Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

A thieno[3,4-*b*]thiophene-based small-molecule donor with a π-extended dithienobenzodithiophene core for solution-processed organic solar cells

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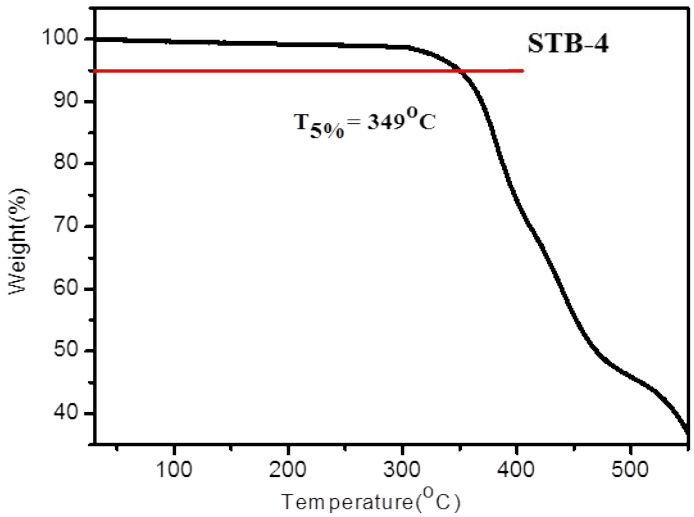


Fig. S1 Thermal gravimetric analysis (TGA) curves of **STB-4**

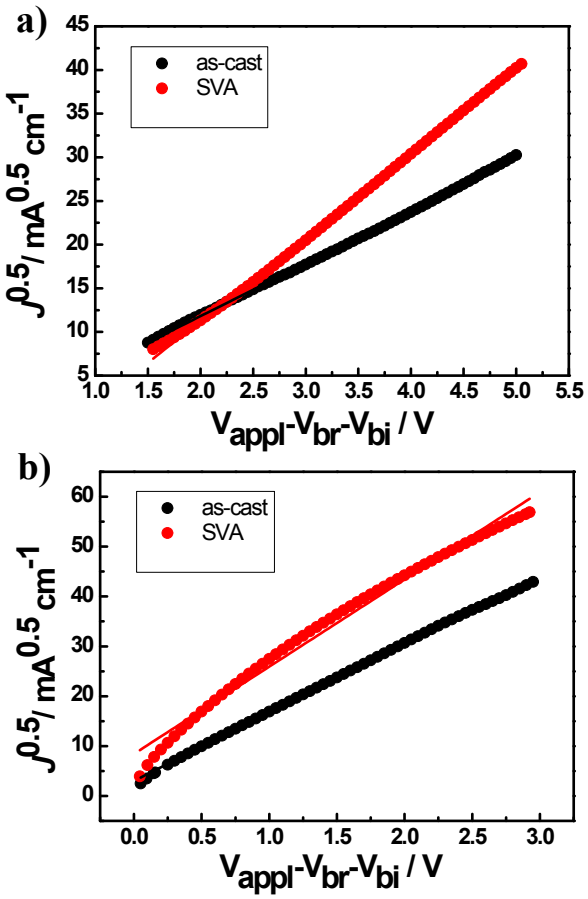


Fig. S2 $J^{0.5}$ vs V plots: STB-4/$PC_{71}BM$ (1:0.8, w/w) hole-only diode (a) and electron-only diode (b) without and with SVA.

UV-VIS of the Blend Film

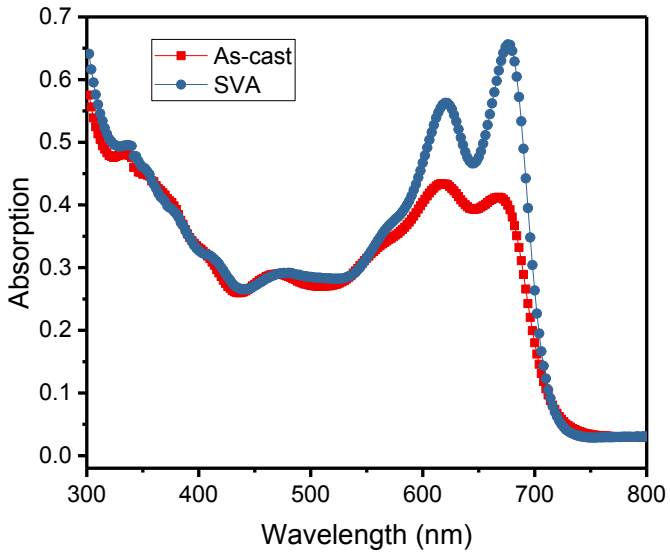


Fig. S3 UV-VIS of the blend film before and after SVA

2D GIWAXS

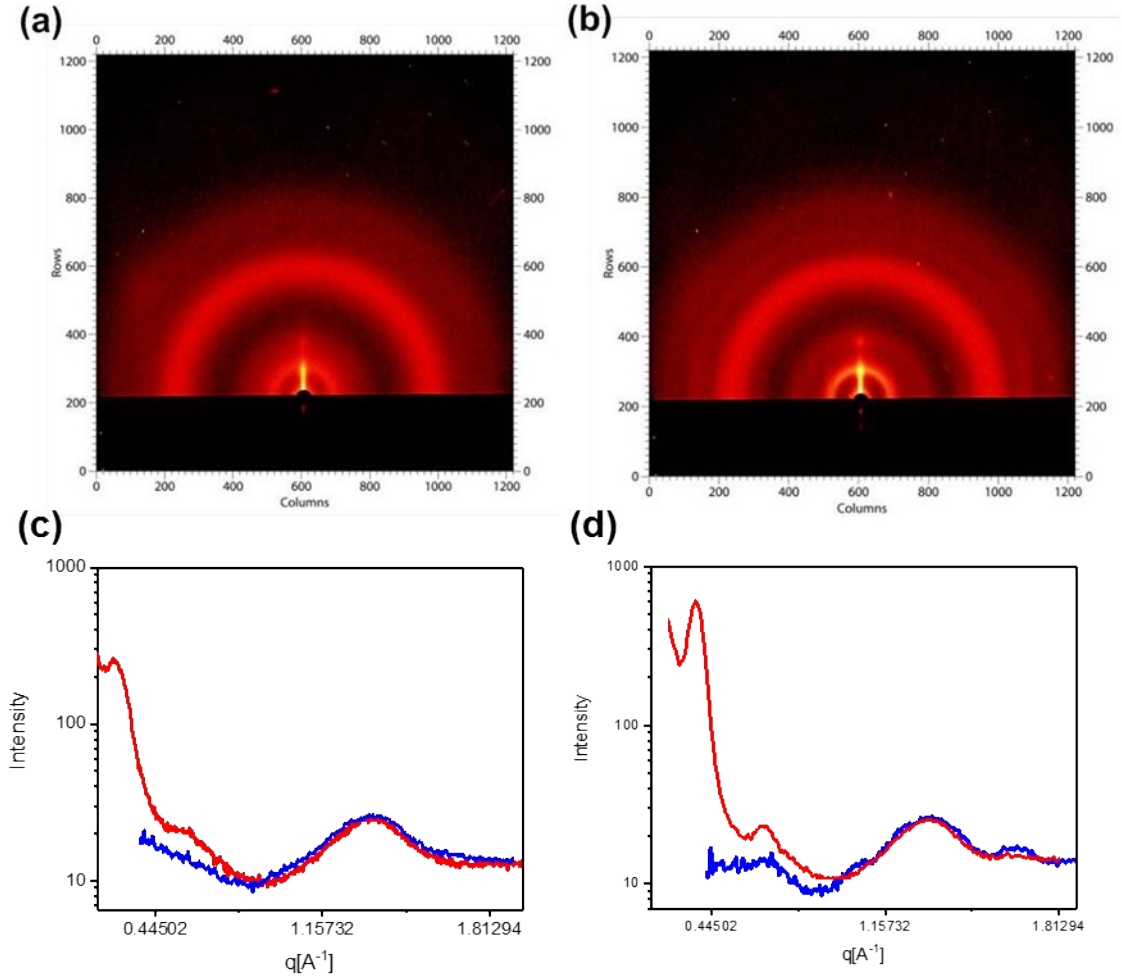


Fig. S4 2D GIWAXS patterns for STB-4-based blend films before (a) and after (b) SVA treatment; (c) and (d) in-plane (blue) and out-of-plane (red) X-ray scattering profiles extracted from the 2-D GIXD images.

2D GIXD scattering images and the corresponding out-of-plane (OOP) and in-plane (IP) line cut proles are shown in Fig. S4. As-cast STB-4:$PC_{71}BM$ blended thin films showed crystalline features, with the lamellae packing distance of 24.1 Å and a $PC_{71}BM$ scattering ring at 1.35 $Å^{-1}$. The π–π stacking peak was quite weak, and no obvious crystal orientation was evident. After SVA, a sharp scattering of (100) peak showed up at 0.31 $Å^{-1}$, which corresponds to a decreased lamella packing distance of 20.3 Å with stronger molecular interactions. The obvious (200) peak at the OOP direction further demonstrated the enhanced crystallinity, which was well matched with the increased hole and electron mobilities. Moreover, a weak peak was found in the IP direction at approximately 1.65 $Å^{-1}$ after SVA and resulted in the stacking distance of 3.80 Å which may be attributed to the π–π interactions, indicating the edge-on orientations to the substrate.

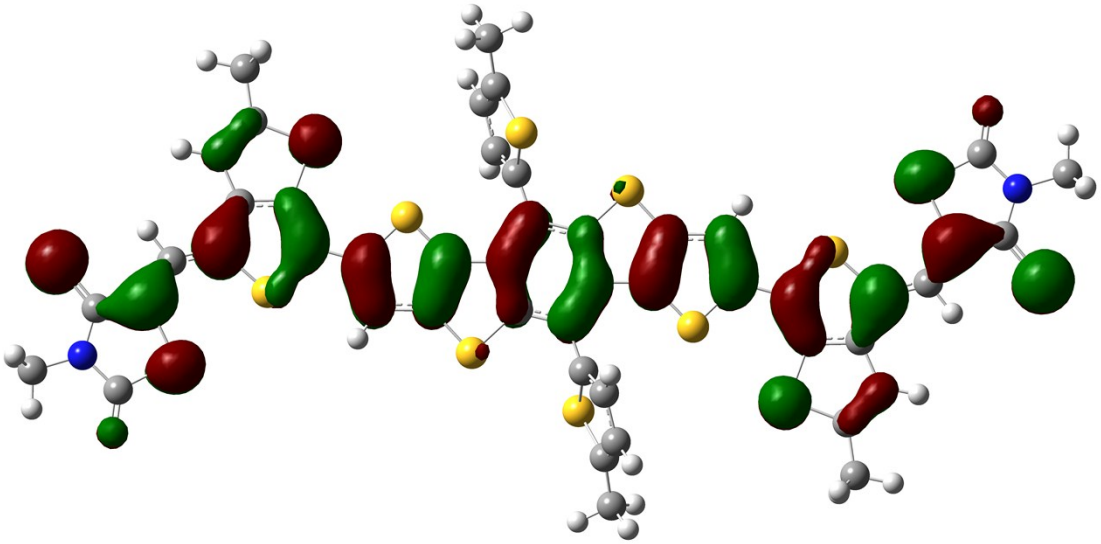
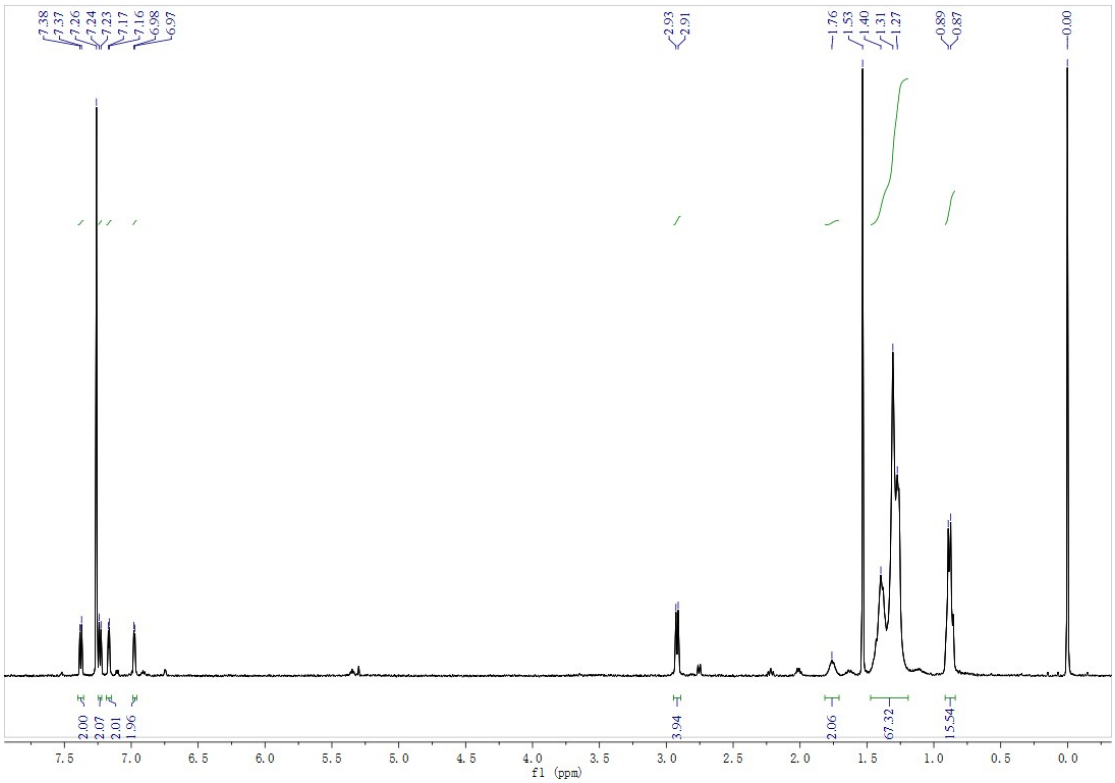


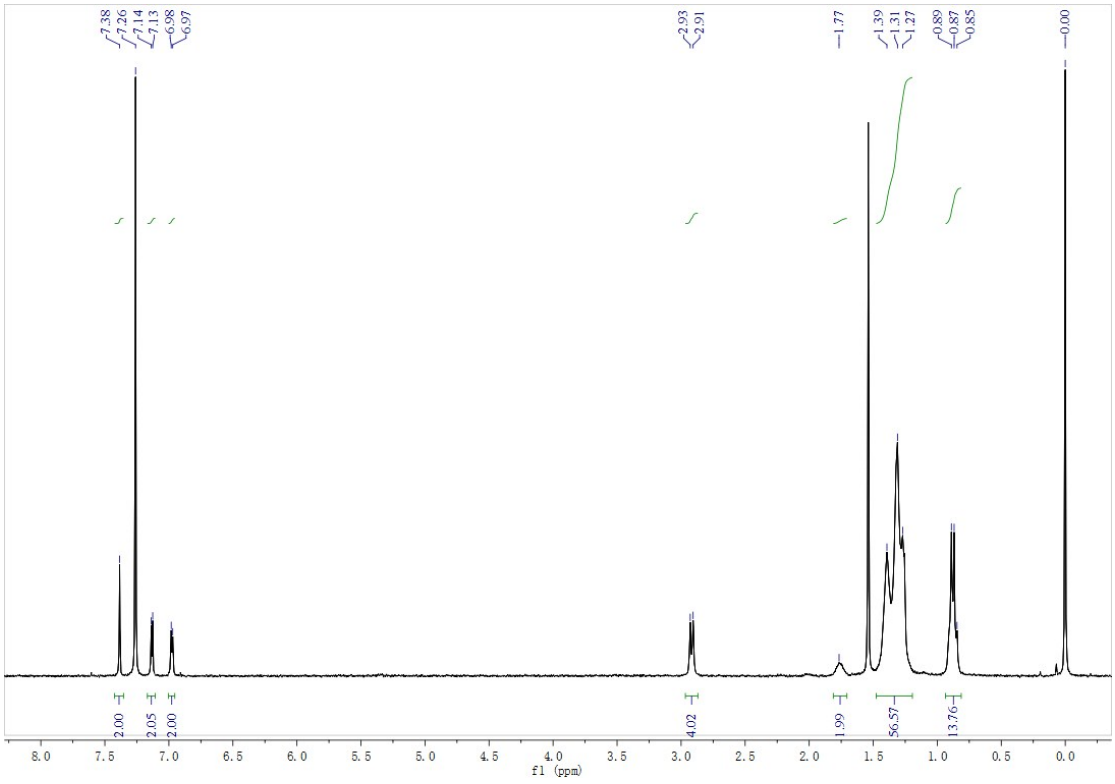
Fig. S5 SOMO orbital of **STB-4** cation.

NMR Charts

5,10-Bis(5-(2-hexyldecyl)thiophen-2-yl)dithieno[2,3-*d*':2',3'-*d*']benzo[1,2-*b*:4',5'-*b*']dithiophene(2)

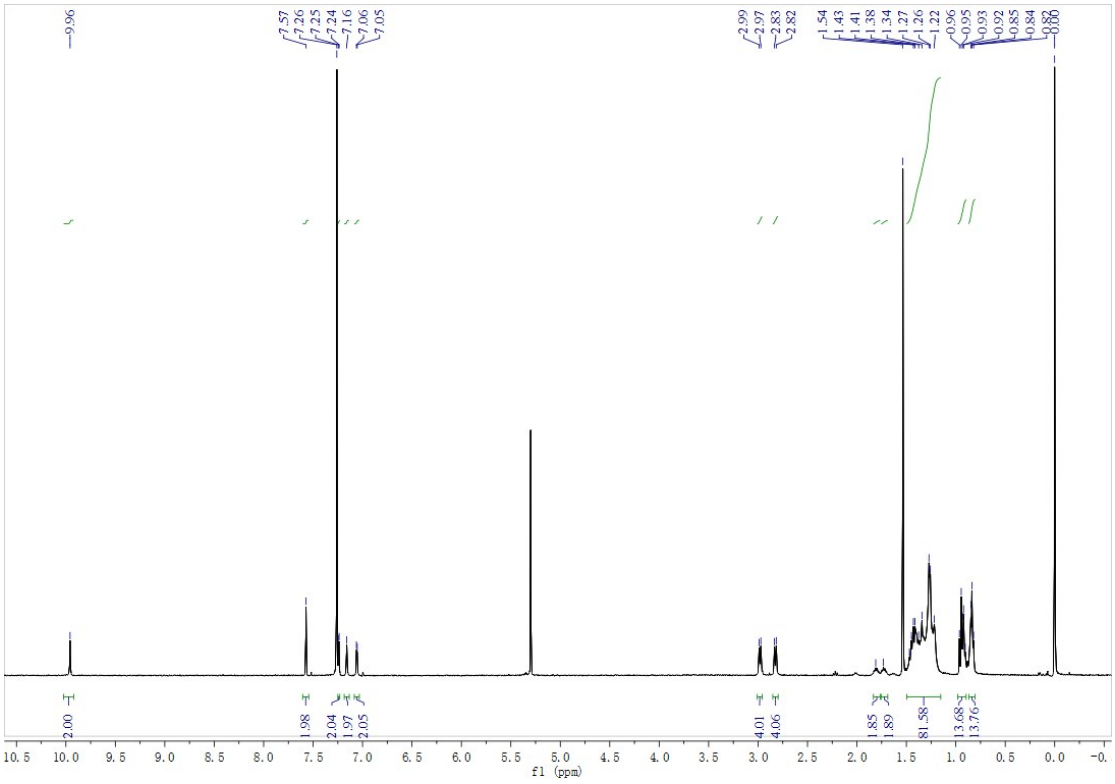


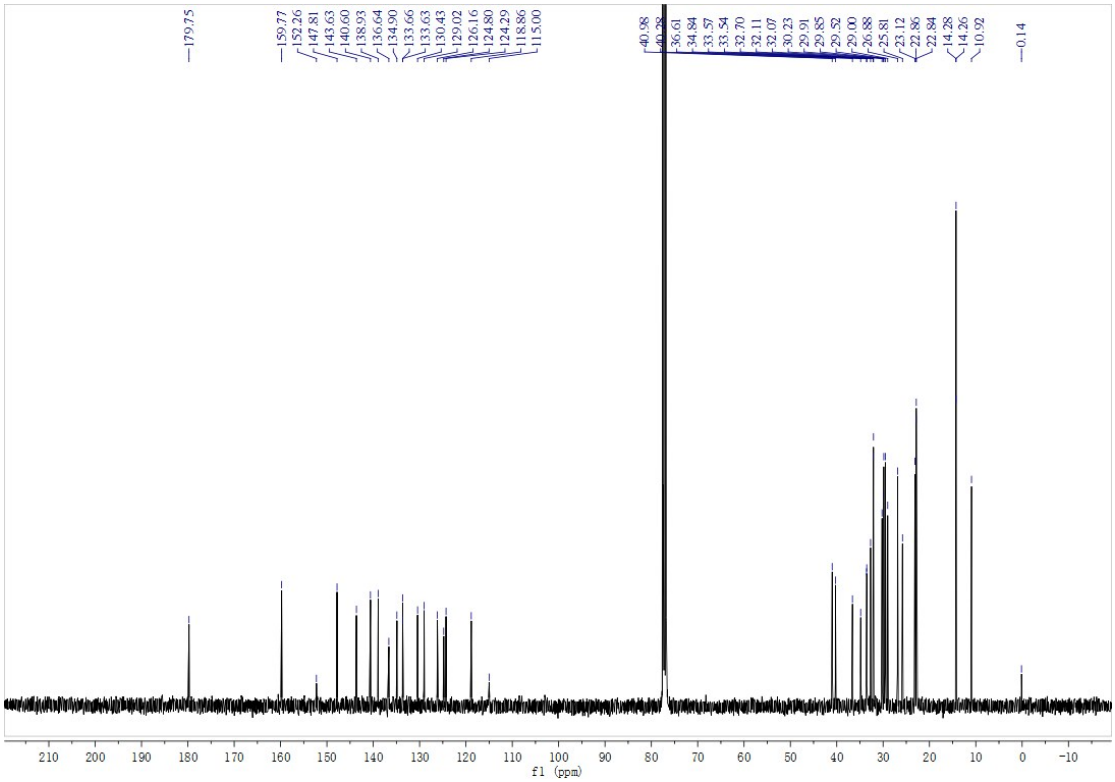
5,10-bis(5-(2-hexyldecyl)thiophen-2-yl)-2,7-iodo-dithieno[2,3-d':2',3'-d']benzo[1,2-b:4',5'-b']dithiophene(3)



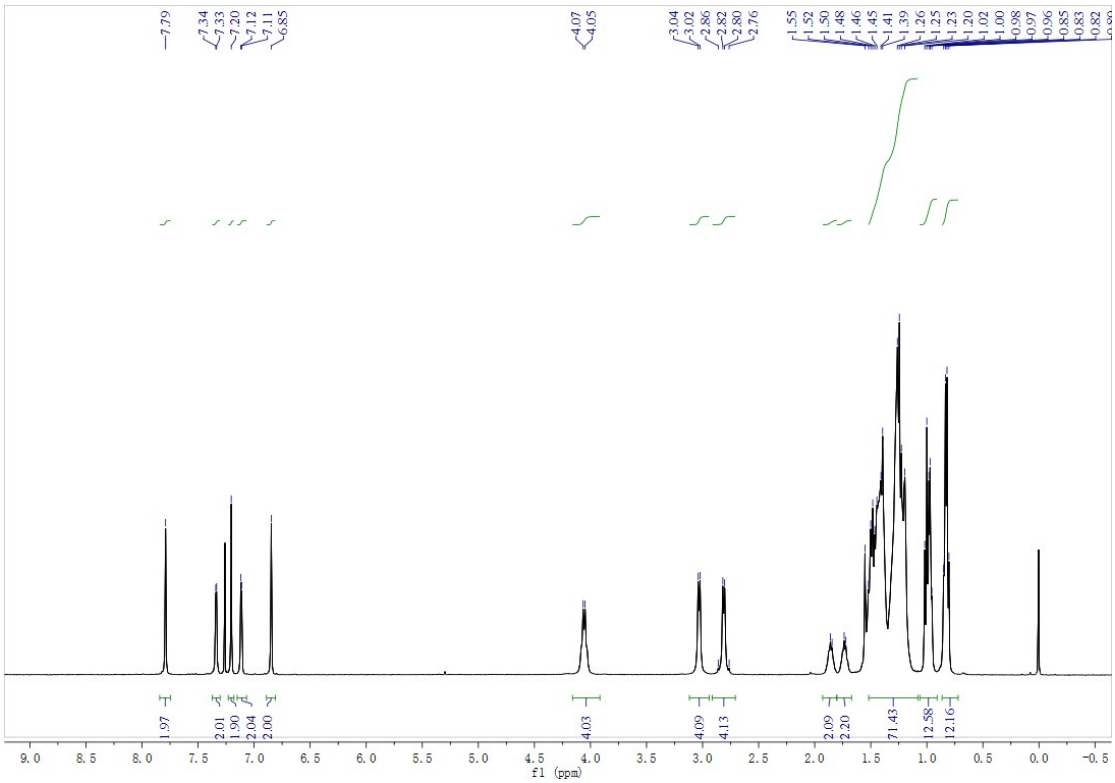
4,4'-(5,10-Bis(5-(2-hexyldecyl)thiophen-2-yl)dithieno[2,3-*d*':2',3'-*d*']benzo[1,2-*b*:4',5'-*b*']dithiophene-2,7-

diyl)bis(2- ethylhexyl)thieno[3,4-b]thiophene-6-carbaldehyde)(5)





(5*Z*,5'*Z*)-5,5'-((4,4'-(5,10-Bis(5-(2-hexyldecyl)thiophen-2-yl))dithieno[2,3-*d*':2',3'-*d*']benzo[1,2-*b*:4',5'-*b*']dithiophene-2,7-diyl)bis(2-(2-ethylhexyl)thieno[3,4-*b*]thiophene-4,6-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one)(STB-4).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7.33
7.20
7.12
7.11
6.85
4.07
4.05
3.04
3.02
2.86
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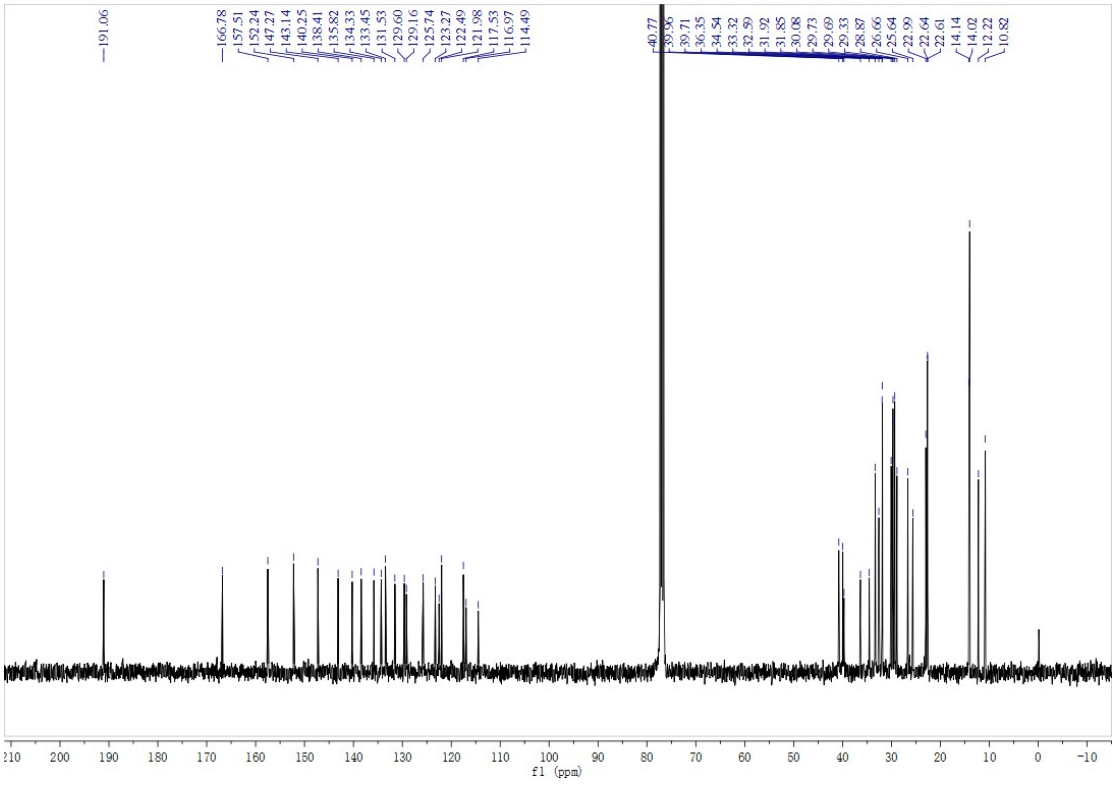
2.80
2.76
1.55
1.52
1.50
1.48
1.46
1.45
1.41
1.39
1.26
1.25
1.23
1.20
1.02
1.00
0.98
0.97
0.96
0.85
0.83
0.82
1.97
2.01
1.90
2.04
2.00
4.03
4.09
4.13
2.09
2.20
71.43
12.58
12.16
f1 (ppm)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166.78
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152.24
147.27
143.14
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138.41
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134.33
133.45
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129.60
129.16
125.74
123.27
122.49
121.98
117.53
116.97
114.49
40.77
39.96
39.71
36.35
34.54
33.32
32.59
31.92
31.85
30.08
29.73
29.69
29.33
28.87
26.66
25.64
22.99
22.64
22.61
14.14
14.02
12.22
10.82
f1 (ppm)