceptor for efficient non-fullerene solar cells

Haijun Fan,[a] Thomas Vergote,[a] Shengjie Xu,[a] Shanshan Chen,[c] Changduk Yang[c] and Xiaozhang Zhu*[ab]

[a]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[b]University of Chinese Academy of Sciences, Beijing 100049, China

[c]Department of Energy Engineering, School of Energy and Chemical Engineering, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and technology (UNIST), Ulsan 689-798, South Korea

*Author to whom correspondence should be addressed. E-mail: xzzhu@iccas.ac.cn.

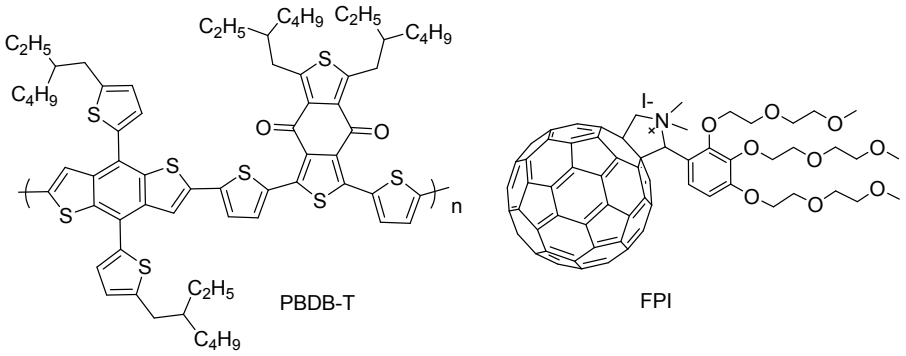


Fig. S1 Molecular structure of PBDB-T and FPI.

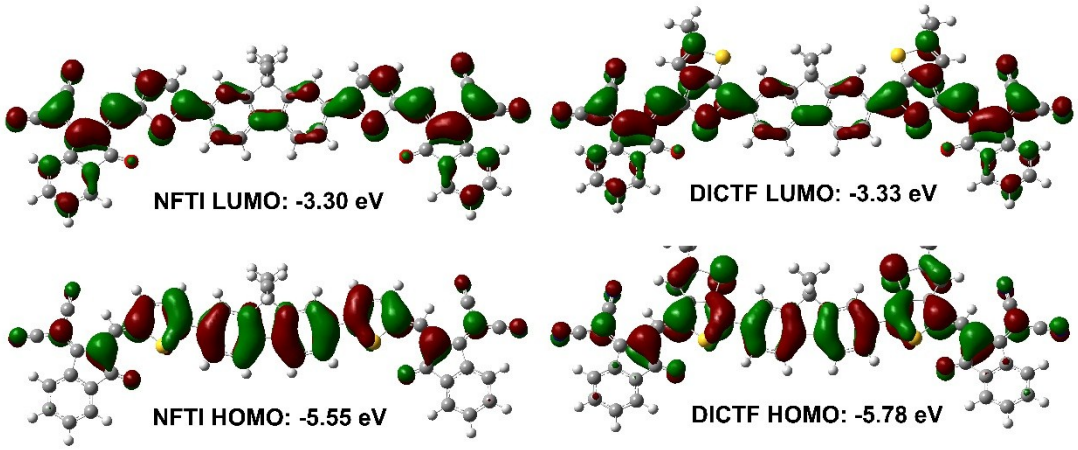


Fig. S2 Theoretical calculation on energy leves of NFTI and DICTF.

Table S1 Photovoltaic parameters of solar cells based on PBDB-T:NFTI films of different blending ratios, measured under illumination of AM 1.5 G, 100 mW cm^{-2}.

D:A (w/w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)[a)]
1:0.5	0.934	7.78	0.52	3.82(3.59)
1:0.9	0.923	8.93	0.57	4.75(4.48)
1:1.3	0.923	8.39	0.60	4.66(4.45)
1:1.7	0.921	7.48	0.61	4.19(4.04)

[a)] bracketed is the averaged PCE value statistically collected from 24 devices.

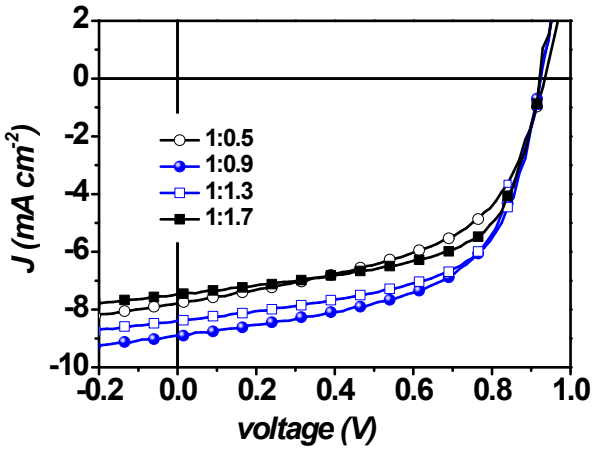


Fig. S3 *J-V* curves of solar cells based on PBDB-T:NFTI films of different blending ratios

Table S2 Photovoltaic parameters of solar cells based on PBDB-T:NFTI films of different amount of DPE additive, measured under illumination of AM 1.5 G, 100 mW cm^{-2}.

DPE(v/v%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)[a)]
0.5	0.914	9.51	0.56	4.95(4.74)
1	0.909	10.45	0.57	5.46(5.29)
2	0.895	10.51	0.57	5.46(5.31)
3	0.887	10.93	0.58	5.66(5.46)
5	0.904	9.83	0.61	5.44(5.29)

[a)] bracketed is the averaged PCE value statistically collected from 24 devices.

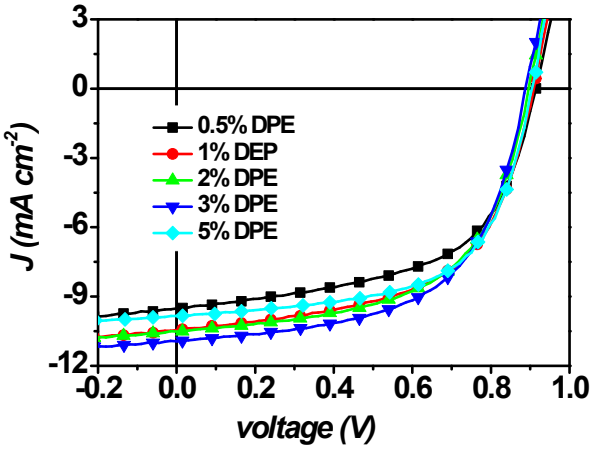


Fig. S4 *J-V* curves of solar cells based on PBDB-T:NFTI films of different DPE contents.

Table S3 Photovoltaic parameters of solar cells based on PBDB-T:NFTI films under different thermal annealing temperature, measured under illumination of AM 1.5 G, 100 mW cm^{-2}.

TA temperature	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)[a)]
No	0.904	9.83	0.61	5.44(5.28)
60 °C	0.900	10.35	0.58	5.44(5.30)
80 °C	0.892	9.97	0.65	5.79(5.62)
100 °C	0.894	11.47	0.60	6.23(6.08)
120 °C	0.902	11.54	0.61	6.33(6.10)
140 °C	0.888	11.67	0.60	6.20(6.01)

[a)] bracketed is the averaged PCE value statistically collected from 24 devices.

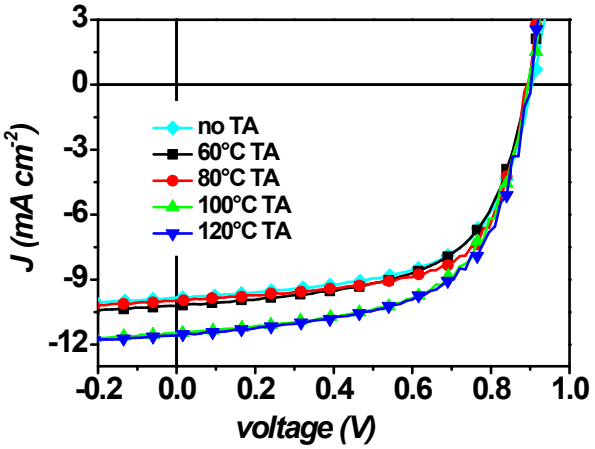


Fig. S5 *J-V* curves of solar cells based on PBDB-T:NFTI films under different

thermal annealing temperature.

Table S4 Photovoltaic parameters of solar cells based on PBDB-T:NFTI films processed in different solvents, measured under illumination of AM 1.5 G, 100 mW cm^{-2}.

solvent	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)[a)]
DCB	0.902	11.54	0.61	6.33(6.10)
CB	0.909	13.60	0.60	7.42(7.25)
CF	0.887	15.32	0.54	7.41(7.23)

[a)] bracketed is the averaged PCE value statistically collected from 24 devices.

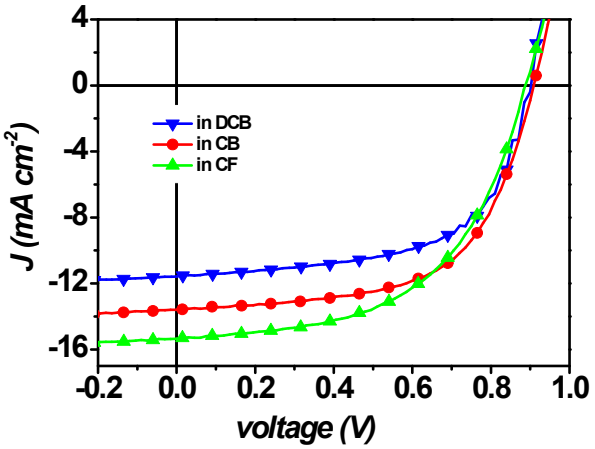


Fig. S6 *J-V* curves of solar cells based on PBDB-T:NFTI films processed in different solvents.

Table S5 Photovoltaic parameters of solar cells based on PBDB-T:NFTI films processed in use of DPE and F4-TCNQ binary additives, measured under illumination of AM 1.5 G, 100 mW cm^{-2}.

F4-TCNQ content(w/w%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)[a]
without	0.898(0.896)	16.22(16.18)	0.57(0.56)	8.34(8.14)
0.005	0.896(0.895)	17.49(17.40)	0.55(0.54)	8.69(8.37)
0.01	0.902(0.901)	17.82(17.77)	0.56(0.55)	9.02(8.89)
0.05	0.883(0.880)	17.77(17.65)	0.54(0.53)	8.50(8.24)

[a)] bracketed is the averaged PCE value statistically collected from 24 devices. All devices adopt FPI electron transporting layers.

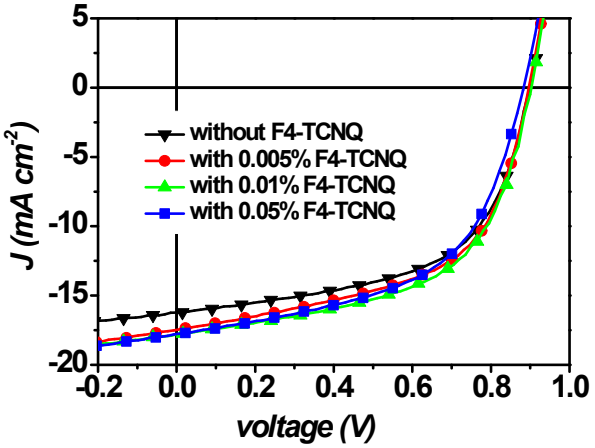


Fig. S7 *J-V* curves of solar cells based on PBDB-T:NFTI films processed in use of different amount of F4-TCNQ.

Table S6 Comparison on photovoltaic parameters of NFTI-based solar cells with different active areas, measured under AM 1.5G, 100 mW cm^{-2} simulated solar illumination.

F4-TCNQ content(w/w%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
without	0.898(0.896)	16.22(16.18)	0.57(0.56)	8.34(8.14)[a]
	0.878(0.878)	15.29(15.28)	0.59(0.58)	8.02(7.89)[b]
0.01	0.902(0.901)	17.82(17.77)	0.56(0.55)	9.02(8.89)[a]
	0.883(0.880)	16.81(16.56)	0.59(0.59)	8.75(8.61)[b]

[a)] device active area: 3.08 mm^2. [b)] device active area: 9.24 mm^2.

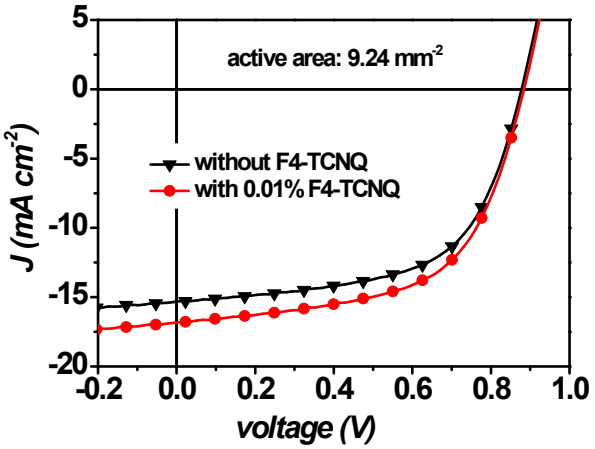


Fig. S8 *J-V* curves of solar cells based on PBDB-T:NFTI films with active area of 9.24 mm^2.

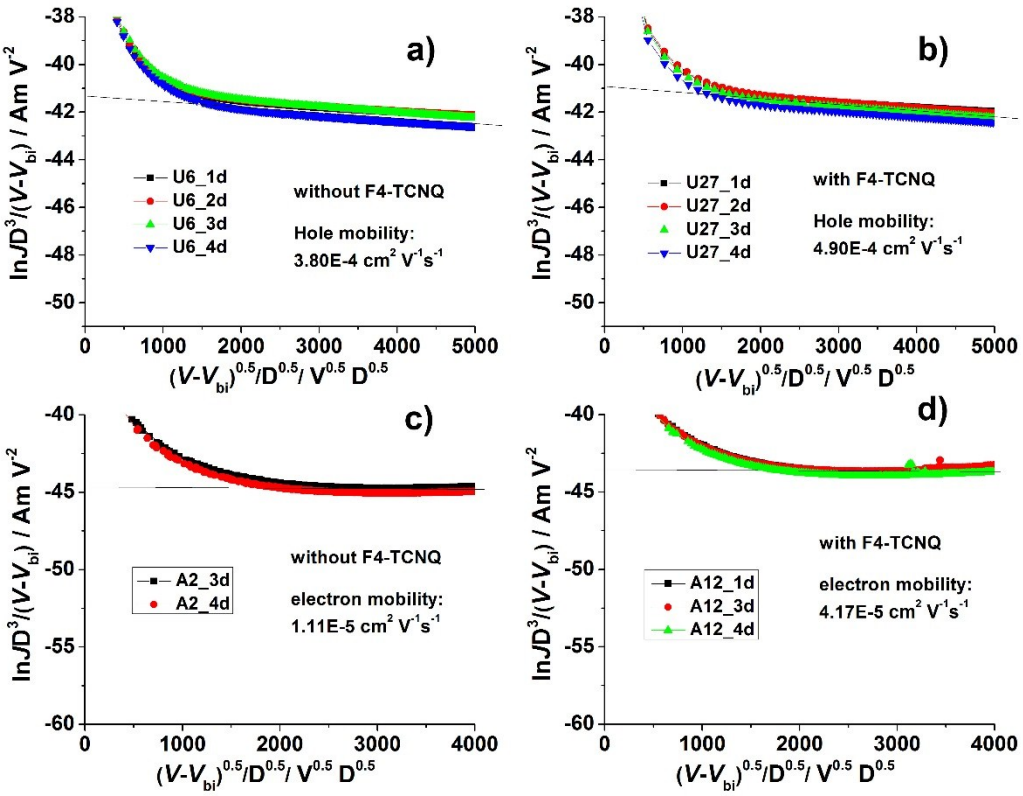


Fig. S9 Hole and electron mobility of PBDB-T:NFTI device by SCLC method.

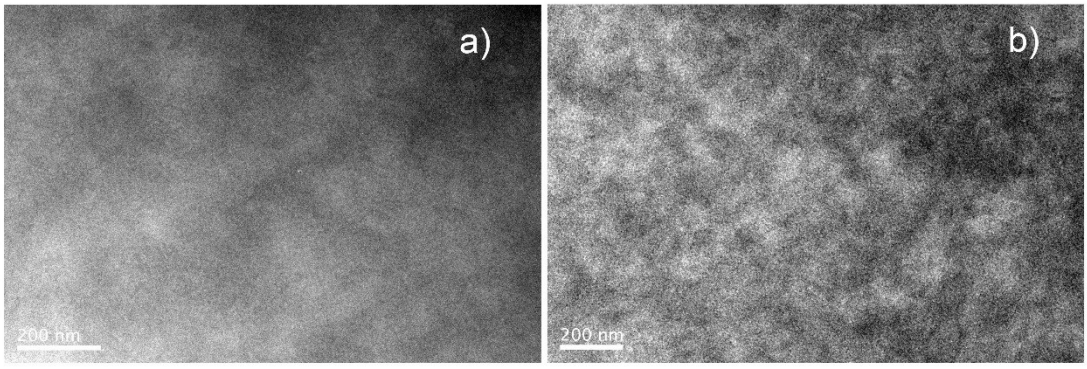
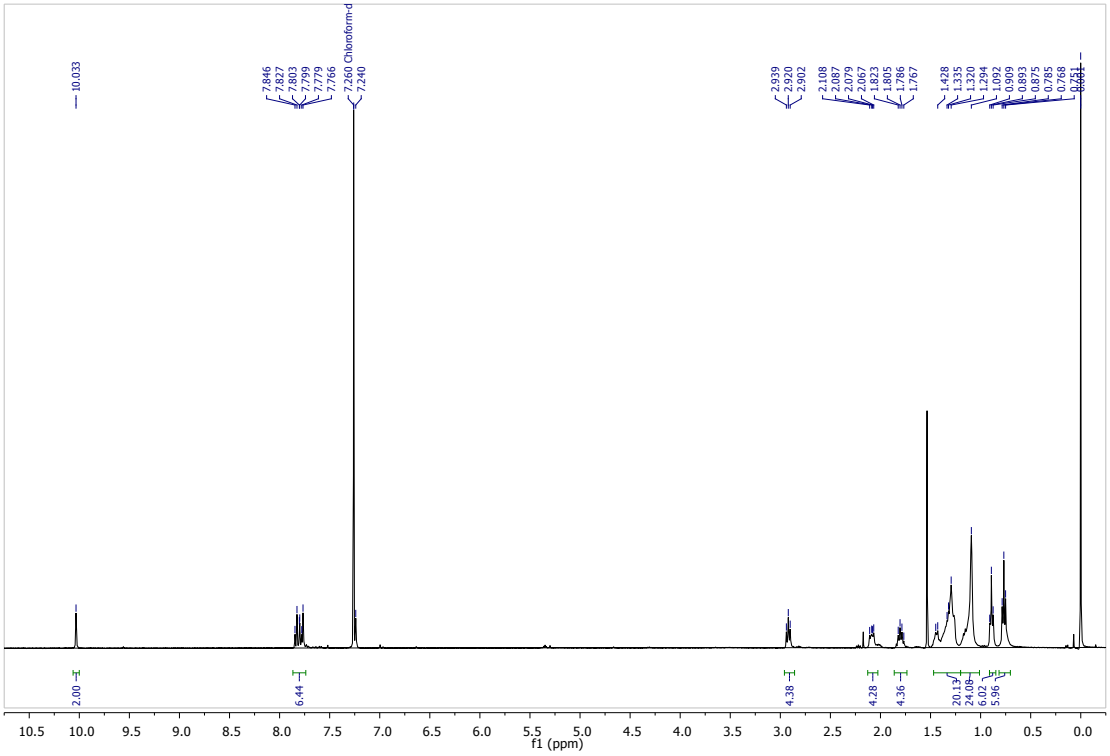
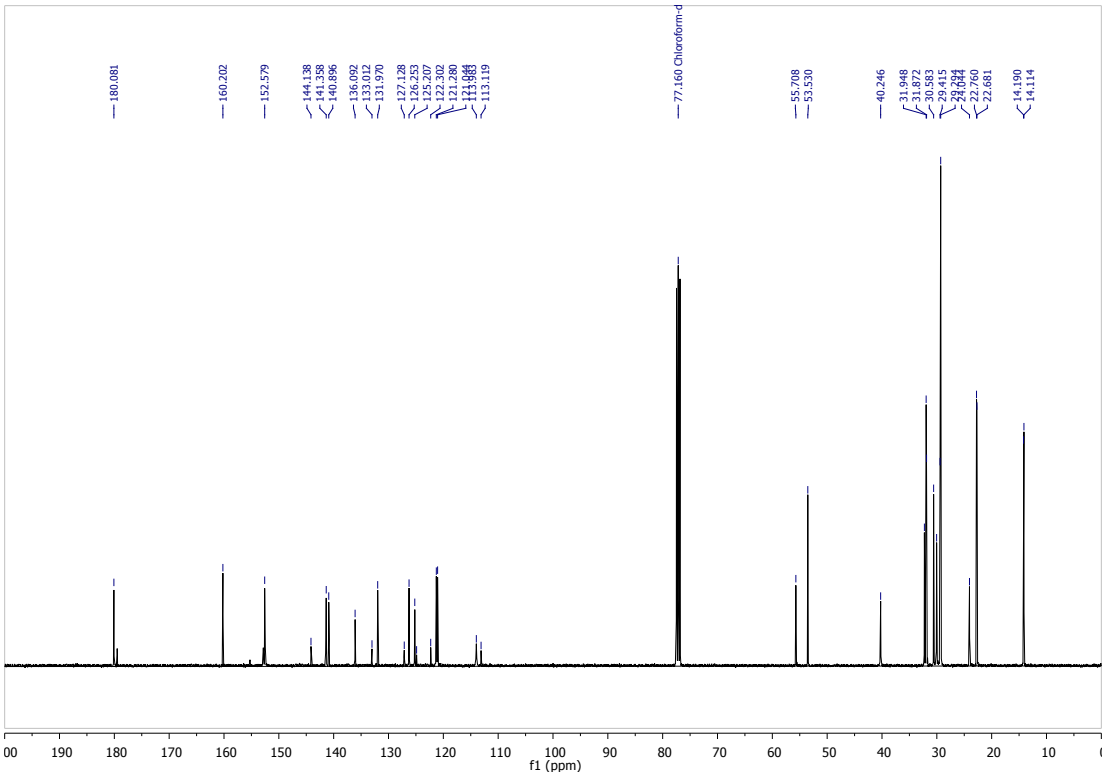


Fig. S10 TEM images for PBDB-T:NFTI film (a) processed without or (b) with F4-TCNQ additives.

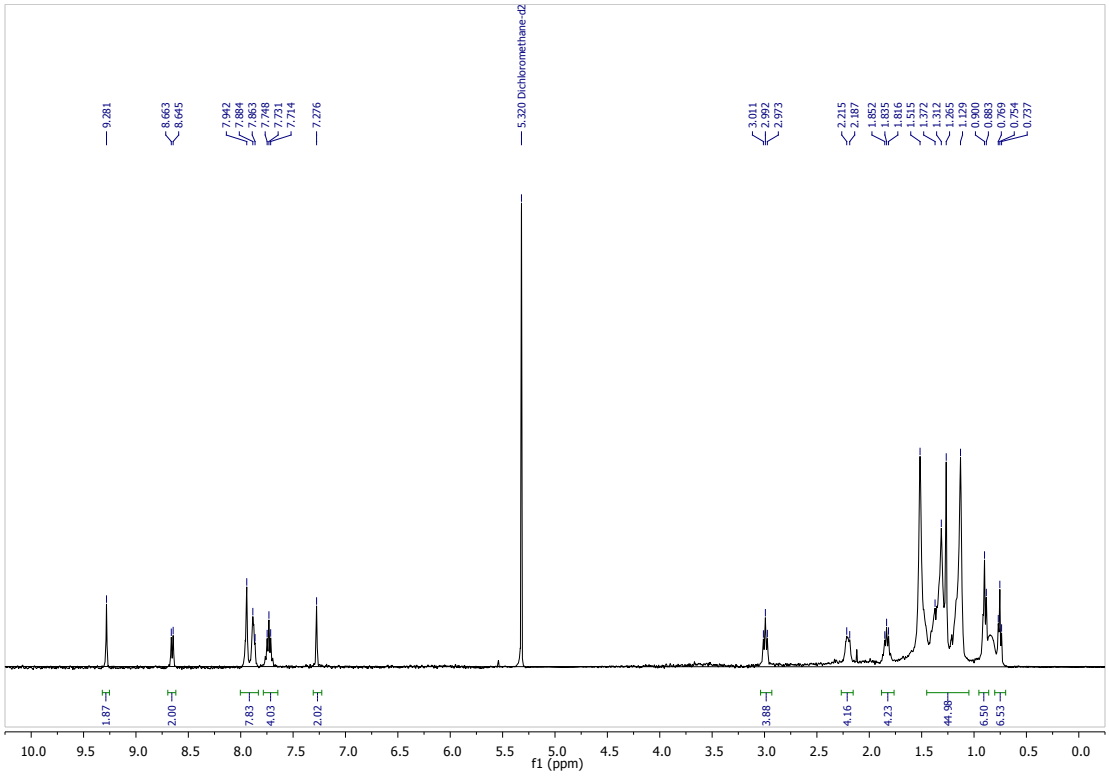
NMR Charts

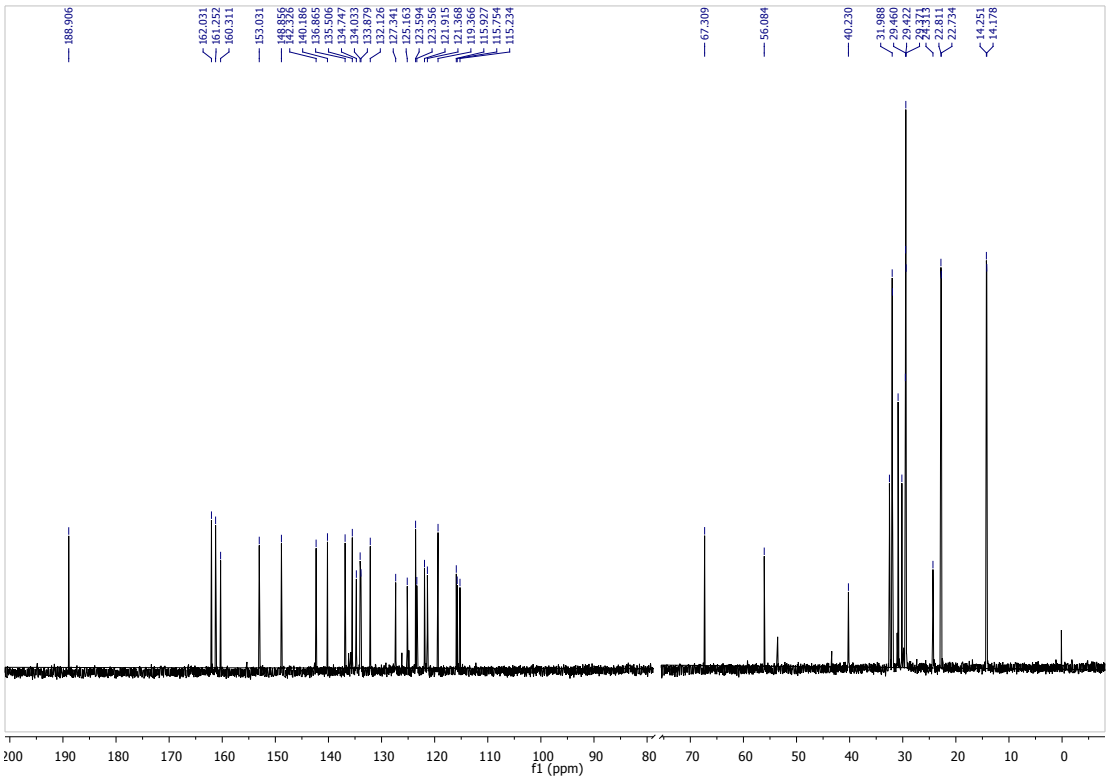
6,6’-(9,9-Dioctyl-9*H*-fluorene-2,7-diyl)bis(2-octylthieno[3,4-*b*]thiophene-4-carbaldehyde) (3)





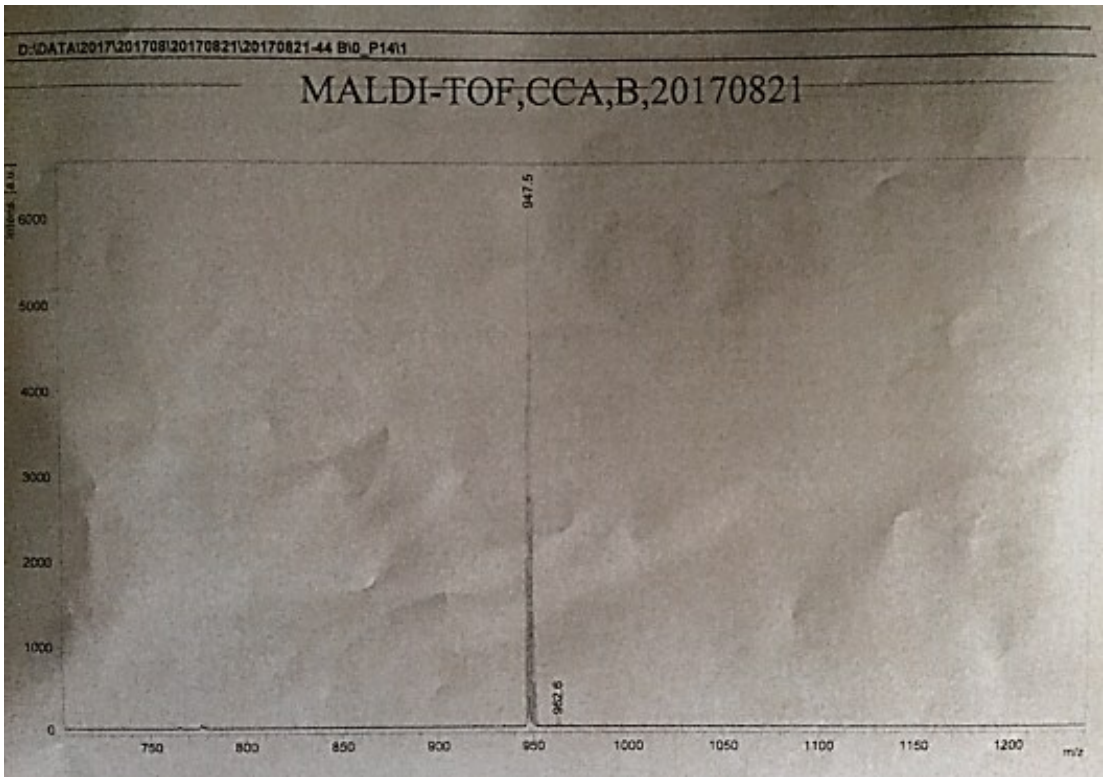
2,2'-((((9,9-Dioctyl-9*H*-fluorene-2,7-diyl)bis(2-octylthieno[3,4-*b*]thiophene-6,4-diyl))bis(methylene))bis(3-oxo-2,3-dihydro-1*H*-indene-2-yl-1-ylidene)) dimalononitrile (NFTI):





MALDI-TOF Mass Spectrum

6,6'-(9,9-Dioctyl-9*H*-fluorene-2,7-diyl)bis(2-octylthieno[3,4-*b*]thiophene-4-carbaldehyde) (3)



2,2'-((((9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(2-octylthieno[3,4-b]thiophene-6,4-diyl))bis(methylene))bis(3-oxo-2,3-dihydro-1H-indene-2-yl-1-ylidene))dimalononitrile (NFTI).