Supporting Information

Tuning the molecular packing and energy level of fullerene acceptors for polymer solar cells

Chengbo Tian,[a*] Miaomiao Chen,[b] Hanrui Tian,[b] Ziang Nan,[b] Yuming Liang,[a] and Zhanhua Wei,[a*]

[a] College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, China

[b] Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Corresponding Author：

*Email: cbtian@hqu.edu.cn, weizhanhua@hqu.edu.cn

Contents

1) Characterization for BTCMA, BTCBA, MBTCMA, and MBTCBA.

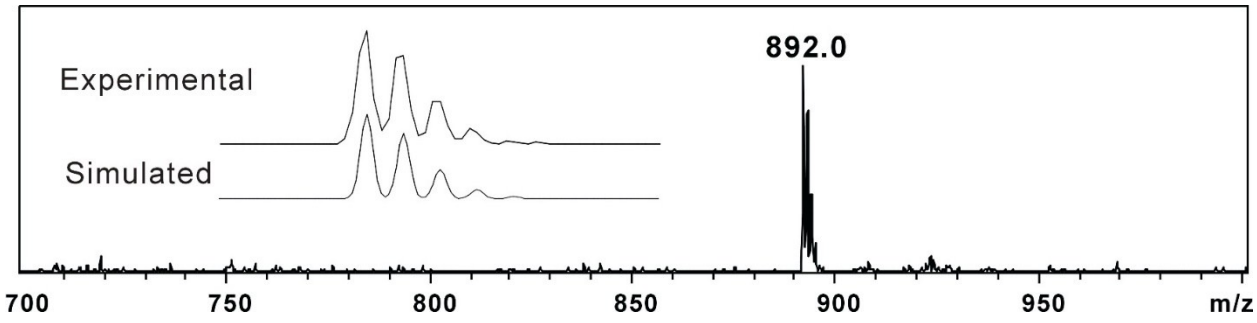

Figure S1. APCI-MS spectrum of BTCMA.

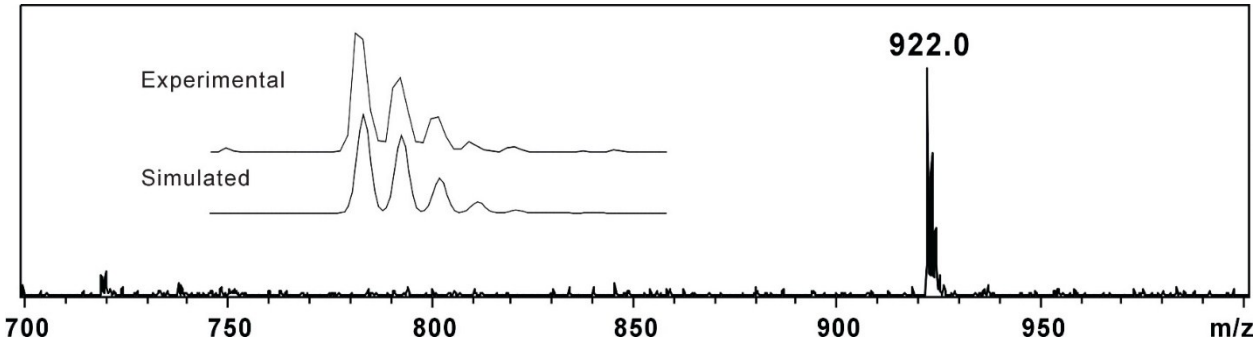

Figure S2. APCI-MS spectrum of MBTCMA.

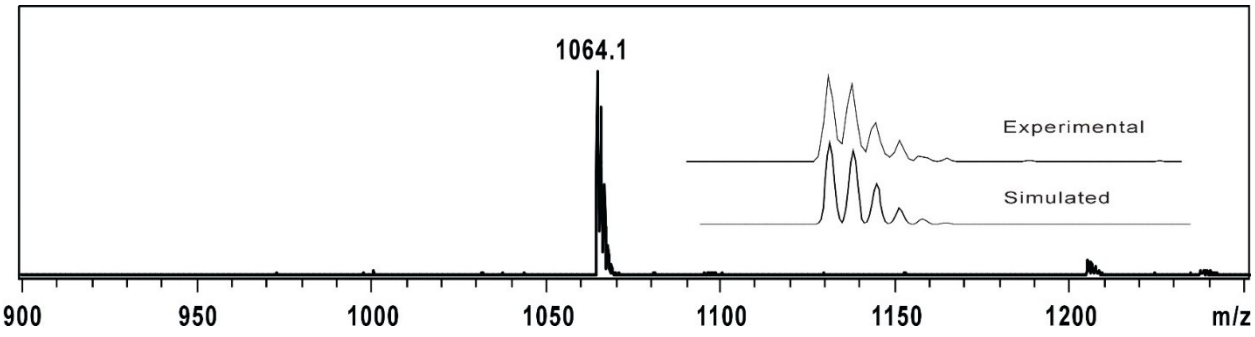

Figure S3. APCI-MS spectrum of BTCBA.

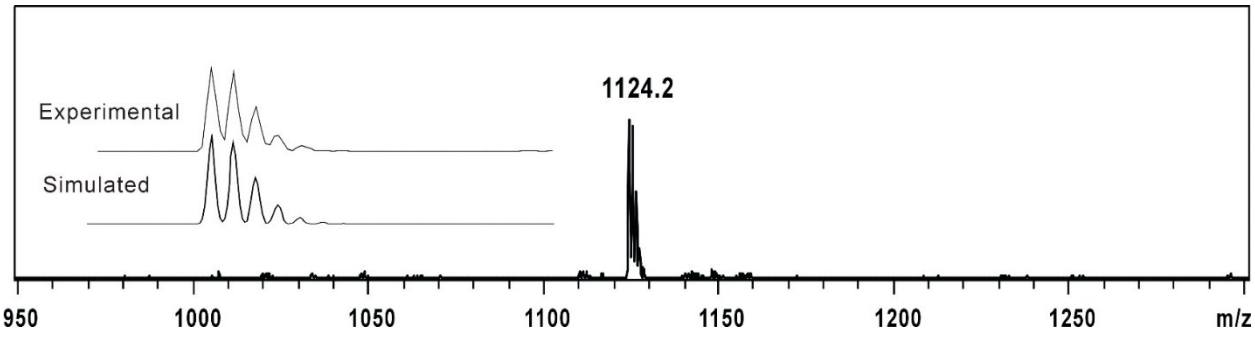

Figure S4. APCI-MS spectrum of MBTCBA.

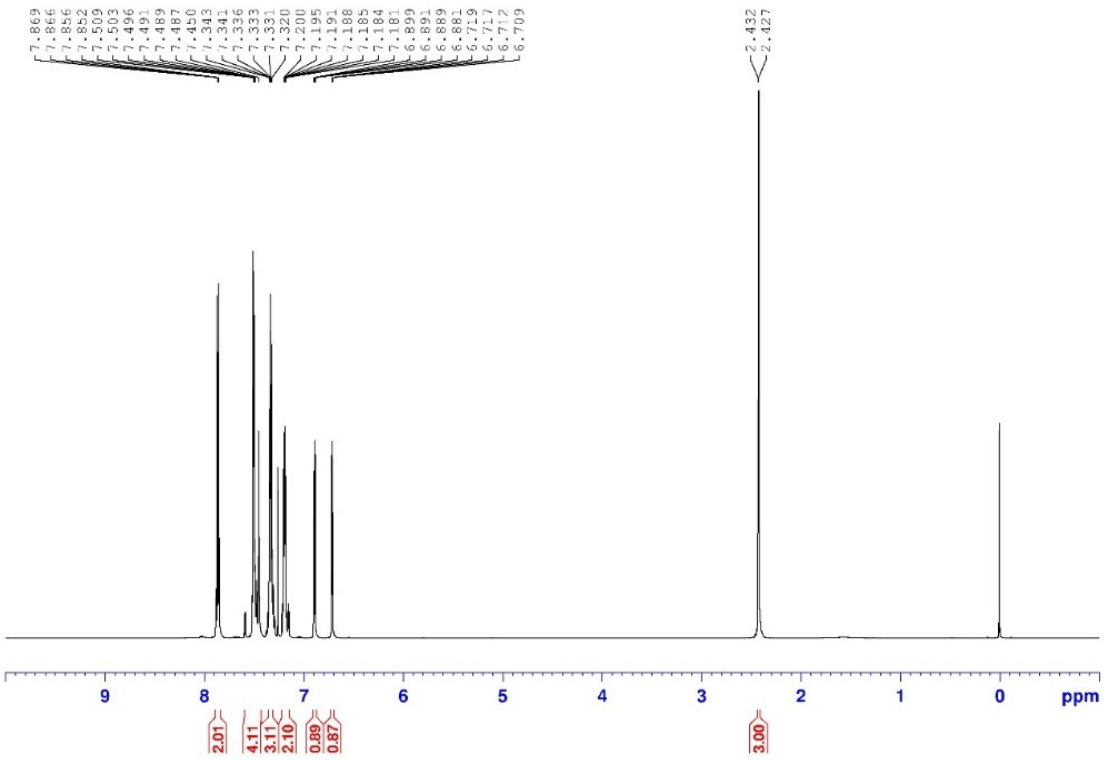

Figure S5. ^{1}H-NMR spectrum of 2-benzoylthiophene *p*-tosylhydrazone.

^{1}H NMR (500MHz, $CDCl_3$): δ (ppm) 7.87-7.85 (m, 2H), 7.59-7.45 (m, 4H), 7.36-7.31 (m, 3H), 6.90-6.88 (m, 1H), 6.72-6.71 (m, 1H), 2.43 (m, 3H).

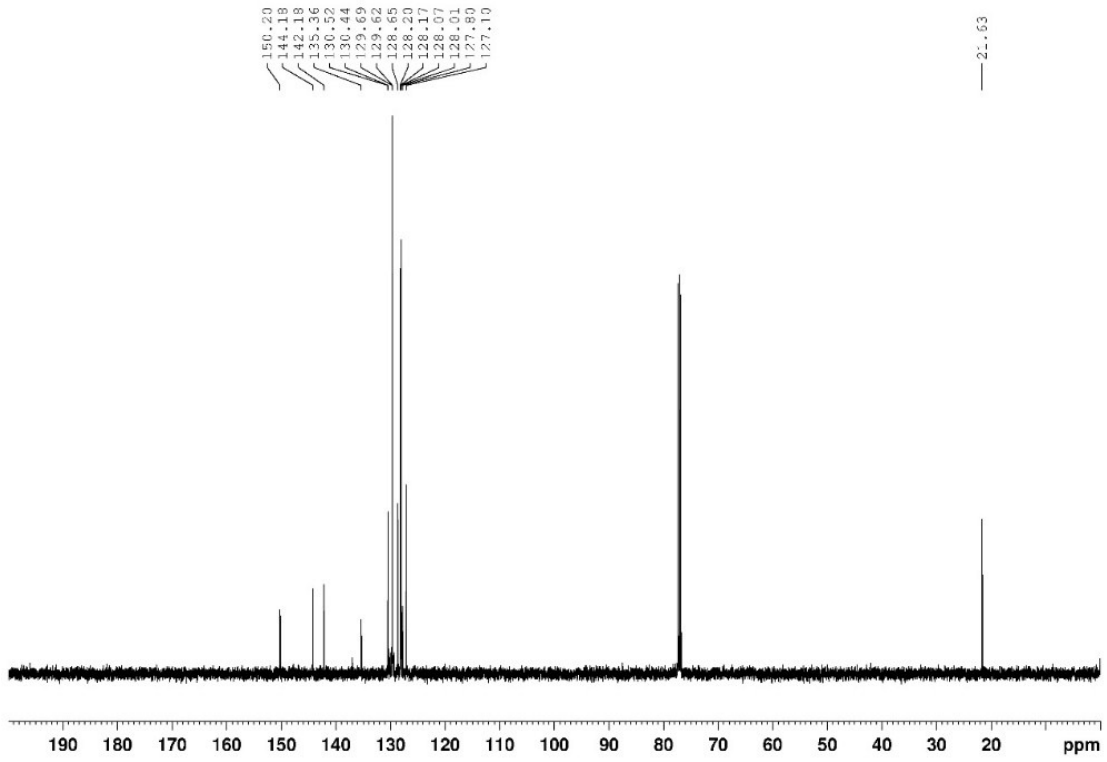

Figure S6. ^{13}C-NMR spectrum of 2-benzoylthiophene *p*-tosylhydrazone.

^{13}C NMR (125MHz, $CDCl_3$): δ (ppm) 150.20, 144.18, 142.18, 135.36, 130.52, 130.44, 129.69, 129.62, 128.65, 128.20, 128.17, 128.07, 128.01, 127.79, 127.10, 21.63.

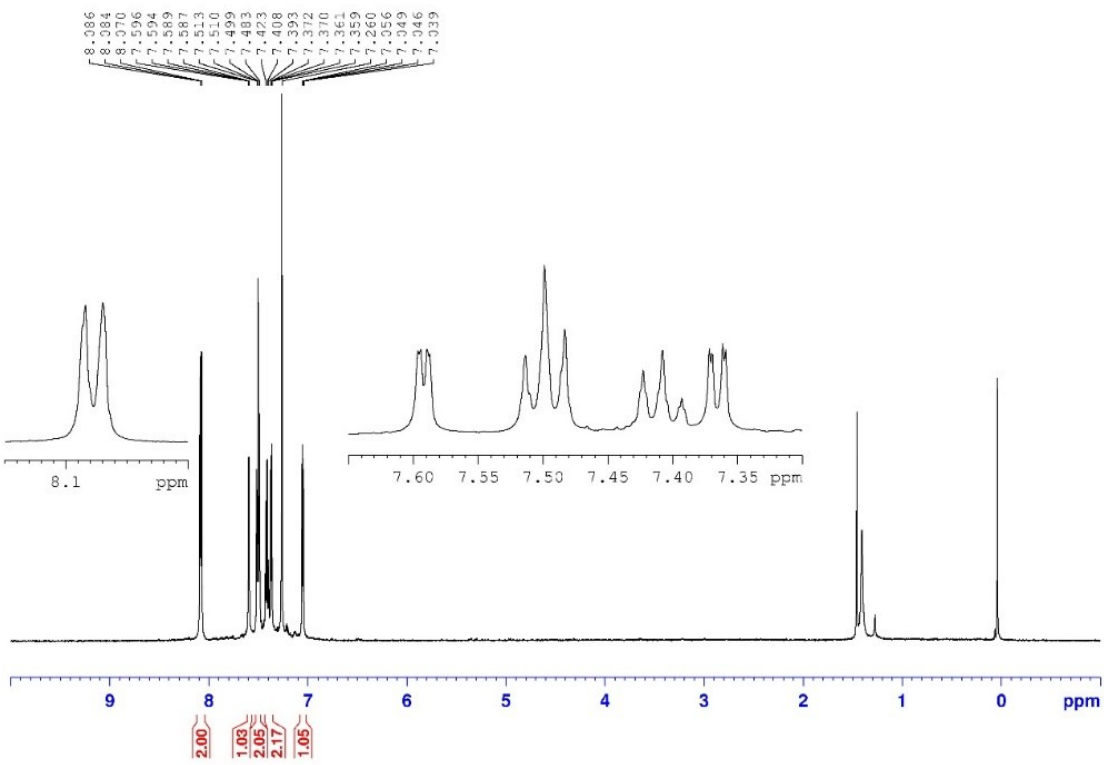

Figure S7. ^{1}H-NMR spectrum of BTCMA.

^{1}H NMR (500MHz, $CDCl_3/CS_2$): δ (ppm) 8.09-8.07 (m, 2H), 7.60-7.59 (m, 1H), 7.51-7.48 (m, 2H), 7.42-7.36 (m, 2H), 7.06-7.04 (m, 1H).

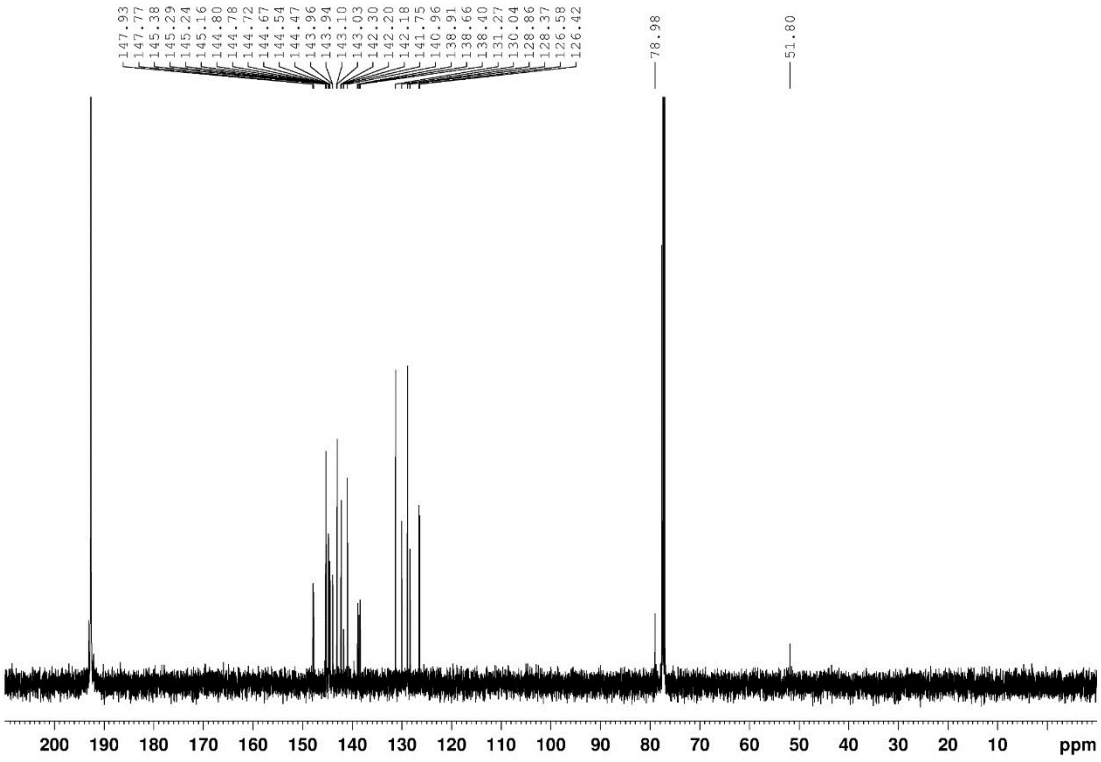

Figure S8. ^{13}C-NMR spectrum of BTCMA.

^{13}C NMR (125MHz, $CDCl_3/CS_2$): δ (ppm) 147.93, 147.77, 145.38, 145.29, 145.24, 145.16, 144.80, 144.78, 144.72, 144.67, 144.54, 144.47, 143.96, 143.94, 143.10, 143.03, 142.30, 142.20, 142.18, 141.75, 140.96, 138.91, 138.66, 138.39, 131.27, 130.04, 128.86, 128.37, 126.58, 126.42, 78.98, 51.80.

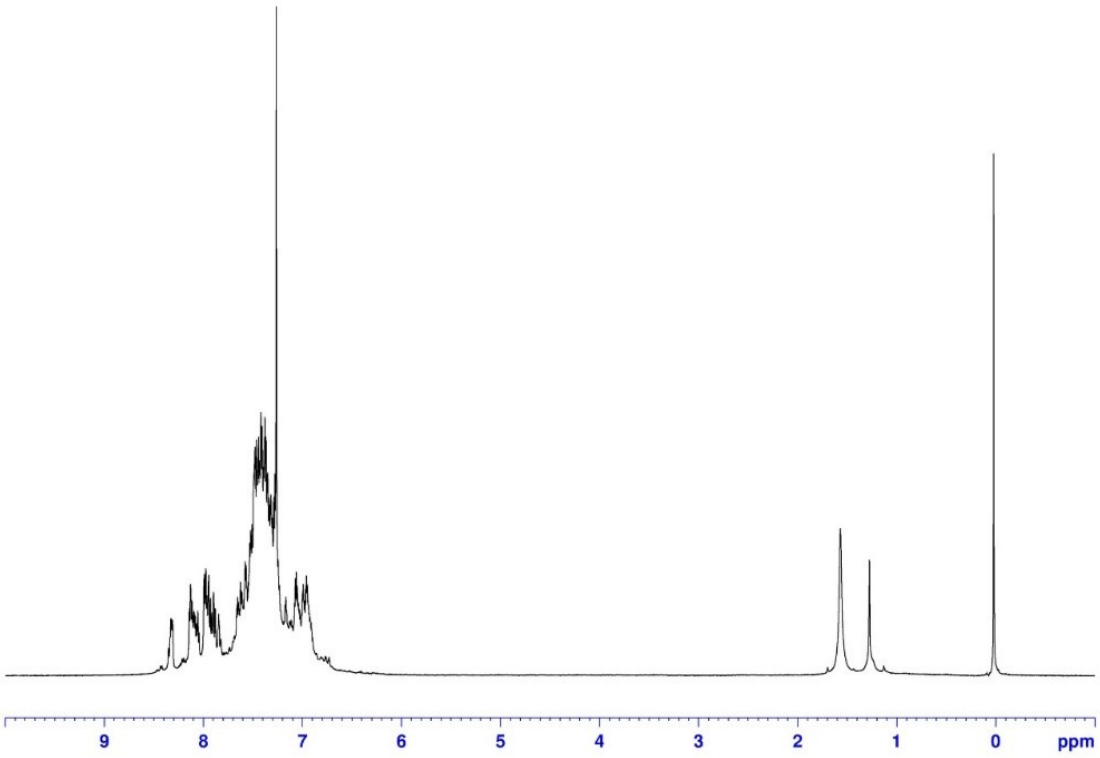

Figure S9. ^{1}H-NMR spectrum of BTCBA

^{1}H NMR (500MHz, $CDCl_3$): δ (ppm) 8.36-6.88 (m, 16H)

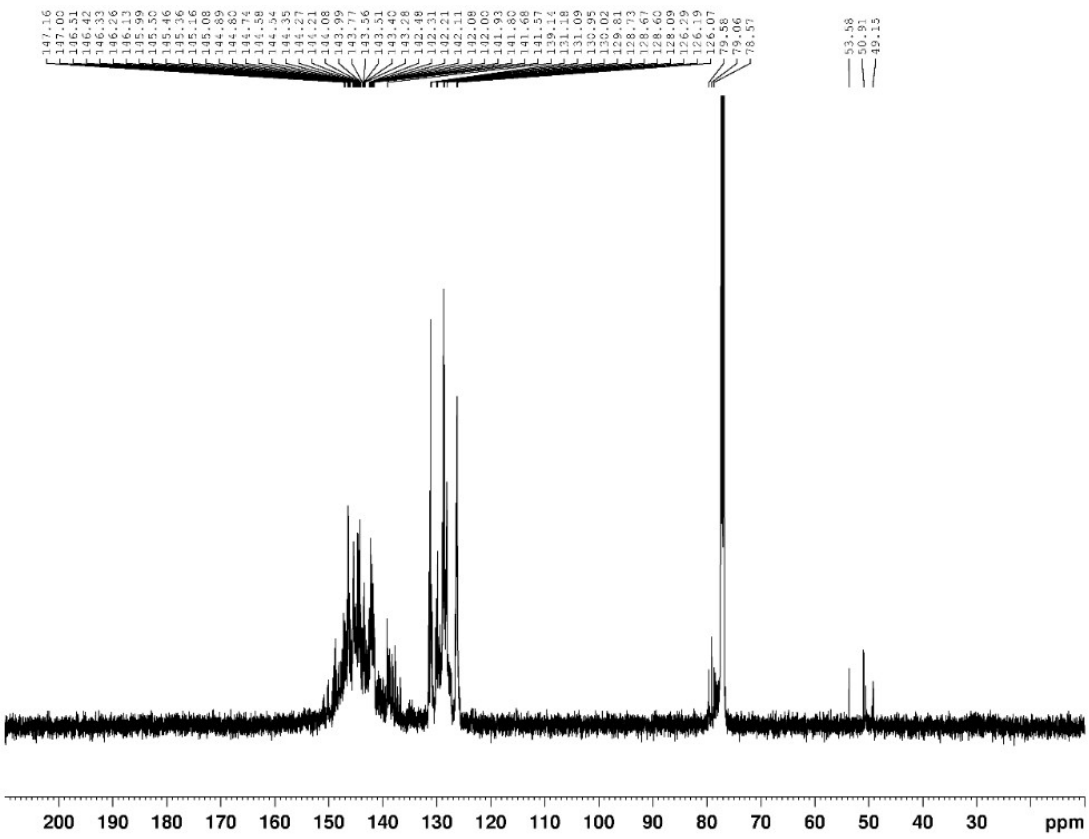

Figure S10. ^{13}C-NMR spectrum of BTCBA

^{13}C NMR (125MHz, $CDCl_3/CS_2$): δ (ppm) 147.16, 146.99, 146.51, 146.42, 146.33, 146.26, 146.13, 145.99, 145.50, 145.46, 145.36, 145.16, 145.08, 144.89, 144.80, 144.74, 144.58, 144.54, 144.35, 144.27, 144.21, 144.08, 143.99, 143.77, 143.56, 143.51, 143.40, 143.28, 142.48, 142.31, 142.21, 142.11, 142.08, 142.00, 141.93, 141.80, 141.68, 141.57, 139.14, 131.18, 131.09, 130.95, 130.02, 129.81, 128.73, 128.67, 128.60, 128.09, 126.29, 126.19, 126.07, 79.58, 79.05, 78.57, 53.58, 50.91, 49.15, 29.69.

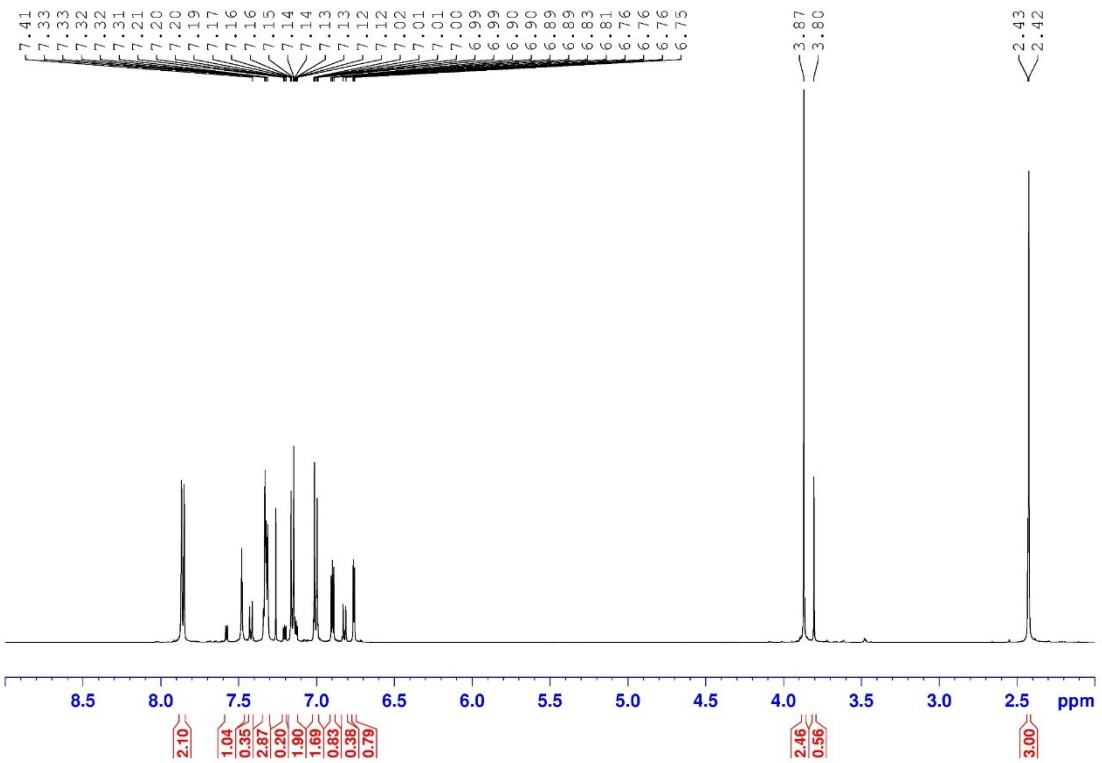

Figure S11. ^{1}H-NMR spectrum of 2-(4-methoxybenzoyl)thiophene *p*-tosylhydrazone.

^{1}H NMR (500MHz, $CDCl_3$): δ (ppm) 7.86 (d, J=8.3Hz, 2H), 7.58-7.48 (m, 1H), 7.43-6.99 (m, 7H), 6.90-6.75 (m, 2H), 3.87 (s, 2.46H), 3.80 (s, 0.55H), 2.43-2.42 (m, 3H).

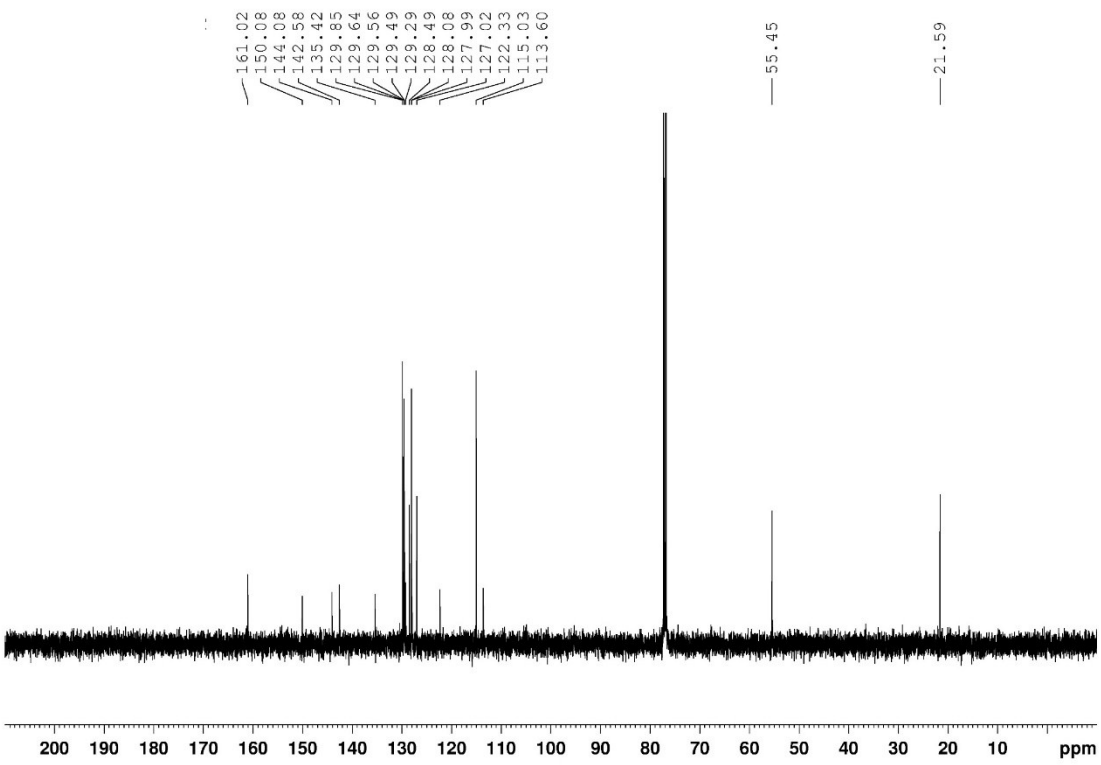

Figure S12. ^{13}C-NMR spectrum of 2-(4-methoxybenzoyl)thiophene *p*-tosylhydrazone.

^{13}C NMR (125MHz, $CDCl_3$): δ(ppm) 161.02, 150.08, 144.08, 142.58, 135.42, 129.85, 129.64, 129.56, 129.49, 129.29, 128.49, 128.08, 127.99, 127.02, 122.33, 115.03, 113.60, 55.45, 21.59.

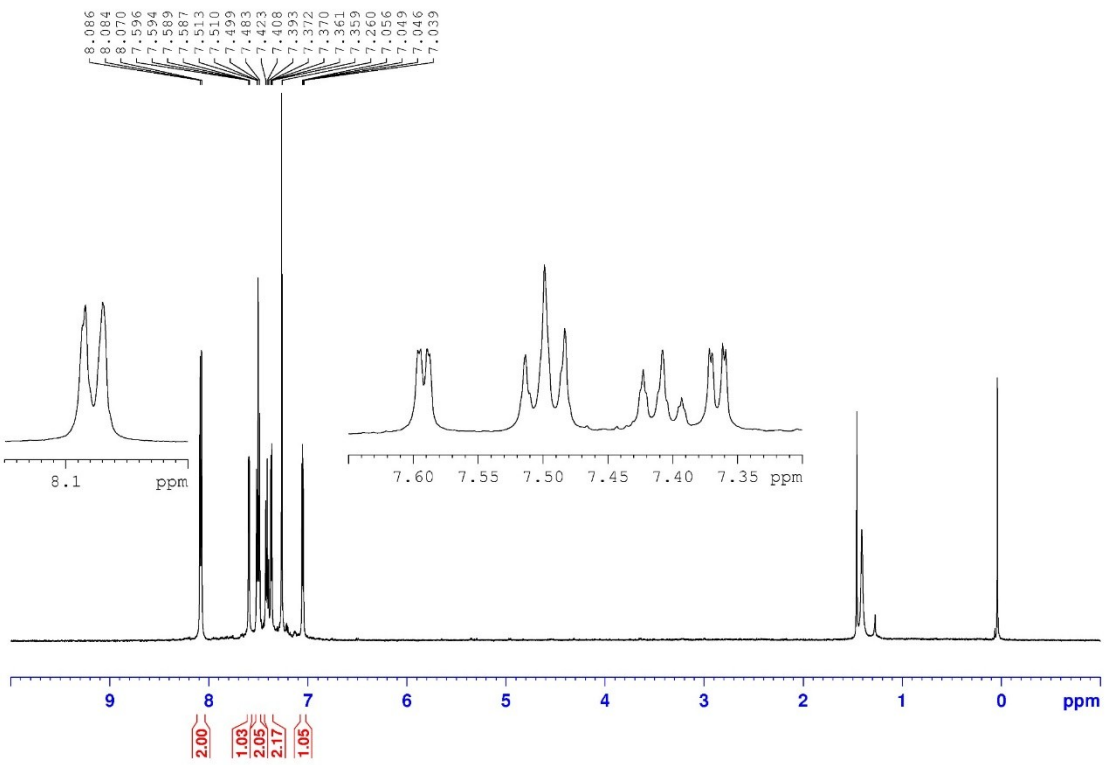

Figure S13. ^{1}H-NMR spectrum of MBTCMA.

^{1}H NMR (500MHz, $CDCl_3/CS_2$): δ (ppm) 8.00-7.96 (m, 2H), 7.57-7.56 (m, 1H), 7.36-7.35 (m, 1H), 7.05-6.99 (m, 3H), 3.87 (s, 3H).

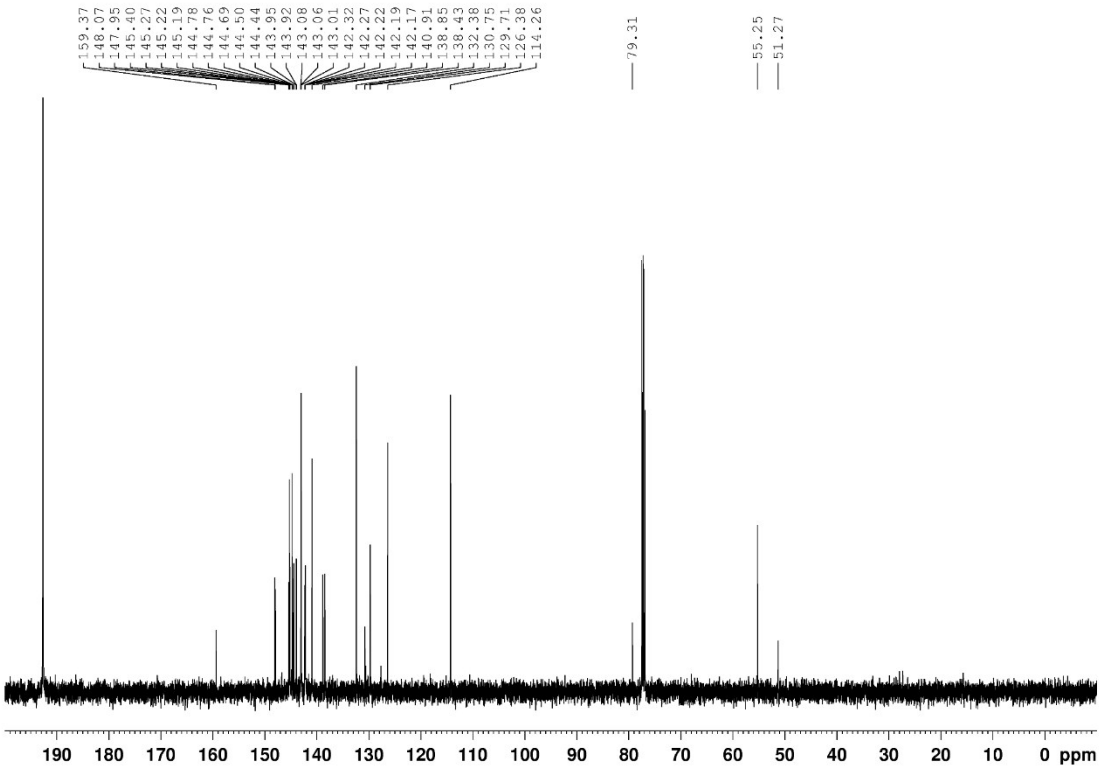

Figure S14. ^{13}C-NMR spectrum of MBTCMA.

^{13}C NMR (125MHz, $CDCl_3/CS_2$): δ (ppm) 159.3724, 148.07, 147.95, 145.40, 145.27, 145.22, 145.19, 144.78, 144.76, 144.69, 144.50, 144.44, 143.95, 143.92, 143.08, 143.06, 143.01, 142.33, 142.27, 142.22, 142.19, 142.17, 140.91, 138.85, 138.43, 132.38, 130.75, 129.71, 126.38, 114.26, 79.31, 55.25, 51.27.

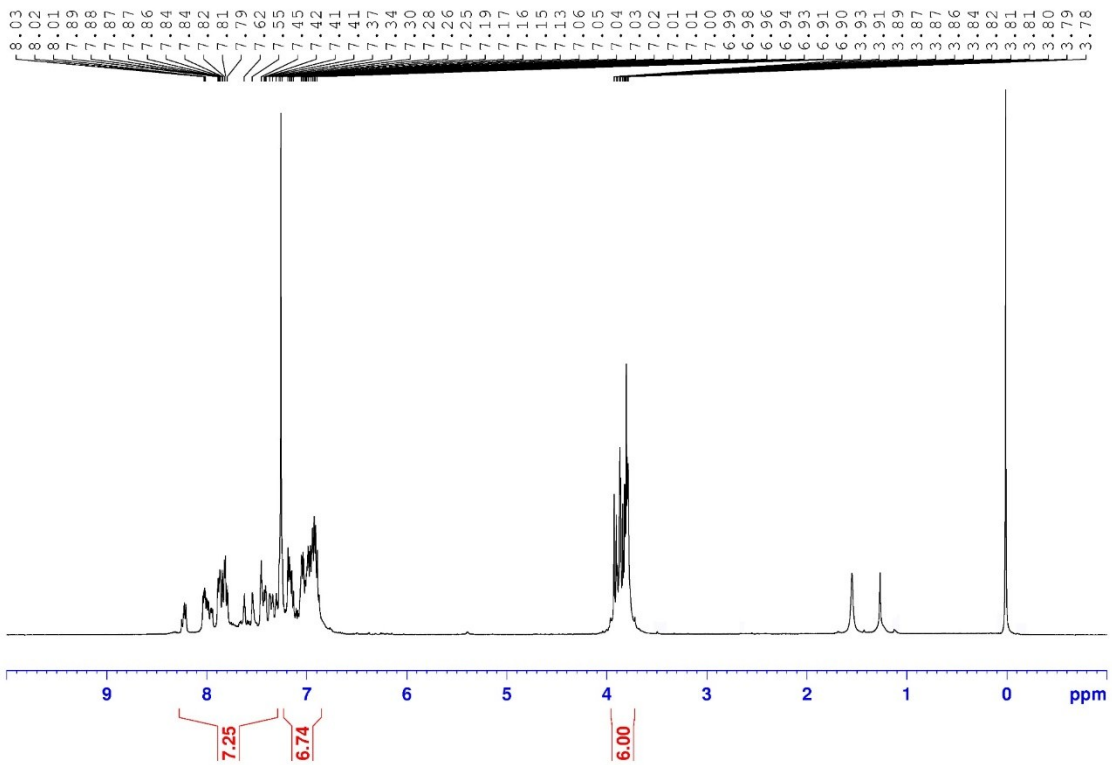

Figure S15. ^{1}H-NMR spectrum of MBTCBA.

^{1}H NMR (500MHz, $CDCl_3$): δ (ppm) 8.27-6.91 (m, 14H), 3.95-3.81 (m, 6H).

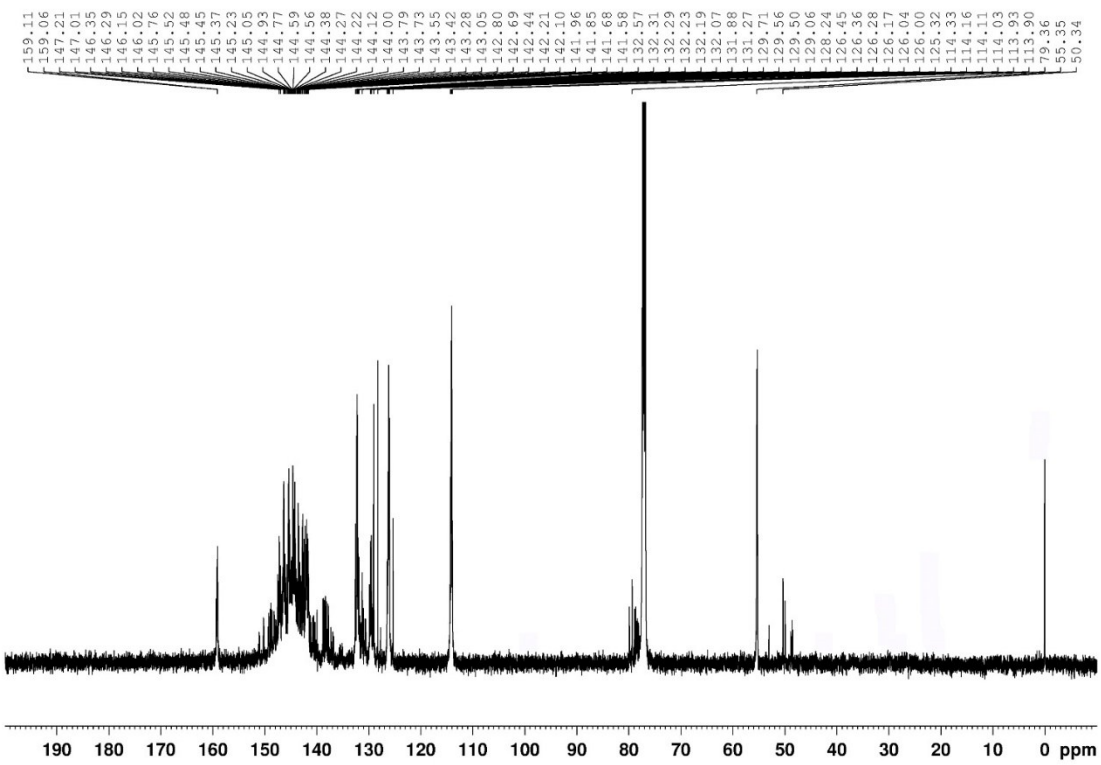

Figure S16. ^{13}C-NMR spectrum of MBTCBA.

^{13}C NMR (125MHz, $CDCl_3$): δ (ppm) 159.24, 159.20, 159.11, 159.06, 147.21, 147.01, 146.35, 146.29, 146.15, 146.02, 145.76, 145.52, 145.48, 145.45, 145.37, 145.23, 145.05, 144.93, 144.77, 144.59, 144.56, 144.38, 144.27, 144.22, 144.12, 144.00, 143.80, 143.73, 143.55, 143.42, 143.28, 143.05, 142.80, 142.69, 142.44, 142.21, 142.10, 141.96, 141.85, 141.68, 141.58, 132.57, 132.31, 132.29, 132.23, 132.19, 132.07, 131.88, 131.27, 129.86, 129.71, 129.56, 129.50, 129.06, 128.24, 126.45, 126.36, 126.28, 126.17, 126.04, 126.00, 125.32, 114.33, 114.16, 114.11, 114.03, 113.93, 113.90, 79.91, 79.36, 78.85, 78.67, 55.35, 50.34, 49.94.

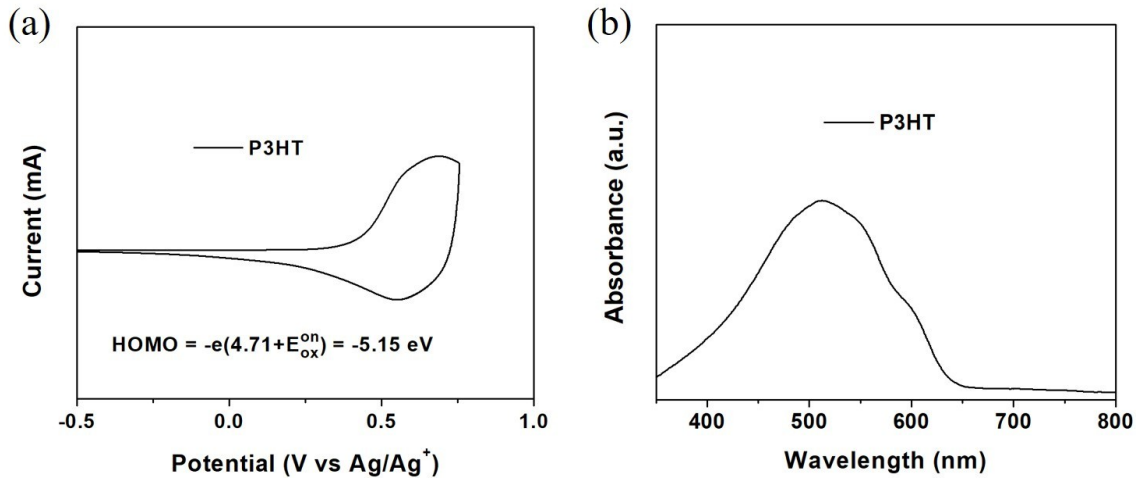

Figure S17. (a) Cyclic voltammetric curve of P3HT film with 0.1 M Bu_4NPF_6 at a scan rate of 100 mV/s. (b) UV-Vis absorption spectrum of the P3HT film.

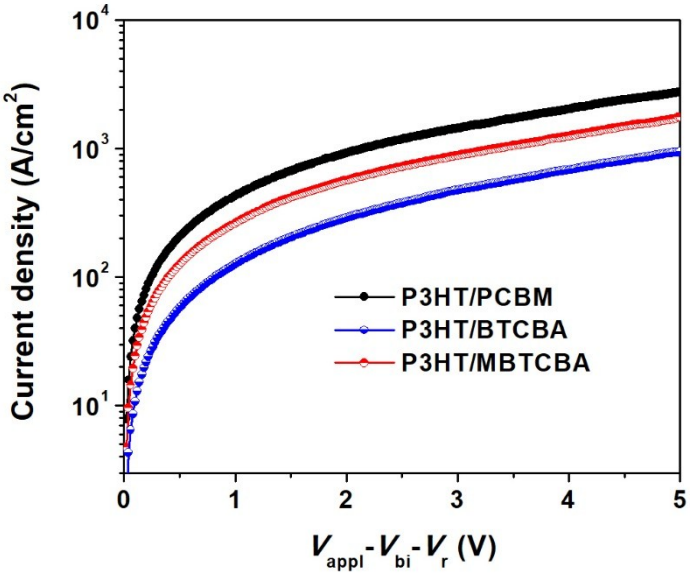

Figure S18. Measured space-charge limited *J–V* characteristics of the P3HT/PCBM, P3HT/BTCBA and P3HT/MBTCBA blend devices under dark conditions for hole-only devices with structure of ITO/PEDOT:PSS/blend film/MoO_3/Au.

2) X-ray crystallographic data for BTCMA and MBTCMA.

Single crystals of BTCMA (or MBTCMA) suitable for X-ray diffraction studies were obtained by solvent evaporation from their toluene solutions. The diffraction data of compound BPCMA and ACMA were collected on an Agilent SuperNova X-Ray single-crystal diffractometer using Cu Kα (λ =1.54184 Å) micro-focus X-ray sources at 100 K. The data were processed using CrysAlisPro, and the structure was solved and refined using full-matrix least-squares method based on F2.[S1, S2]

CCDC 1907607 (for BTCMA) and CCDC 1907608 (for MBTCMA) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Sample and crystal data for BTCMA.

Chemical formula	$C_{71}H_8S$
Formula weight	892.83
Temperature (K)	100
Radiation, wavelength	Cu Kα, 1.54184
Crystal color	black
Crystal size (mm)	0.15 × 0.12 × 0.10
Crystal system	Orthogonal
Space group	*Pca21*
a (Å)	19.670(3)
b (Å)	10.318(9)
c (Å)	17.107(4)
Alpha (deg)	90.00
Beta (deg)	90.00
Gamma (deg)	90.00
Cell volume ($Å^3$)	3472.4(3)
Z	4
F(000)	1800
Goodness-of-fit on F^2	1.102
Reflections with $I>2\sigma(I)$	4523
Final *R* indices[$I>2\sigma(I)$]	R_1=0.0760, ωR_2=0.2189

Table S2. Sample and crystal data for MBTCMA.

Chemical formula	$C_{72}H_{10}OS$
Formula weight	922.86
Temperature (K)	100
Radiation, wavelength	Cu Kα, 1.54184
Crystal color	black
Crystal size (mm)	0.12 × 0.15 × 0.12
Crystal system	monoclinic
Space group	*P21/c*
a (Å)	19.501(2)
b (Å)	17.532(8)
c (Å)	21.185(7)
Alpha (deg)	90.00
Beta (deg)	98.027(2)
Gamma (deg)	90.00
Cell volume ($Å^3$)	7172.6(3)
Z	8
F(000)	3728
Goodness-of-fit on F^2	1.056
Reflections with $I>2\sigma(I)$	9879
Final *R* indices[$I>2\sigma(I)$]	R_1=0.0561, ωR_2=0.1655

References

[S1] G.M. Sheldrick, Phase annealing in SHELX-90: direct methods for larger structures, Acta Crystallogr. A., 46 (1990) 467-473.

[S2] G. Sheldrick, SHELXL-97 program for crystal structure solution and refinement; University of Göttingen: Göttingen, Germany, (1997).