Supporting Information

Insight of thin-film stacking modes of π-expanded quinoidal molecules on charge transport property via side-chain engineering

Cheng Zhang,[a,d] Dafei Yuan,[a,d] Hao Wu,[a,d] Eliot Gann,[b] Lars Thomsen,[c] Christopher R. McNeill,*[,b] Chong-an Di,*[,a] Xiaozhang Zhu,*[,a,d] and Daoben Zhu[a]

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

[b]Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia

[c]Australian Synchrotron, 800 Blackburn Rd Clayton, VIC 3168, Australia

[d]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

xzzhu@iccas.ac.cn

dicha@iccas.ac.cn

christopher.mcneill@monash.edu

Contents

Part 1. Physical properties

1-1. Cyclic voltammogram of 2DQTT-n.

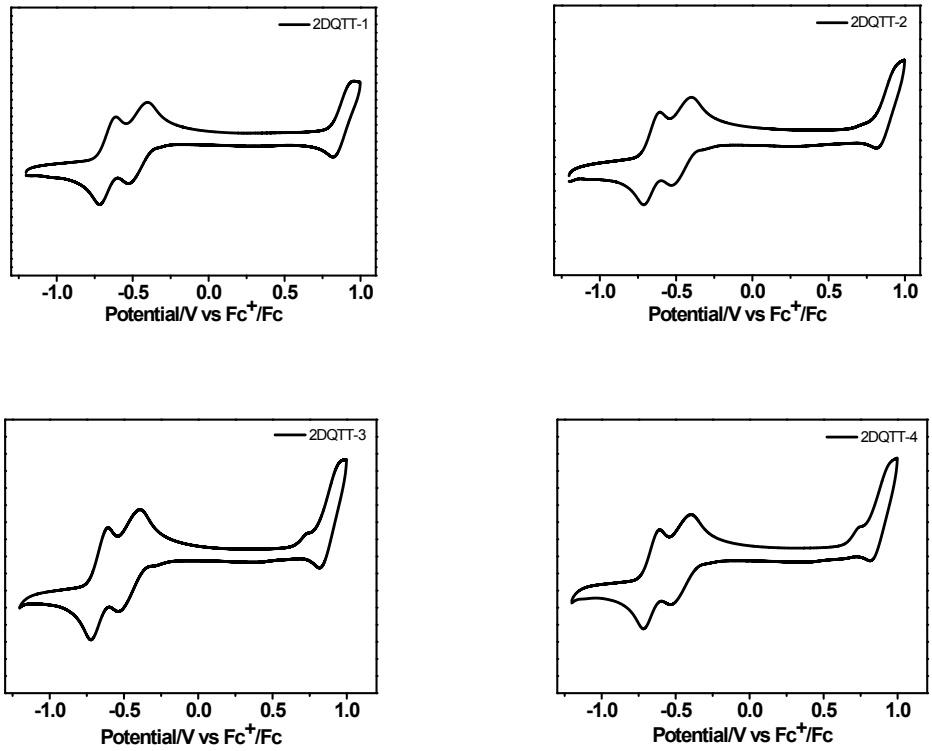
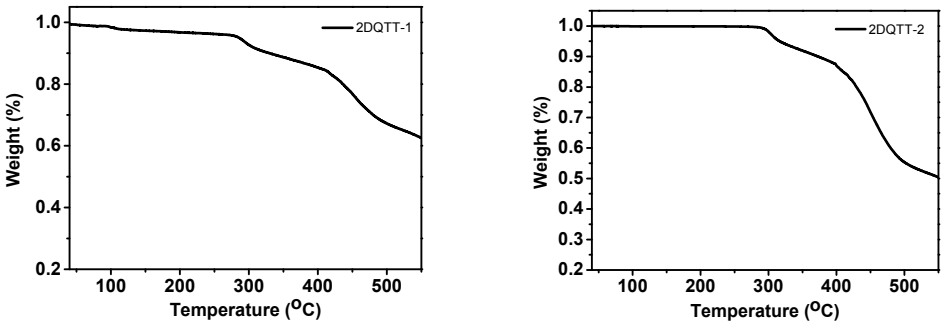


Figure S1. Cyclic voltammogram of **2DQTT-1**, **2DQTT-2**, **2DQTT-3**, and **2DQTT-4** in diluted CH_2Cl_2 solution with scan rate of 100 mV s^{-1}.

1-2. TGA data for 2DQTTs.



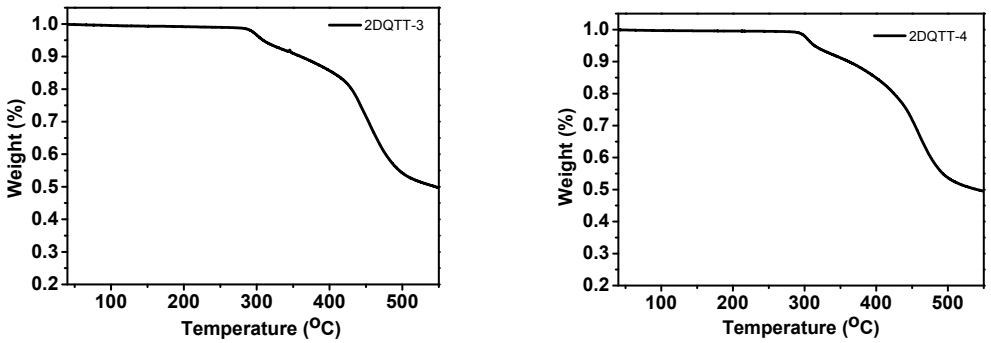


Figure S2. Thermal gravimetric analysis (TGA) curves of compounds **2DQTT-1**, **2DQTT-2**, **2DQTT-3**, and **2DQTT-4**.

Part 2. Thin film characterization

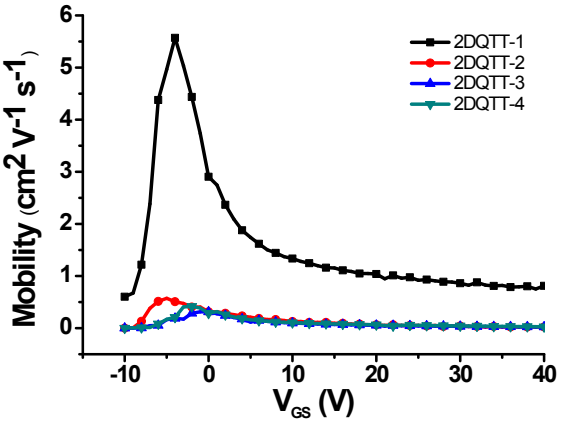


Figure S3. The mobility as a function of gate voltage for **2DQTT** based OTFTs with BGBC structure.

Fabrication of BGTC OTFTs: The thin films of organic active layer were deposited on OTS-treated SiO_2/Si substrates by spin coating from their $CHCl_3$ solution. Thereafter, the deposited thin films were annealed at different temperatures. Gold source and drain contacts (30 nm in thickness) were deposited on the organic layer by vacuum evaporation through a shadow mask, according a bottom-gate top contact configuration. The channel length and width were 80 and 8800 μm, respectively.

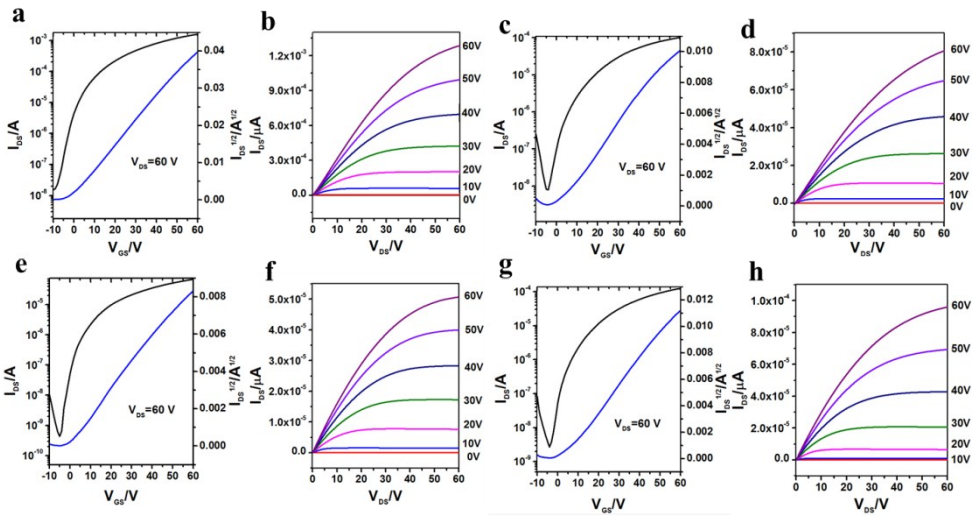


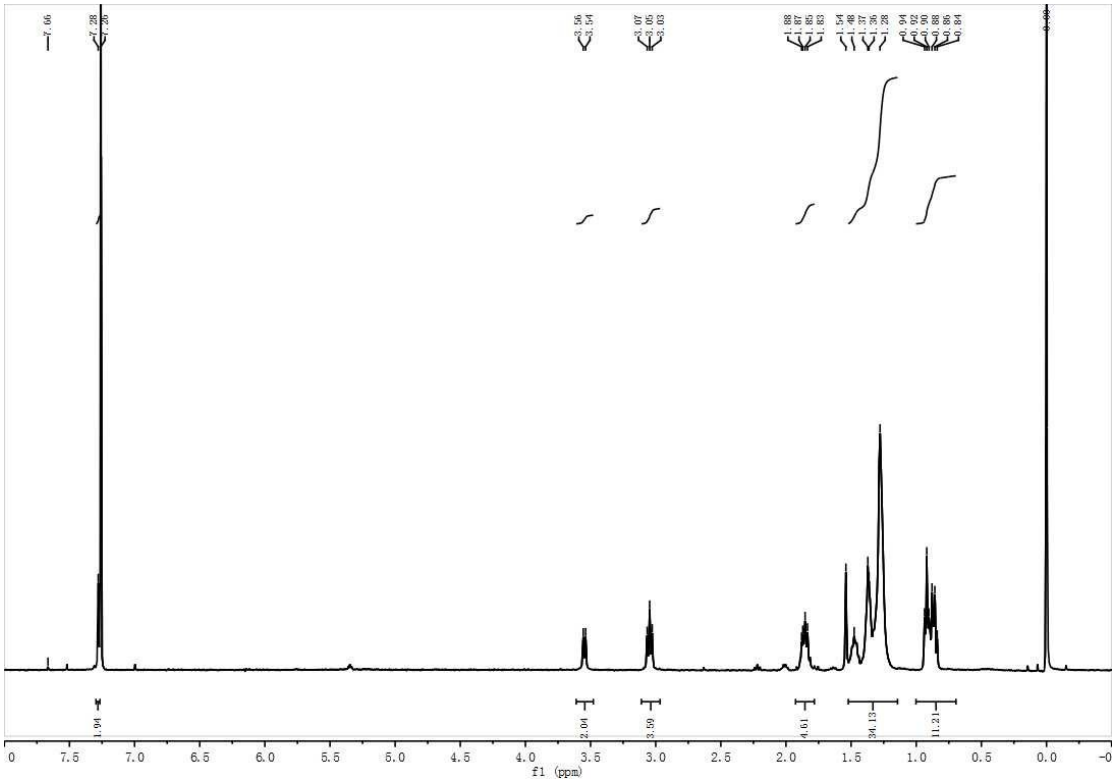
Figure S4. Transfer and output characteristics of BGTC OTFTs based on (a, b) **2DQTT-1**; (c, d) **2DQTT-2**; (e, f) **2DQTT-3**, and (g, h) 2**DQTT-4**, respectively.

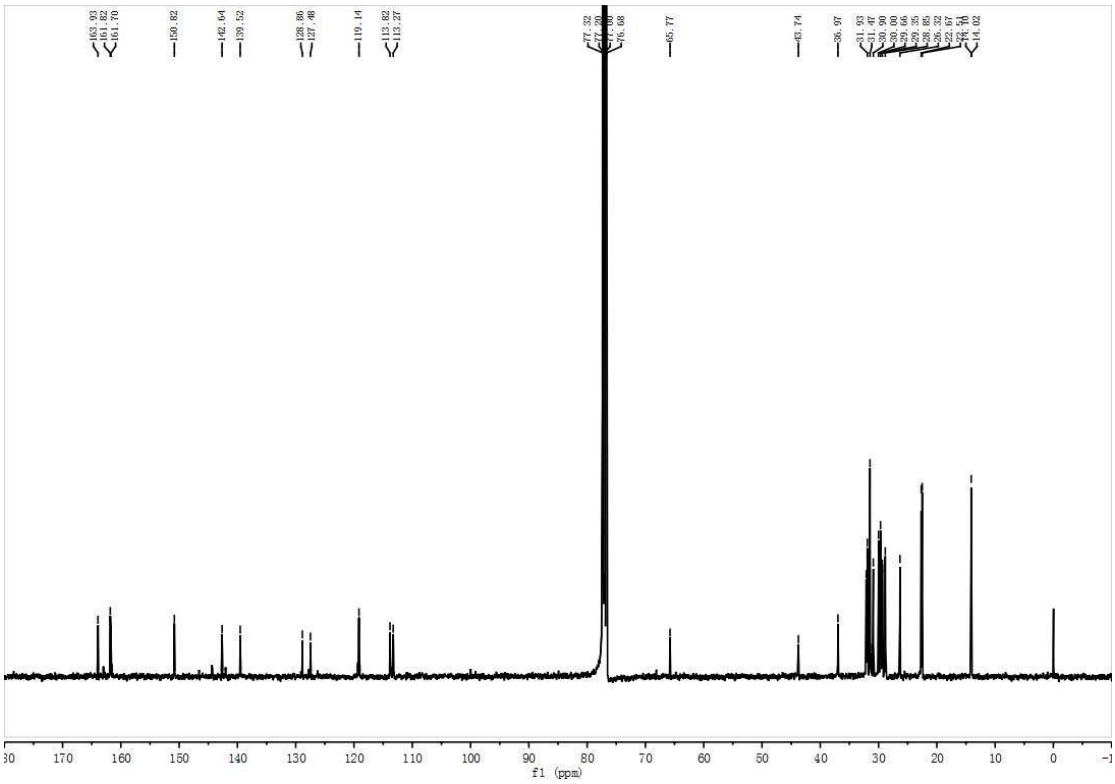
Table S1. Device performance of **2DQTT**-based OTFTs with BGBC and BGTC structures.

Materials	Mobility with BGBC ($cm^2V^{-1}s^{-1}$) Avg(Max)	Mobility with BGTC ($cm^2V^{-1}s^{-1}$) Avg(Max)
2DQTT-1	3.7(4.5)	0.90(1.2)
2DQTT-2	0.47(0.60)	0.15(0.16)
2DQTT-3	0.23(0.34)	0.07(0.08)
2DQTT-4	0.30(0.43)	0.10(0.11)

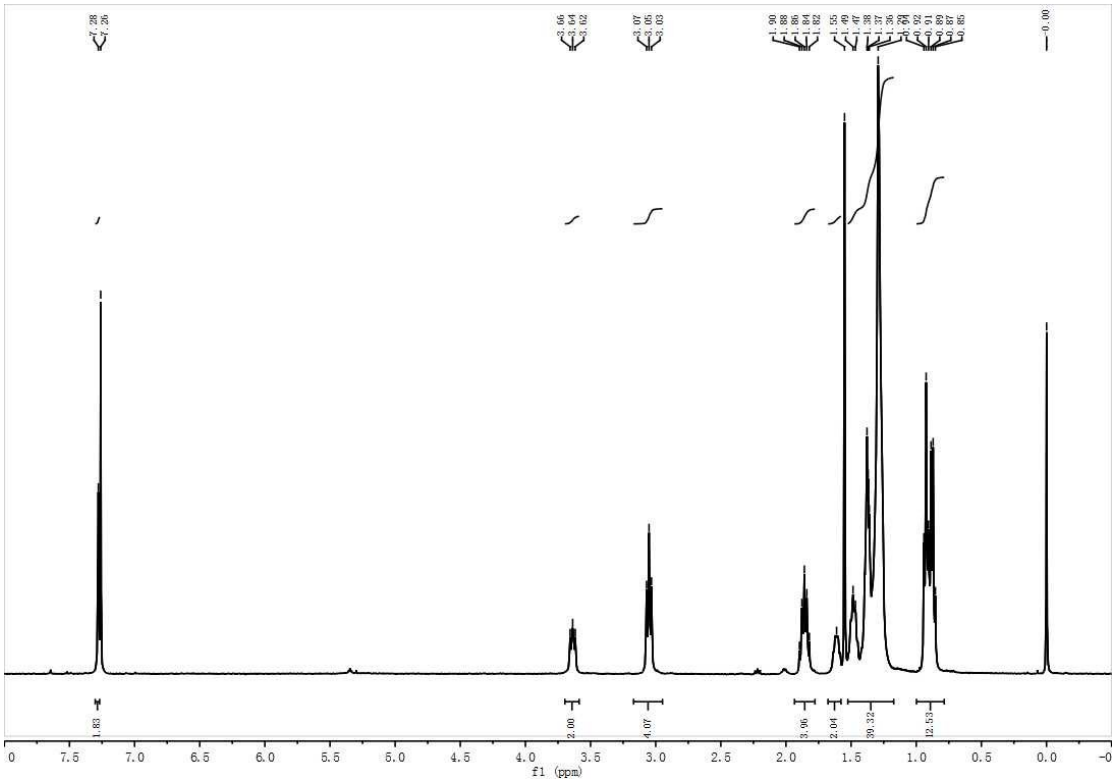
Part 3. NMR Charts

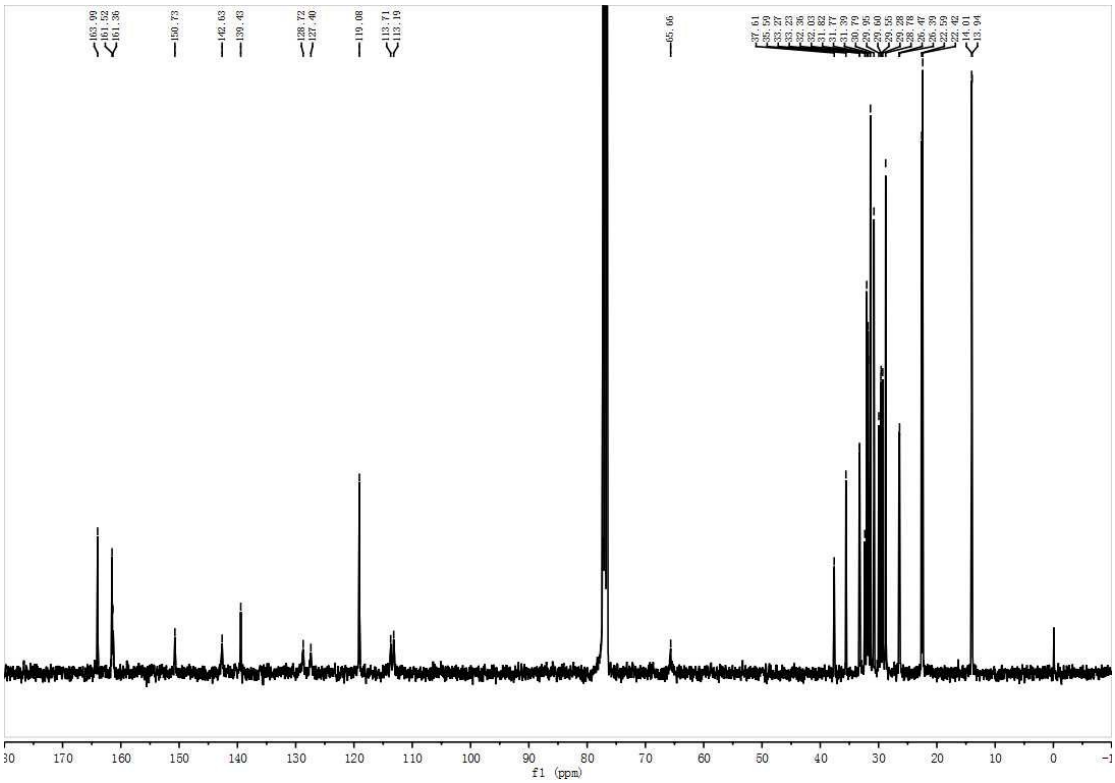
2,2'-((4*E*,4'*E*)-4,4'-(5-(2-hexyldecyl)-4,6-dioxo-5,6-dihydro-1*H*-thieno[3,4-*c*]pyrrole-1,3(4*H*)-diylidene)bis(2-hexylthieno[3,4-*b*]thiophene-6,4(4*H*)-diylidene))dimalononitrile (2DQTT-1)



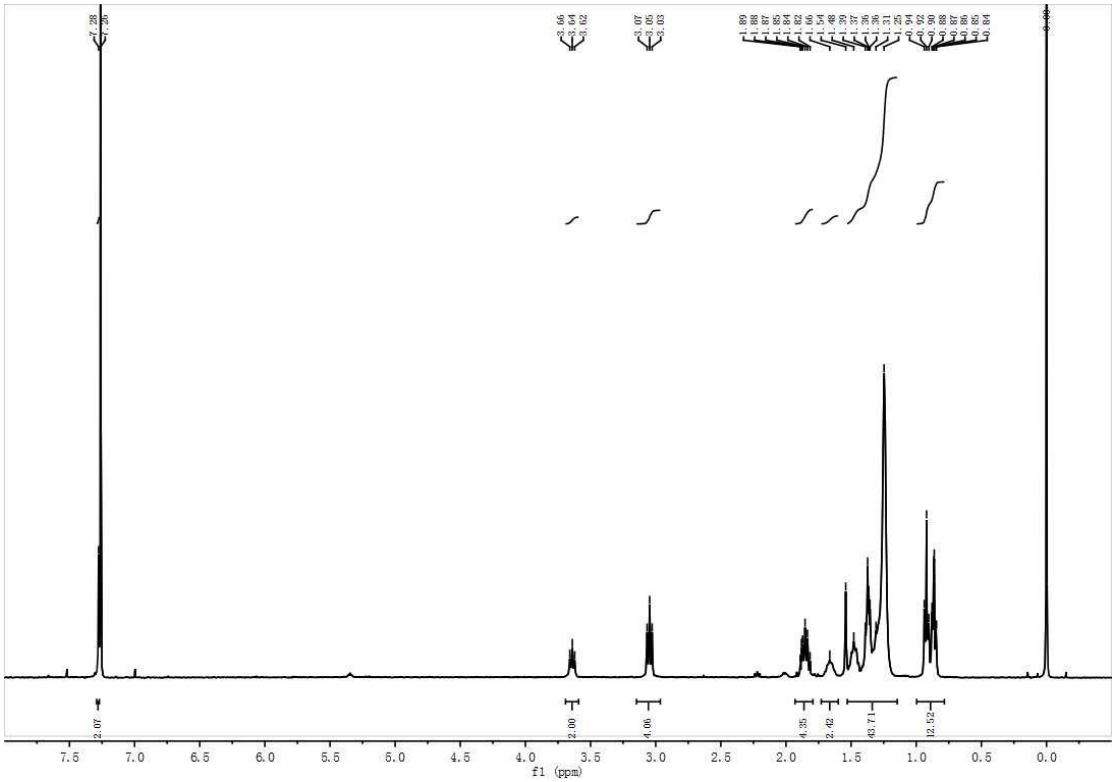


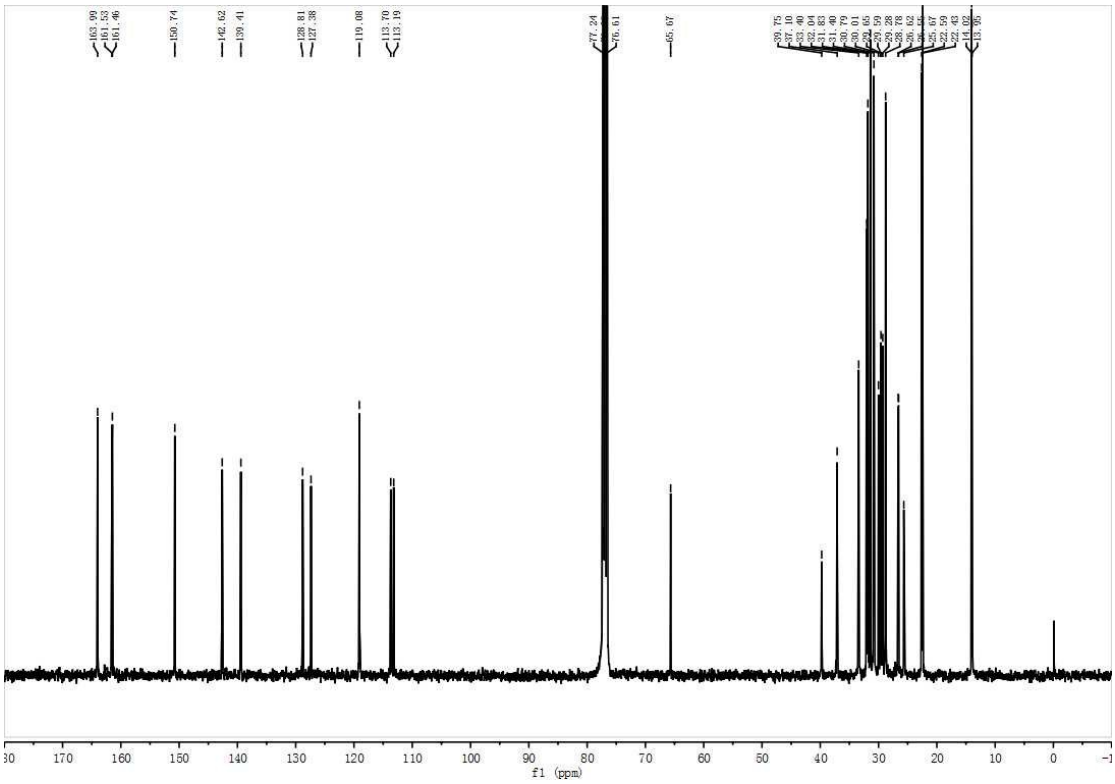
2,2'-((4*E*,4'*E*)-4,4'-(5-(3-hexylundecyl)-4,6-dioxo-5,6-dihydro-1*H*-thieno[3,4-*c*]pyrrole-1,3(4*H*)-diylidene)bis(2-hexylthieno[3,4-*b*]thiophene-6,4(4*H*)-diylidene))dimalononitrile (2DQTT-2)





2,2'-((4*E*,4'*E*)-4,4'-(5-(4-hexyldodecyl)-4,6-dioxo-5,6-dihydro-1*H*-thieno[3,4-*c*]pyrrole-1,3(4*H*)-diylidene)bis(2-hexylthieno[3,4-*b*]thiophene-6,4(4*H*)-diylidene))dimalononitrile (2DQTT-3)





2,2'-((4*E*,4'*E*)-4,4'-(5-(5-hexyltridecyl)-4,6-dioxo-5,6-dihydro-1*H*-thieno[3,4-*c*]pyrrole-1,3(4*H*)-diylidene)bis(2-hexylthieno[3,4-*b*]thiophene-6,4(4*H*)-diylidene))dimalononitrile (2DQTT-4)