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Electronic Supplementary Information

Tetraphenylethylene Substituted Thienothiophene and Dithienothiophene Derivatives; Synthesis, Optical Properties and OLED Devices

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1. Materials

All the reagents were purchased from Aldrich and Acros, used without further purification. All the solvents used in the syntheses were technical grade and freshly distilled prior to use. The solvents used in spectroscopic measurements were spectroscopic grade. Flash chromatography was performed with ≤ 0.063 μm Silica Gel.

NMR spectroscopy

^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 and 126 MHz, respectively, spectrometer. Proton and carbon chemical shifts are reported in parts per million downfield from tetramethyl silane, TMS.

Mass spectrometry

Mass spectra were recorded on Thermo LCQ-Deca ion trap mass instruments.

Thermal properties

Thermalgravimetric analysis (TGA) as performed on PerkinElmer Diamond TA/TGA with a heating rate of 10 °C min $^{-1}$ under a nitrogen flow.

Optical spectroscopy

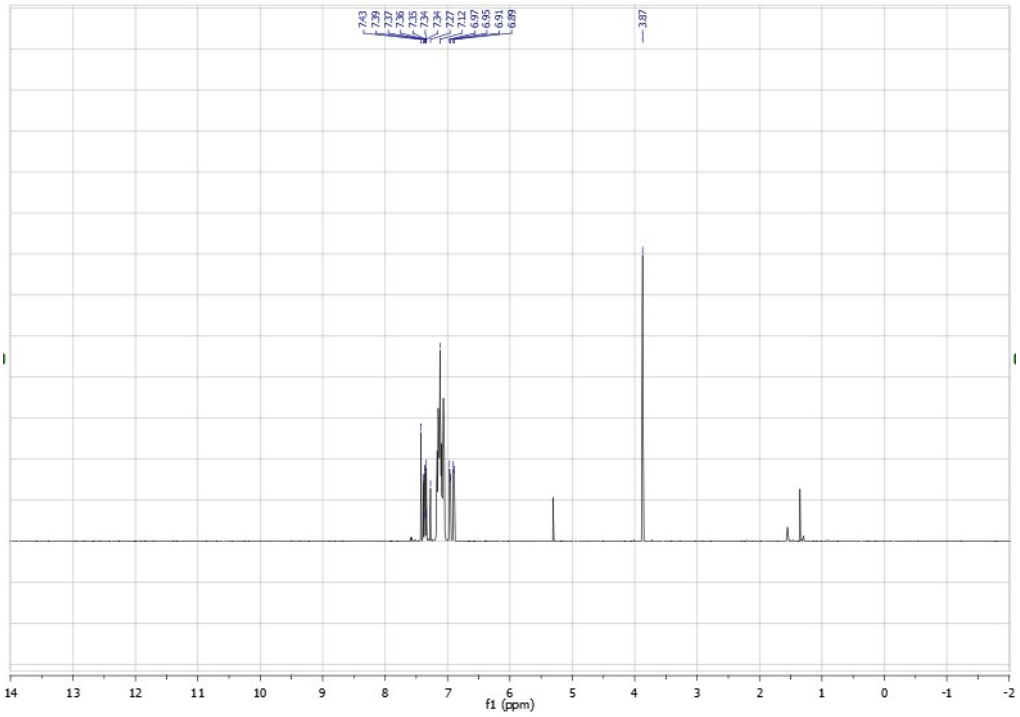
Fluorescence spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer. UV-vis measurements were recorded on a HITACHI U-0080D spectrophotometer.

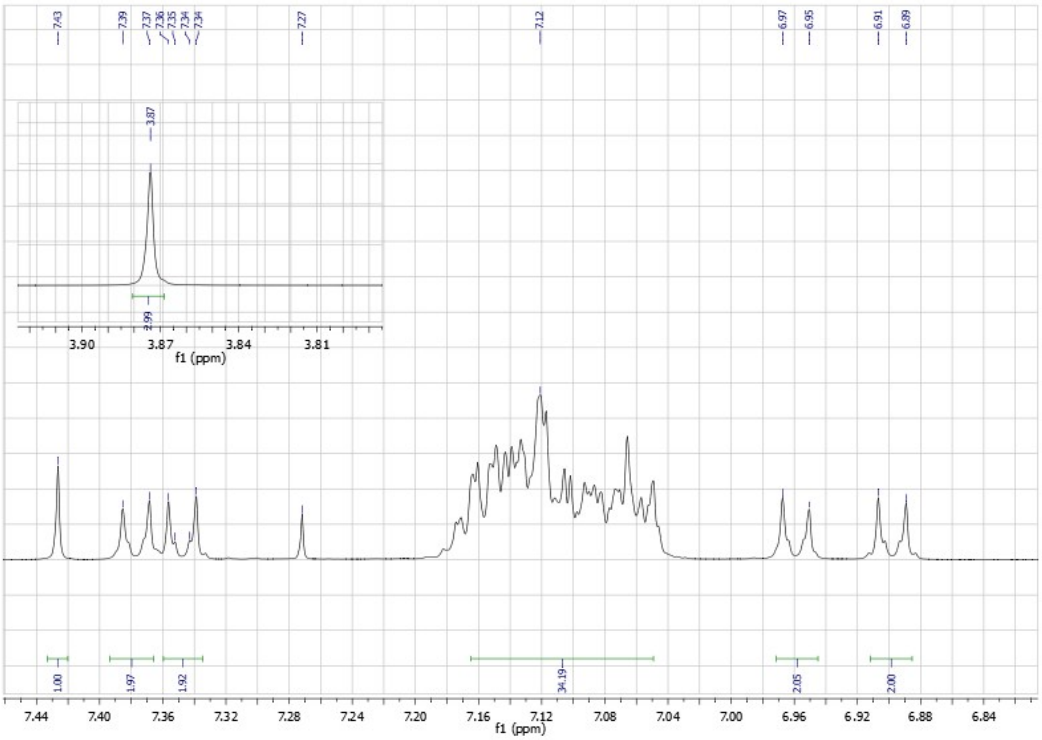
OLED fabrication and characterization

The ITO/glass substrates were supplied in patterned form (120 nm, 15 Ω sq^{-1}, Kintec Company) and sequentially cleaned in detergent PCC-54 solution (2 wt %. dispersed in H_2O), deionized water, acetone, and isopropyl alcohol by ultrasonication and dried under N_2 gas flow. Subsequently, the substrates were exposed to an oxygen plasma for 5 min. Then, NPB (N,N′-Di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine), molecules 1-3, TPBi (1,3,5-Tris(1-phenyl-1H-benzo[d]imidazole-2-yl)benzene), tris-(8-hydroxyquinoline) aluminum (Alq_3), LiF and Al layers were deposited under vacuum (10^{-6} mbar) using a thermal evaporation technique. The active emission area was 9.0 mm^2. A Hamamatsu PMA-12 C10027 Photonic Multichannel Analyzer and digital multimeter (2427-C 3A Keithley) were used to measure current density, luminance, voltage characteristics and efficiency of the devices. A stylus profiler (KLA Tencor P-6) was used to determine the thickness of the organic layers.

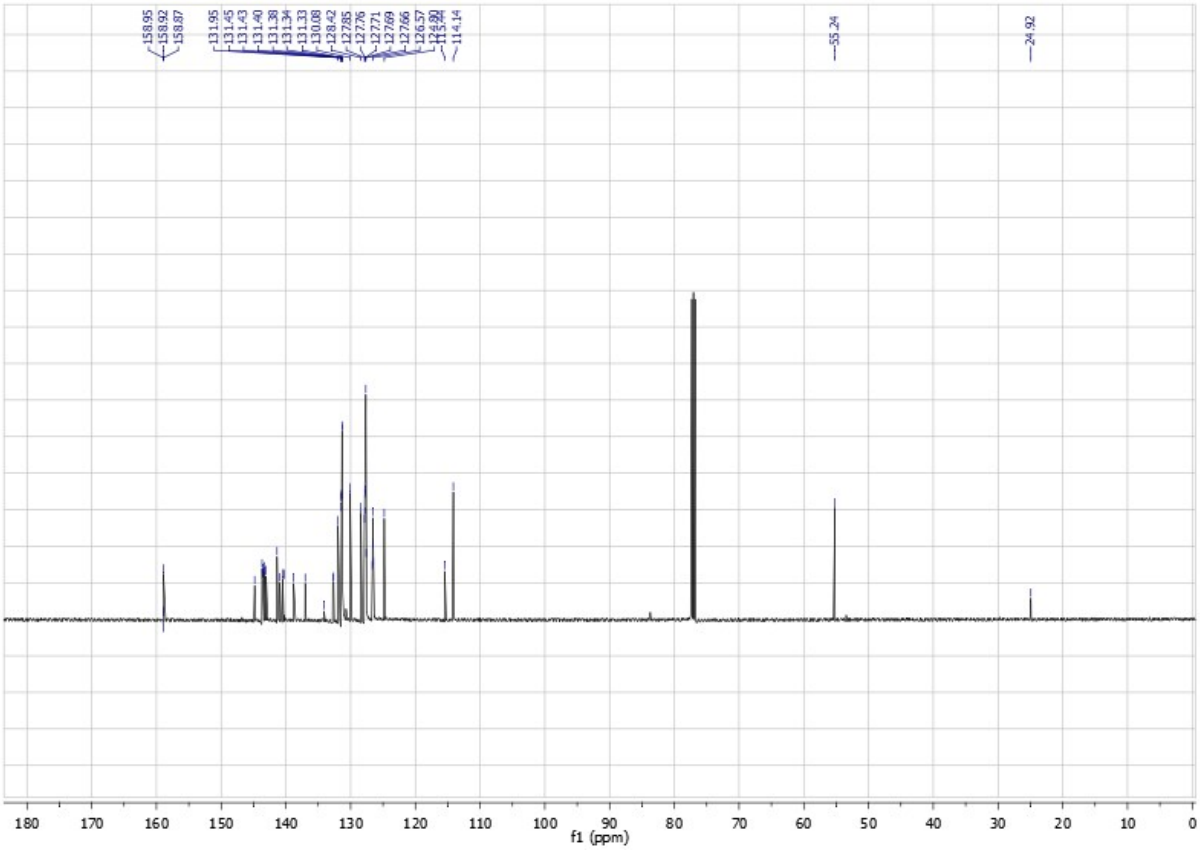
2. NMR Spectra

^{1}H NMR of TPE2-TT

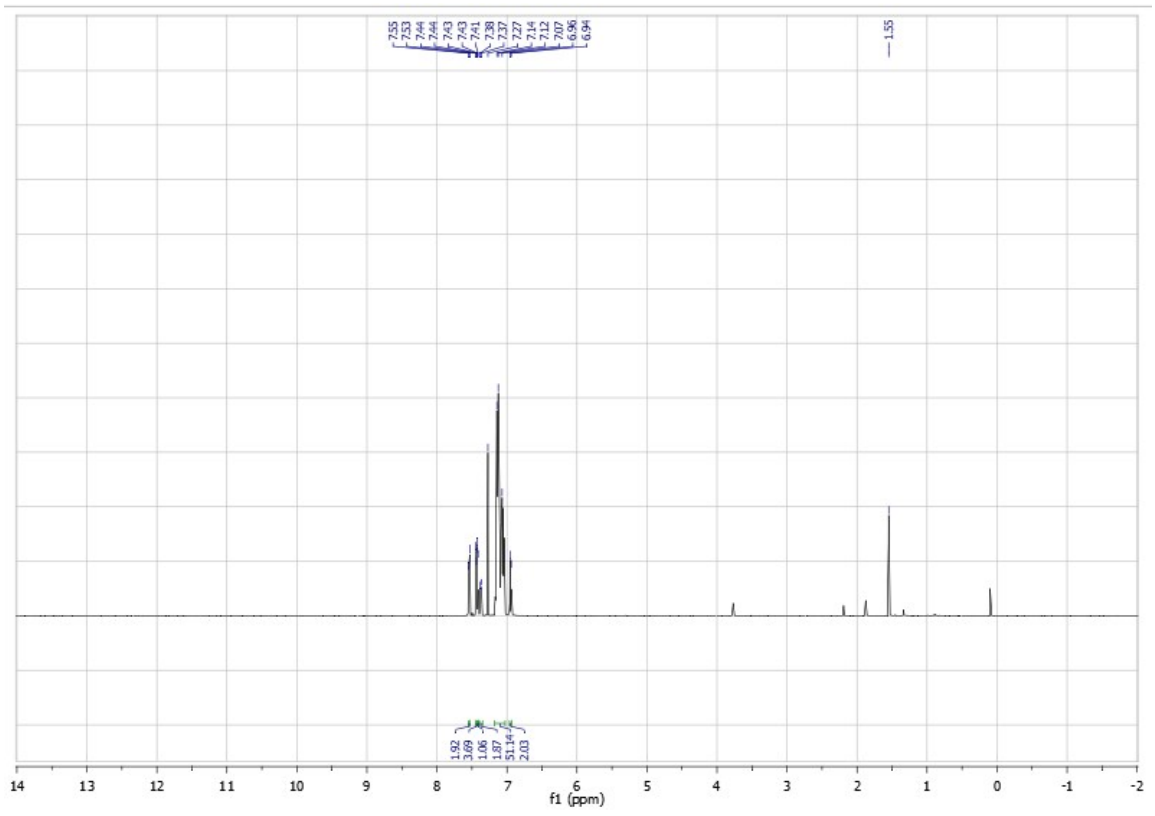


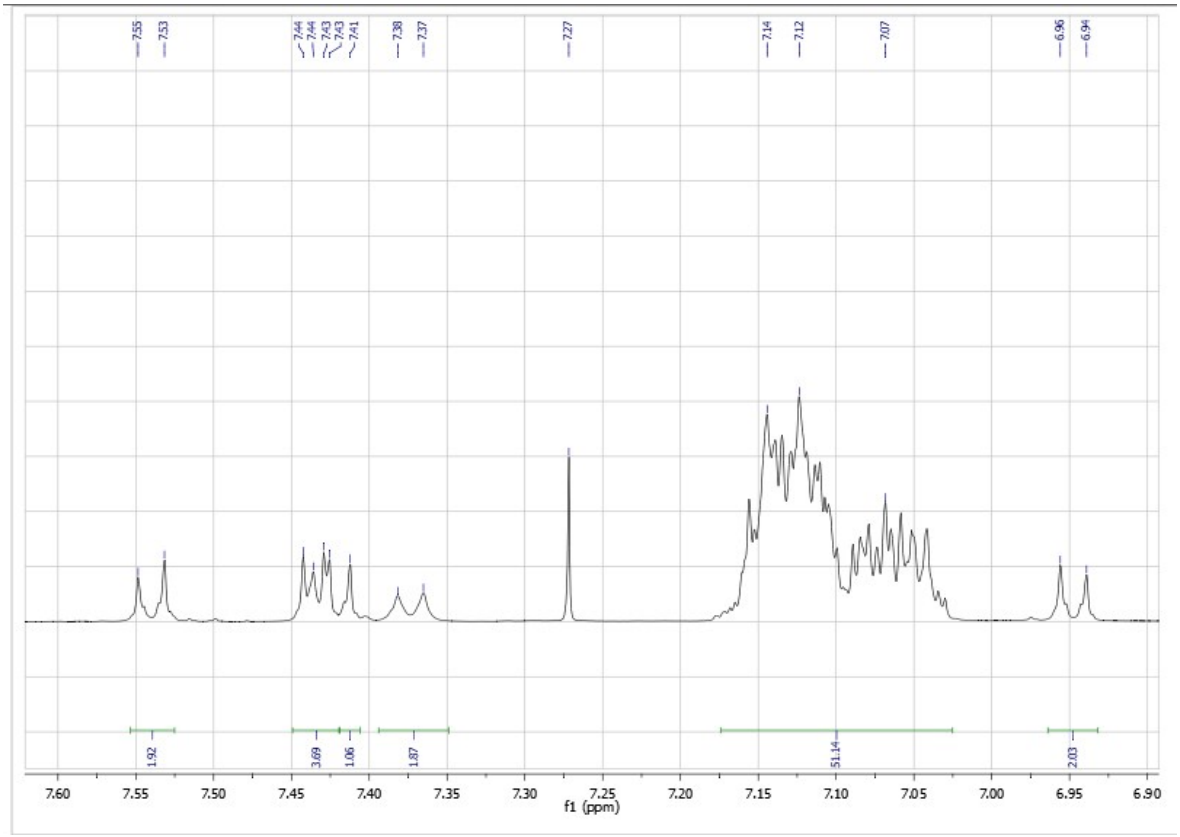


^{13}C NMR of TPE2-TT

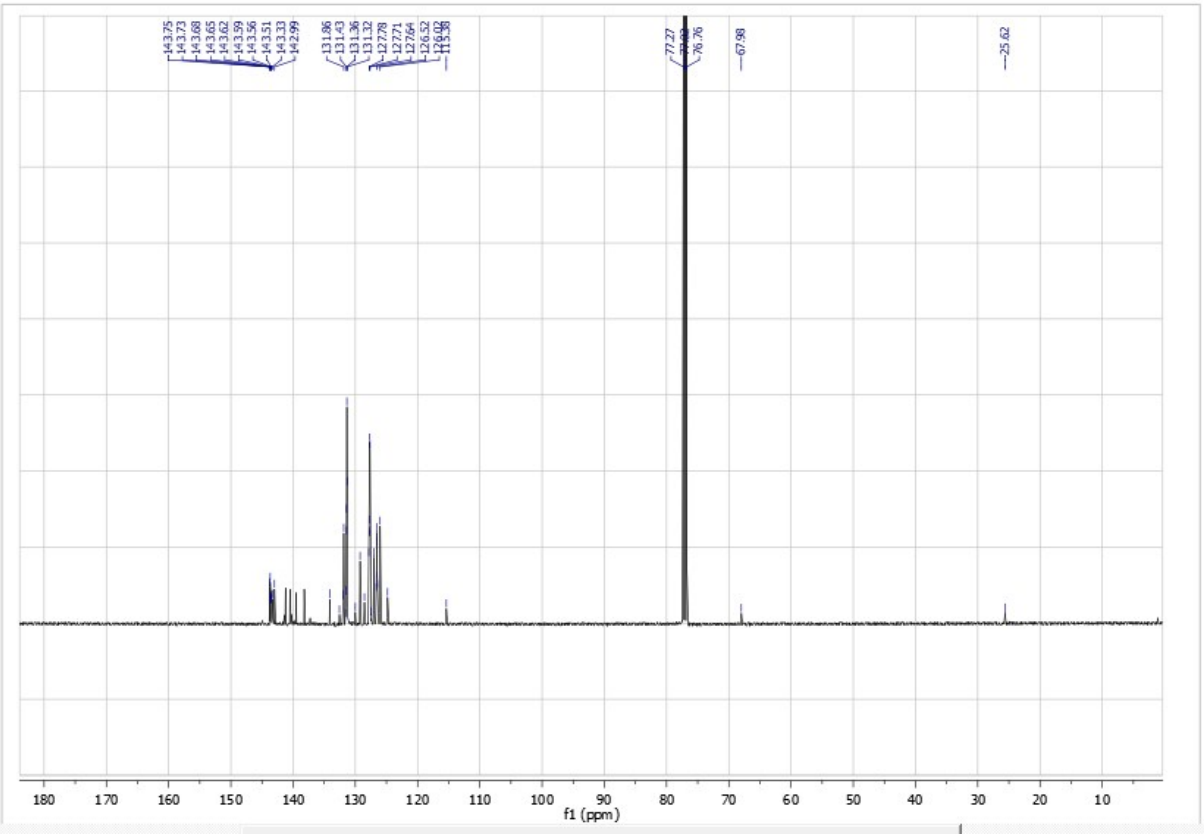


^{1}H NMR of TPE3-TT

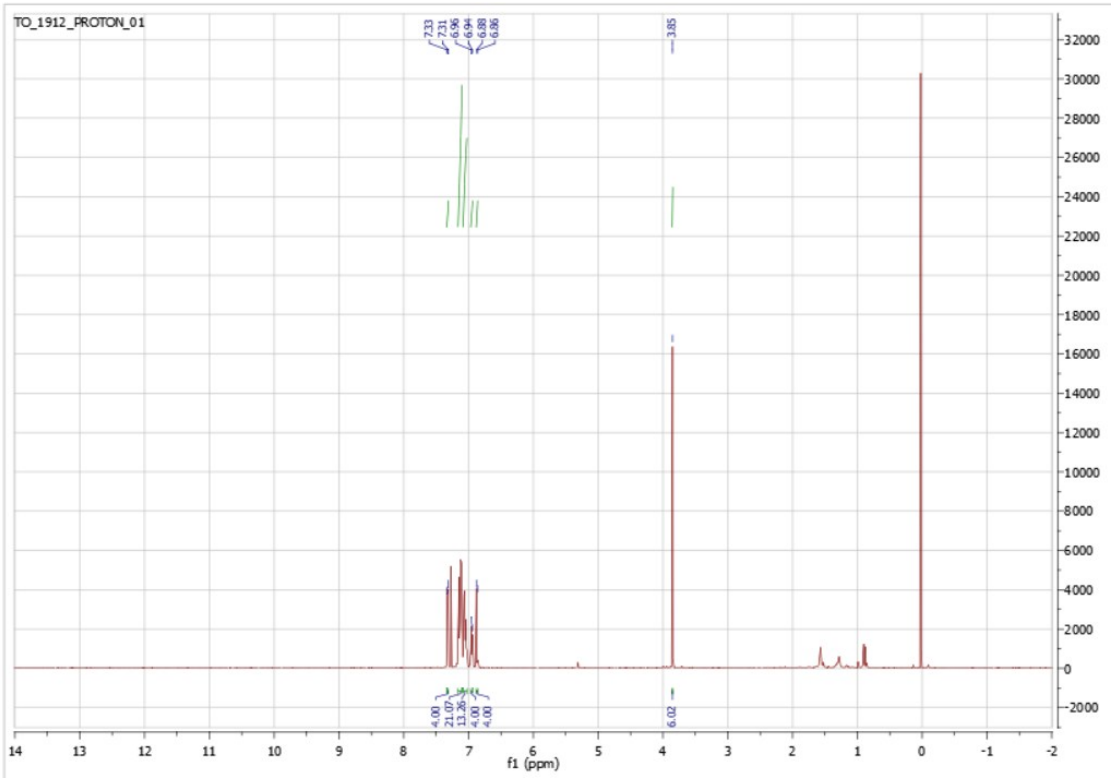


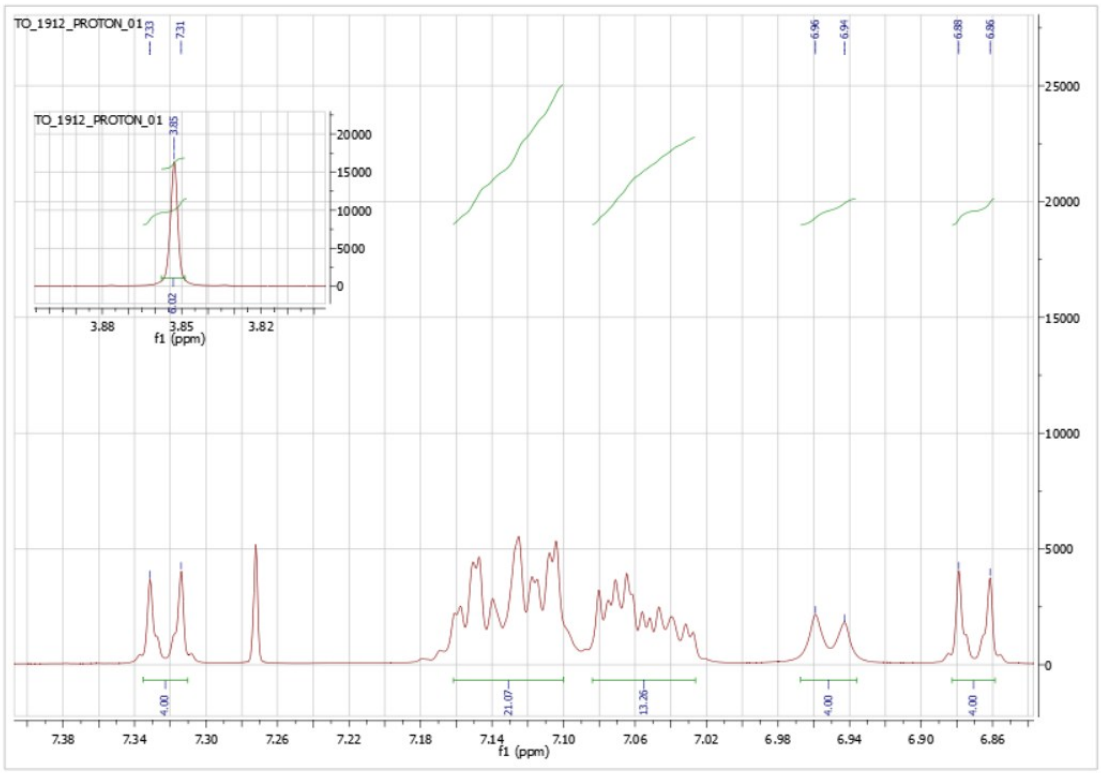


^{13}C NMR of TPE3-TT

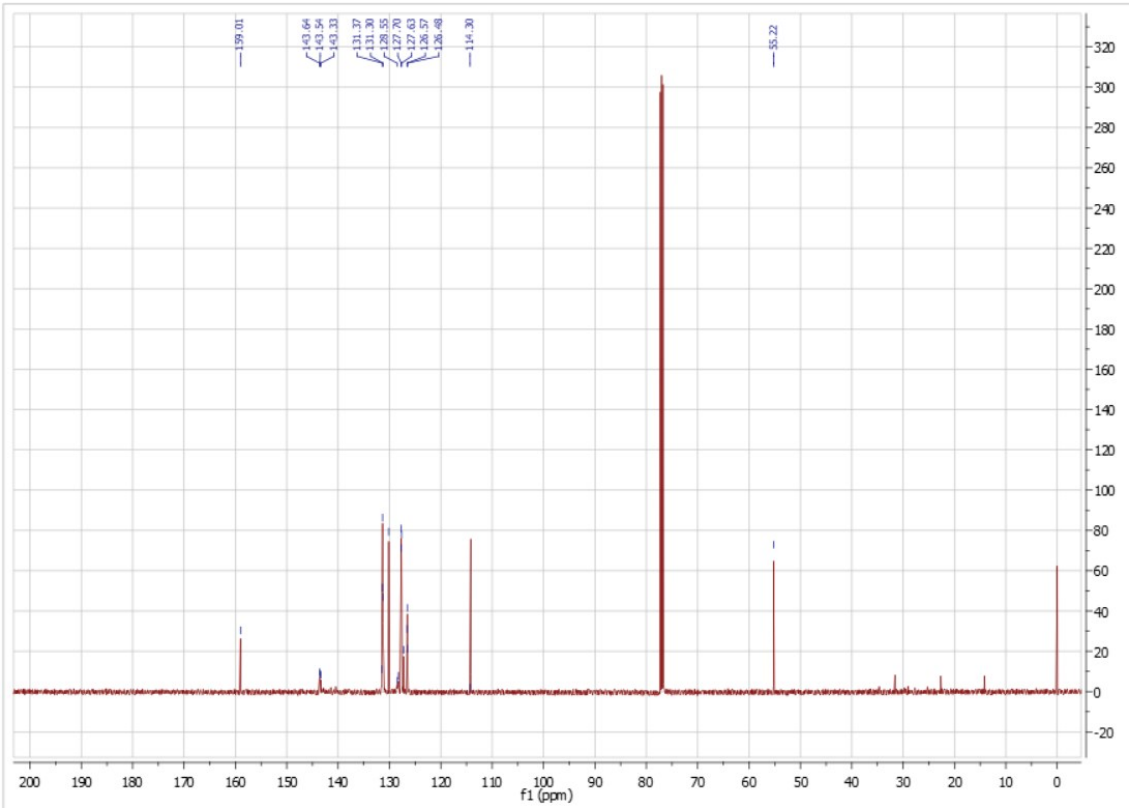


^{1}H NMR of TPE2-DTT



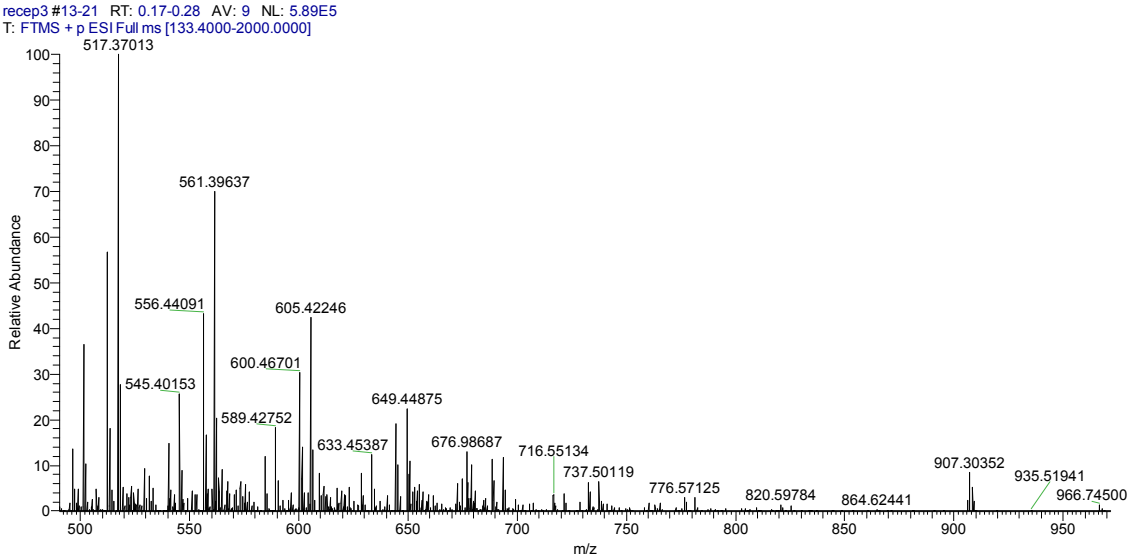


^{13}C NMR of TPE2-DTT



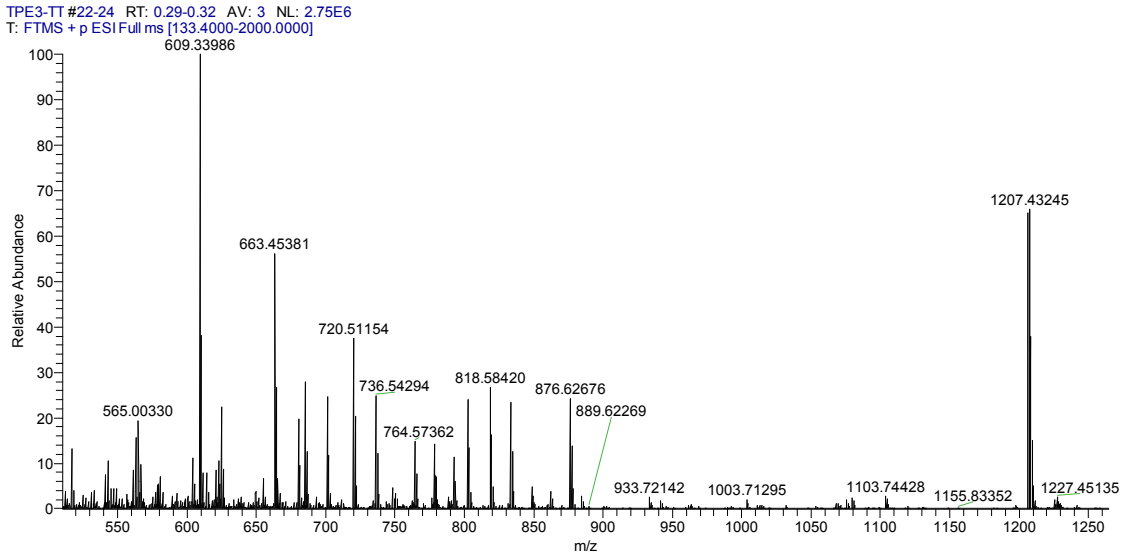
3. Mass Spectra

HRMS of TPE2-TT



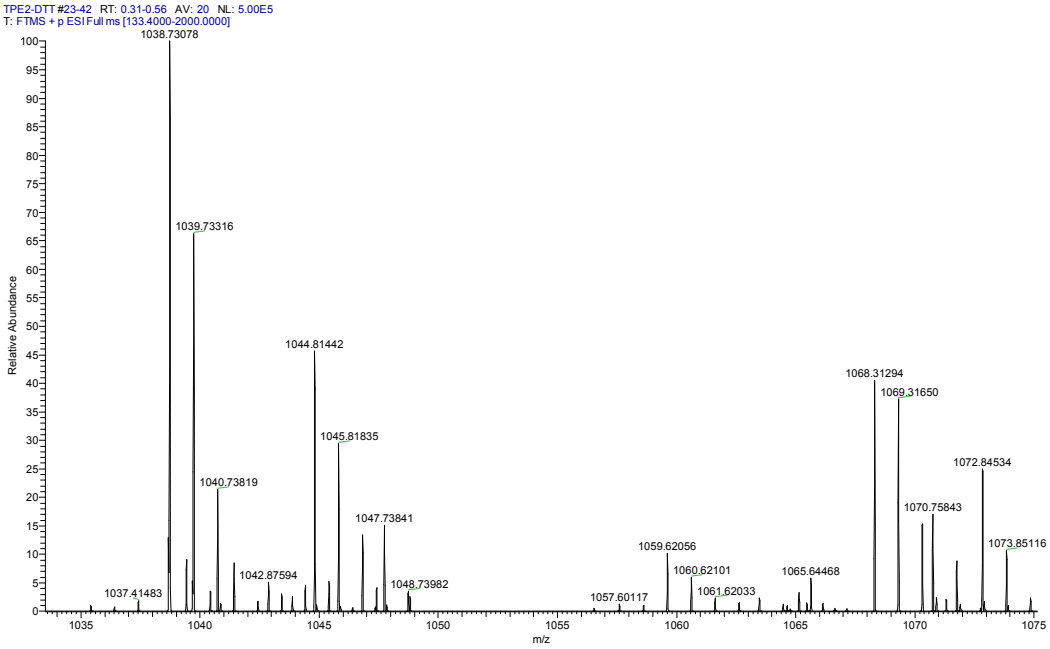
m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
907.30352	907.30628	-3.05	42.5	$C_{65}H_{47}OS_2$

HRMS of TPE3-TT



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1207.43245	1207.43657	-3.41	59.5	$C_{90}H_{63}OS_2$

HRMS of TPE2-DTT



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
1068.31294	1068.31239	0.51	49.0	C_{74} H_{52} O_2 S_3

4. X-Ray Crystallography Details

For single crystal X-ray analysis, the crystal was mounted on a cryomount and was attached to a goniometer head on a Bruker D8 VENTURE diffractometer equipped with PHOTON 100 detector and was measured with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) using 1.0° of Ω and Φ rotation frames at 130 K using Oxford Cryostream 700 cooling device. The structure was solved using Olex2 and olex2.solve structure solution program using Charge Flipping method and was refined with the olex2.refine refinement package using Gauss-Newton minimization. Molecular drawings are generated using OLEX2. Ver. 1.2-dev [1,2].

Further details on crystal data, data collection and refinements are included in the supporting information and can also be found by downloading CCDC 1916908 via https://www.ccdc.cam.ac.uk/structures/ .

Table S1 Crystal data and structure refinement for TPE2-DTT.

Empirical formula C74H58O5S3
Formula weight 1117.43
Temperature/K 131.82
Crystal system triclinic
Space group P-1
a/Å 12.366(19)
b/Å 14.86(3)
c/Å 17.64(3)
α/° 111.33(5)
β/° 93.80(5)
γ/° 96.37(5)
Volume/Å^3 2981(9)
Z 2
ρcalcg/cm^3 1.2447
μ/mm^{-1} 0.177
F(000) 1169.2
Crystal size/mm^3 0.5 × 0.05 × 0.03
Radiation Mo Kα (λ = 0.71073)
2Θ range for data collection/° 4.14 to 50
Index ranges $-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-21 \leq l \leq 21$
Reflections collected 114302
Independent reflections 10477 [Rint = 0.1352, Rsigma = 0.0984]
Data/restraints/parameters 10477/0/727
Goodness-of-fit on F2 1.009
Final R indexes [I>=2σ (I)] R1 = 0.0745, wR2 = 0.2209
Final R indexes [all data] R1 = 0.1382, wR2 = 0.2820
Largest diff. peak/hole / e Å^{-3} 1.82/-1.35

Table S2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for TPE2-DTT. Ueq is defined as 1/3 of of the trace of the orthogonalized UIJ tensor.

Atom *x y z* U(eq)

S1 5129.9(9) 1989.5(8) 4673.6(7) 20.5(3)
S2 2339.2(9) 3322.2(8) 5290.1(7) 22.1(3)
S3 5539.9(9) 4831.7(8) 6006.5(7) 21.4(3)
O1 -88(3) 7270(3) 6973(3) 46.1(11)
O2 -1265(3) -693(3) 3509(2) 37.1(9)
C1 4460(4) 3898(3) 5564(3) 20.2(11)
C2 4318(4) 2867(3) 5089(3) 19.7(10)
C3 3216(4) 2468(3) 4905(3) 19.6(10)

C4 3472(4) 4240(3) 5730(3) 20.0(11)
C5 3559(4) 5264(3) 6204(3) 20.8(11)
C6 4639(4) 5672(3) 6423(3) 19.7(11)
C7 3985(4) 1077(3) 4279(3) 18.7(10)
C8 3013(4) 1431(3) 4453(3) 18.1(10)
C9 1893(4) 863(3) 4224(3) 19.9(10)
C10 1642(4) -10(3) 4354(3) 21.9(11)
C11 1059(4) 1191(3) 3870(3) 24.4(11)
C12 605(4) -545(3) 4125(3) 23.7(11)
C13 -218(4) -219(3) 3758(3) 24.8(11)
C14 20(4) 658(4) 3636(3) 29.1(12)
C15 -1504(4) -1637(4) 3576(3) 34.9(13)
C16 4154(4) 62(3) 3805(3) 17.4(10)
C17 3389(4) -527(3) 3135(3) 21.3(11)
C18 5062(4) -329(3) 3993(3) 19.0(10)
C19 3506(4) -1491(3) 2716(3) 20.4(11)
C20 5169(4) -1305(3) 3559(3) 19.4(10)
C21 4377(4) -1907(3) 2932(3) 20.0(10)
C22 4441(4) -2964(3) 2488(3) 22.1(11)
C23 3562(4) -3670(3) 2323(3) 24.2(11)
C24 2555(4) -3500(3) 2759(3) 28.2(12)
C25 2657(4) -3042(4) 3610(3) 32.7(13)
C26 1741(5) -2941(4) 4025(4) 41.6(15)
C27 707(5) -3280(4) 3615(5) 51.2(18)
C28 586(5) -3748(4) 2760(5) 50.6(17)
C29 1513(4) -3861(4) 2345(4) 39.4(14)
C30 3553(4) -4679(3) 1712(3) 29.7(12)
C31 3881(5) -4815(4) 951(3) 34.9(13)
C32 3231(4) -5498(3) 1905(3) 34.0(13)
C33 3918(5) -5749(4) 393(4) 48.6(16)
C34 3294(5) -6419(4) 1358(4) 48.4(17)
C35 3631(5) -6549(4) 598(4) 51.9(18)
C36 5537(4) -3202(3) 2217(3) 21.5(11)
C37 5969(4) -3992(3) 2323(3) 30.9(13)
C38 6153(4) -2642(3) 1866(3) 25.4(11)
C39 6952(5) -4236(4) 2046(3) 36.2(14)
C40 7154(4) -2881(4) 1601(3) 30.3(12)
C41 7545(4) -3689(4) 1684(3) 37.1(14)
C42 2595(4) 5780(3) 6400(3) 19.4(10)
C43 1664(4) 5347(3) 6615(3) 25.9(12)
C44 746(4) 5813(3) 6803(3) 27.5(12)
C45 2561(4) 6708(3) 6367(3) 27.8(12)
C46 1672(4) 7168(4) 6557(3) 33.1(13)
C47 757(4) 6729(4) 6777(3) 32.0(13)
C48 -1032(5) 6821(4) 7199(4) 51.8(17)
C49 5116(4) 6680(3) 6975(3) 18.5(10)
C50 6067(4) 7161(3) 6826(3) 20.0(10)
C51 4641(4) 7163(3) 7682(3) 22.2(11)
C52 5084(4) 8101(3) 8208(3) 23.0(11)
C53 6520(4) 8098(3) 7358(3) 18.4(10)

C54 6035(4) 8598(3) 8050(3) 22.4(11)
C55 6564(4) 9597(3) 8624(3) 19.8(10)
C56 7784(4) 9681(3) 8762(3) 20.9(11)
C57 8268(4) 8997(3) 8988(3) 27.9(12)
C58 8473(4) 10392(3) 8611(3) 27.6(12)
C59 9381(4) 9005(4) 9053(3) 36.7(14)
C60 10055(4) 9698(4) 8872(3) 39.5(14)
C61 9597(4) 10393(4) 8665(3) 36.6(13)
C62 6003(4) 10353(3) 8958(3) 20.5(11)
C63 4833(4) 10332(3) 8683(3) 21.1(11)
C64 4426(4) 9941(3) 7860(3) 23.0(11)
C65 4106(4) 10752(3) 9243(3) 23.3(11)
C66 3351(4) 9950(3) 7594(3) 26.2(12)
C67 3025(4) 10745(3) 8981(3) 26.2(12)
C68 2646(4) 10355(3) 8163(3) 29.6(12)
C69 6550(4) 11281(3) 9636(3) 23.3(11)
C70 7209(4) 11258(3) 10298(3) 26.5(12)
C71 6377(4) 12211(3) 9640(3) 31.9(13)
C72 6867(5) 13044(4) 10270(4) 42.4(15)
C73 7688(4) 12107(4) 10935(3) 33.1(13)
C74 7521(5) 13006(4) 10920(3) 41.2(15)
O1aa 373(5) 7175(4) 1220(4) 91.2(17)
O0aa 9108(6) 6653(5) 9670(4) 120(2)
O3 697(7) 5474(6) 9905(5) 149(3)

Table S3 Anisotropic Displacement Parameters (Å2×103) for TPE2-DTT. The

Anisotropic displacement factor exponent takes the form:

-2π2[h2a*2U11+2hka*b*U12+…].

Atom U11 U22 U33 U12 U13 U23

S1 21.2(7) 14.2(6) 23.5(7) 4.0(5) 2.8(5) 3.4(5)
S2 19.3(7) 13.3(6) 29.8(7) 2.9(5) 3.6(5) 3.1(5)
S3 19.7(7) 14.6(6) 26.3(7) 3.1(5) 3.1(5) 3.1(5)
O1 34(2) 42(2) 72(3) 26.8(19) 20(2) 24(2)
O2 23(2) 35(2) 51(2) -6.0(16) -6.6(17) 17.0(18)
C1 18(3) 19(2) 21(3) 0(2) 1(2) 5(2)
C2 22(3) 17(2) 20(3) 6(2) 2(2) 5(2)
C3 25(3) 14(2) 19(2) 2(2) 1(2) 5(2)
C4 20(3) 14(2) 23(3) 1.8(19) 2(2) 5(2)
C5 28(3) 16(2) 20(3) 4(2) 5(2) 8(2)
C6 22(3) 15(2) 23(3) 6(2) 9(2) 7(2)
C7 18(3) 18(2) 18(2) 1.5(19) 0(2) 5(2)
C8 24(3) 13(2) 16(2) 3.7(19) 3(2) 4.1(19)
C9 21(3) 17(2) 19(3) 1(2) 3(2) 3(2)
C10 24(3) 17(2) 22(3) 2(2) 0(2) 6(2)
C11 29(3) 17(2) 27(3) 6(2) 3(2) 8(2)
C12 27(3) 20(2) 24(3) 0(2) 4(2) 9(2)
C13 19(3) 27(3) 25(3) -1(2) 0(2) 8(2)
C14 26(3) 31(3) 31(3) 7(2) -3(2) 12(2)

C15 30(3) 29(3) 38(3) -5(2) 8(3) 5(2)
C16 22(3) 13(2) 17(2) 0.7(19) 3(2) 5.8(19)
C17 20(3) 20(2) 27(3) 5(2) 4(2) 12(2)
C18 21(3) 17(2) 17(2) 3(2) 3(2) 4(2)
C19 20(3) 17(2) 19(3) 1(2) 2(2) 1(2)
C20 18(2) 21(2) 21(3) 8(2) 3(2) 8(2)
C21 20(3) 17(2) 22(3) 3(2) 4(2) 5(2)
C22 28(3) 13(2) 23(3) 3(2) 1(2) 6(2)
C23 31(3) 14(2) 26(3) 6(2) -3(2) 6(2)
C24 29(3) 14(2) 42(3) 2(2) -1(2) 13(2)
C25 35(3) 28(3) 34(3) 1(2) 3(3) 12(2)
C26 46(4) 31(3) 49(4) 6(3) 18(3) 15(3)
C27 37(4) 36(3) 91(6) 10(3) 28(4) 31(4)
C28 29(3) 43(4) 81(5) 0(3) 1(3) 27(4)
C29 35(3) 30(3) 48(4) 5(3) -5(3) 11(3)
C30 33(3) 20(3) 31(3) 3(2) -9(2) 6(2)
C31 48(4) 23(3) 28(3) 6(2) 0(3) 4(2)
C32 48(3) 19(3) 33(3) -1(2) -11(3) 11(2)
C33 56(4) 38(4) 35(3) 5(3) 0(3) -4(3)
C34 61(4) 21(3) 55(4) 2(3) -17(3) 9(3)
C35 64(4) 17(3) 56(4) 11(3) -9(3) -8(3)
C36 31(3) 11(2) 18(2) 5(2) -3(2) 0(2)
C37 44(3) 21(3) 26(3) 13(2) 4(2) 6(2)
C38 28(3) 21(3) 25(3) 8(2) -3(2) 6(2)
C39 46(4) 26(3) 38(3) 20(3) 0(3) 11(3)
C40 34(3) 32(3) 29(3) 12(2) 9(2) 13(2)
C41 26(3) 50(3) 30(3) 15(3) 1(2) 6(3)
C42 22(3) 13(2) 21(3) 3.2(19) 3(2) 3(2)
C43 27(3) 16(2) 32(3) 4(2) 3(2) 5(2)
C44 24(3) 25(3) 34(3) 8(2) 3(2) 10(2)
C45 26(3) 25(3) 37(3) 8(2) 6(2) 15(2)
C46 37(3) 20(3) 47(3) 14(2) 8(3) 15(2)
C47 28(3) 29(3) 37(3) 13(2) 3(2) 8(2)
C48 34(3) 53(4) 71(5) 27(3) 19(3) 18(3)
C49 23(3) 10(2) 21(3) 4.7(19) 0(2) 4.4(19)
C50 20(3) 19(2) 21(3) 6(2) 5(2) 7(2)
C51 16(3) 19(2) 31(3) 0.7(19) 3(2) 9(2)
C52 20(3) 20(2) 26(3) 3(2) 3(2) 6(2)
C53 16(2) 12(2) 26(3) 2.7(18) 3(2) 6(2)
C54 18(3) 22(2) 26(3) 4(2) 1(2) 7(2)
C55 25(3) 17(2) 18(2) 1(2) 4(2) 7(2)
C56 17(3) 19(2) 21(3) 2(2) 6(2) 1(2)
C57 24(3) 23(3) 32(3) 3(2) 0(2) 5(2)
C58 26(3) 25(3) 28(3) -1(2) 5(2) 7(2)
C59 31(3) 32(3) 39(3) 6(2) -6(3) 5(3)
C60 21(3) 46(3) 45(4) 5(3) 1(3) 10(3)
C61 23(3) 43(3) 44(3) -1(2) 7(3) 17(3)
C62 21(3) 17(2) 23(3) 1(2) 4(2) 7(2)
C63 23(3) 13(2) 25(3) 0.9(19) 2(2) 6(2)
C64 24(3) 13(2) 30(3) 0(2) 5(2) 7(2)

C65 27(3) 20(2) 23(3) 4(2) 8(2) 8(2)
C66 25(3) 27(3) 28(3) 2(2) -1(2) 14(2)
C67 23(3) 26(3) 31(3) 8(2) 11(2) 10(2)
C68 22(3) 25(3) 45(3) 1(2) 1(2) 19(3)
C69 22(3) 24(3) 20(3) 0(2) 3(2) 5(2)
C70 26(3) 25(3) 29(3) 4(2) 5(2) 11(2)
C71 37(3) 19(3) 36(3) 6(2) -1(2) 7(2)
C72 46(4) 14(3) 56(4) 7(2) -8(3) 2(3)
C73 29(3) 37(3) 28(3) 2(2) -6(2) 6(2)
C74 44(4) 22(3) 40(3) 9(2) -5(3) -9(2)

Table S4 Bond Lengths for TPE2-DTT.

Atom Atom Length/Å Atom Atom Length/Å

S1 C2 1.714(5) C31 C33 1.388(7)
S1 C7 1.756(5) C32 C34 1.372(8)
S2 C3 1.739(5) C33 C35 1.380(9)
S2 C4 1.757(5) C34 C35 1.383(9)
S3 C1 1.726(5) C36 C37 1.409(7)
S3 C6 1.758(5) C36 C38 1.398(7)
O1 C47 1.375(6) C37 C39 1.377(7)
O1 C48 1.432(7) C38 C40 1.388(7)
O2 C13 1.365(6) C39 C41 1.384(8)
O2 C15 1.449(6) C40 C41 1.394(8)
C1 C2 1.438(6) C42 C43 1.398(7)
C1 C4 1.383(7) C42 C45 1.407(7)
C2 C3 1.392(7) C43 C44 1.392(7)
C3 C8 1.438(6) C44 C47 1.376(7)
C4 C5 1.433(6) C45 C46 1.356(7)
C5 C6 1.372(7) C46 C47 1.391(7)
C5 C42 1.480(7) C49 C50 1.398(7)
C6 C49 1.486(6) C49 C51 1.399(7)
C7 C8 1.373(6) C50 C53 1.393(6)
C7 C16 1.481(6) C51 C52 1.388(6)
C8 C9 1.487(6) C52 C54 1.418(7)
C9 C10 1.402(7) C53 C54 1.392(7)
C9 C11 1.393(7) C54 C55 1.503(6)
C10 C12 1.382(7) C55 C56 1.495(7)
C11 C14 1.384(7) C55 C62 1.356(6)
C12 C13 1.393(7) C56 C57 1.397(7)
C13 C14 1.400(7) C56 C58 1.397(7)
C16 C17 1.405(6) C57 C59 1.372(7)
C16 C18 1.395(6) C58 C61 1.387(7)
C17 C19 1.381(6) C59 C60 1.394(8)
C18 C20 1.398(6) C60 C61 1.378(8)
C19 C21 1.397(7) C62 C63 1.488(7)
C20 C21 1.388(6) C62 C69 1.508(6)
C21 C22 1.493(6) C63 C64 1.388(7)
C22 C23 1.360(7) C63 C65 1.403(7)
C22 C36 1.503(7) C64 C66 1.383(7)

C23 C24 1.503(7) C65 C67 1.383(7)
C23 C30 1.494(7) C66 C68 1.386(7)
C24 C25 1.395(8) C67 C68 1.371(7)
C24 C29 1.385(7) C69 C70 1.393(7)
C25 C26 1.381(7) C69 C71 1.420(7)
C26 C27 1.371(8) C70 C73 1.386(7)
C27 C28 1.402(10) C71 C72 1.370(7)
C28 C29 1.395(8) C72 C74 1.381(8)
C30 C31 1.379(8) C73 C74 1.384(8)
C30 C32 1.404(7)

Table S5 Bond Angles for TPE2-DTT.

Atom Atom Atom Angle/° Atom Atom Atom Angle/°

C7 S1 C2 91.7(2) C32 C30 C31 119.2(5)
C4 S2 C3 90.1(2) C33 C31 C30 120.3(5)
C6 S3 C1 91.4(2) C34 C32 C30 120.2(6)
C48 O1 C47 116.2(4) C35 C33 C31 120.1(6)
C15 O2 C13 117.1(4) C35 C34 C32 120.2(6)
C2 C1 S3 137.1(4) C34 C35 C33 119.9(5)
C4 C1 S3 110.6(3) C37 C36 C22 120.3(4)
C4 C1 C2 112.3(4) C38 C36 C22 121.1(4)
C1 C2 S1 137.7(4) C38 C36 C37 118.7(5)
C3 C2 S1 110.7(3) C39 C37 C36 120.4(5)
C3 C2 C1 111.6(4) C40 C38 C36 120.6(4)
C2 C3 S2 113.3(3) C41 C39 C37 120.3(5)
C8 C3 S2 132.0(4) C41 C40 C38 119.7(5)
C8 C3 C2 114.6(4) C40 C41 C39 120.2(5)
C1 C4 S2 112.7(3) C43 C42 C5 120.7(4)
C5 C4 S2 132.3(4) C45 C42 C5 122.2(4)
C5 C4 C1 115.0(4) C45 C42 C43 117.1(4)
C6 C5 C4 110.2(4) C44 C43 C42 121.9(4)
C42 C5 C4 123.1(4) C47 C44 C43 118.9(5)
C42 C5 C6 126.6(4) C46 C45 C42 121.0(5)
C5 C6 S3 112.7(3) C47 C46 C45 121.0(5)
C49 C6 S3 118.2(3) C44 C47 O1 124.1(5)
C49 C6 C5 129.0(4) C46 C47 O1 116.0(4)
C8 C7 S1 112.8(3) C46 C47 C44 119.9(5)
C16 C7 S1 119.1(3) C50 C49 C6 121.7(4)
C16 C7 C8 128.1(4) C51 C49 C6 120.3(4)
C7 C8 C3 110.1(4) C51 C49 C50 118.0(4)
C9 C8 C3 122.8(4) C53 C50 C49 121.1(4)
C9 C8 C7 127.1(4) C52 C51 C49 121.0(4)
C10 C9 C8 121.7(4) C54 C52 C51 121.2(4)
C11 C9 C8 120.2(4) C54 C53 C50 121.5(4)
C11 C9 C10 118.1(4) C53 C54 C52 117.2(4)
C12 C10 C9 121.4(4) C55 C54 C52 122.6(4)
C14 C11 C9 120.8(4) C55 C54 C53 120.0(4)
C13 C12 C10 120.0(4) C56 C55 C54 112.8(4)
C12 C13 O2 124.6(4) C62 C55 C54 123.7(4)

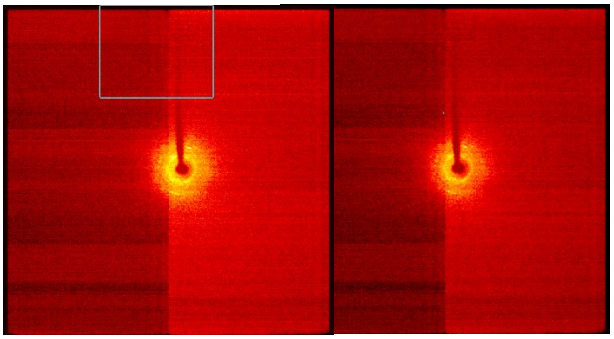
C14 C13 O2 116.5(4) C62 C55 C56 123.4(4)
C14 C13 C12 119.0(4) C57 C56 C55 120.4(4)
C13 C14 C11 120.7(5) C58 C56 C55 121.7(4)
C17 C16 C7 119.5(4) C58 C56 C57 117.8(4)
C18 C16 C7 122.1(4) C59 C57 C56 121.9(5)
C18 C16 C17 118.4(4) C61 C58 C56 120.4(5)
C19 C17 C16 120.0(4) C60 C59 C57 119.7(5)
C20 C18 C16 120.7(4) C61 C60 C59 119.4(5)
C21 C19 C17 122.0(4) C60 C61 C58 120.8(5)
C21 C20 C18 120.9(4) C63 C62 C55 123.1(4)
C20 C21 C19 117.8(4) C69 C62 C55 120.9(4)
C22 C21 C19 120.1(4) C69 C62 C63 116.0(4)
C22 C21 C20 122.1(4) C64 C63 C62 121.5(4)
C23 C22 C21 122.4(4) C65 C63 C62 121.4(4)
C36 C22 C21 115.7(4) C65 C63 C64 117.0(4)
C36 C22 C23 121.8(4) C66 C64 C63 122.2(5)
C24 C23 C22 122.7(4) C67 C65 C63 121.0(4)
C30 C23 C22 121.7(4) C68 C66 C64 119.6(5)
C30 C23 C24 115.6(4) C68 C67 C65 120.7(5)
C25 C24 C23 120.0(4) C67 C68 C66 119.6(5)
C29 C24 C23 121.6(5) C70 C69 C62 121.3(4)
C29 C24 C25 118.2(5) C71 C69 C62 121.3(4)
C26 C25 C24 120.7(5) C71 C69 C70 117.4(4)
C27 C26 C25 121.2(6) C73 C70 C69 121.6(5)
C28 C27 C26 119.0(6) C72 C71 C69 120.2(5)
C29 C28 C27 119.6(6) C74 C72 C71 121.5(5)
C28 C29 C24 121.2(6) C74 C73 C70 120.0(5)
C31 C30 C23 120.0(4) C73 C74 C72 119.3(5)
C32 C30 C23 120.8(5)

Table S6 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for TPE2-DTT.

Atom *x y z* U(eq)

H10 2197(4) -238(3) 4606(3) 26.3(13)
H11 1205(4) 1789(3) 3788(3) 29.3(14)
H12 455(4) -1136(3) 4217(3) 28.5(13)
H14 -537(4) 889(4) 3390(3) 34.9(14)
H15a -1031(19) -2080(8) 3251(17) 52(2)
H15b -1370(30) -1561(5) 4151(4) 52(2)
H15c -2273(8) -1907(11) 3371(19) 52(2)
H17 2792(4) -264(3) 2970(3) 25.5(13)
H18 5613(4) 71(3) 4421(3) 22.9(12)
H19 2979(4) -1882(3) 2267(3) 24.5(13)
H20 5794(4) -1559(3) 3695(3) 23.3(12)
H25 3364(4) -2796(4) 3908(3) 39.3(15)
H26 1828(5) -2631(4) 4605(4) 49.9(18)
H27 83(5) -3198(4) 3906(5) 61(2)

H28 -124(5) -3987(4) 2466(5) 61(2)
H29 1429(4) -4192(4) 1766(4) 47.3(17)
H31 4083(5) -4266(4) 809(3) 41.9(16)
H32 2968(4) -5415(3) 2417(3) 40.8(16)
H33 4140(5) -5839(4) -132(4) 58(2)
H34 3106(5) -6969(4) 1502(4) 58(2)
H35 3665(5) -7187(4) 218(4) 62(2)
H37 5580(4) -4359(3) 2588(3) 37.0(15)
H38 5885(4) -2094(3) 1807(3) 30.4(14)
H39 7226(5) -4783(4) 2104(3) 43.4(16)
H40 7570(4) -2495(4) 1365(3) 36.3(15)
H41 8220(4) -3864(4) 1491(3) 44.6(17)
H43 1658(4) 4715(3) 6634(3) 31.0(14)
H44 122(4) 5505(3) 6947(3) 33.0(14)
H45 3171(4) 7017(3) 6209(3) 33.3(14)
H46 1673(4) 7799(4) 6540(3) 39.7(16)
H48a -1380(20) 6245(18) 6729(8) 78(3)
H48b -810(7) 6630(30) 7653(17) 78(3)
H48c -1554(16) 7287(11) 7370(20) 78(3)
H50 6411(4) 6843(3) 6354(3) 24.0(13)
H51 4005(4) 6844(3) 7805(3) 26.7(13)
H52 4744(4) 8415(3) 8683(3) 27.6(13)
H53 7175(4) 8402(3) 7247(3) 22.1(12)
H57 7814(4) 8512(3) 9101(3) 33.5(14)
H58 8170(4) 10879(3) 8471(3) 33.1(14)
H59 9691(4) 8540(4) 9221(3) 44.1(17)
H60 10824(4) 9691(4) 8891(3) 47.4(17)
H61 10057(4) 10879(4) 8557(3) 43.9(16)
H64 4902(4) 9658(3) 7466(3) 27.5(13)
H65 4359(4) 11045(3) 9811(3) 28.0(13)
H66 3098(4) 9681(3) 7026(3) 31.4(14)
H67 2539(4) 11012(3) 9371(3) 31.4(14)
H68 1906(4) 10363(3) 7987(3) 35.6(15)
H70 7334(4) 10645(3) 10313(3) 31.8(14)
H71 5920(4) 12257(3) 9205(3) 38.3(15)
H72 6754(5) 13661(4) 10259(4) 50.8(18)
H73 8131(4) 12072(4) 11382(3) 39.7(15)
H74 7854(5) 13591(4) 11352(3) 49.5(18)



TPE2-TT **TPE3-TT**

Figure S1. X-ray diffraction patterns (snapchats) of **TPE2-TT** and **TPE3-TT**

References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339-341
2. L. J. Bourhis, O. V. Dolomanov, , R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Crystallogr. A Found Adv*., 2015, **71**, 59-75

5. Computational Analysis

Free enthalpies, Gibbs free energies and cartesian coordinates of **TPE2-TT, TPE3-TT** and **TPE2-DTT** with their optimized structures are fully detailed in the following section.

TPE2-TT

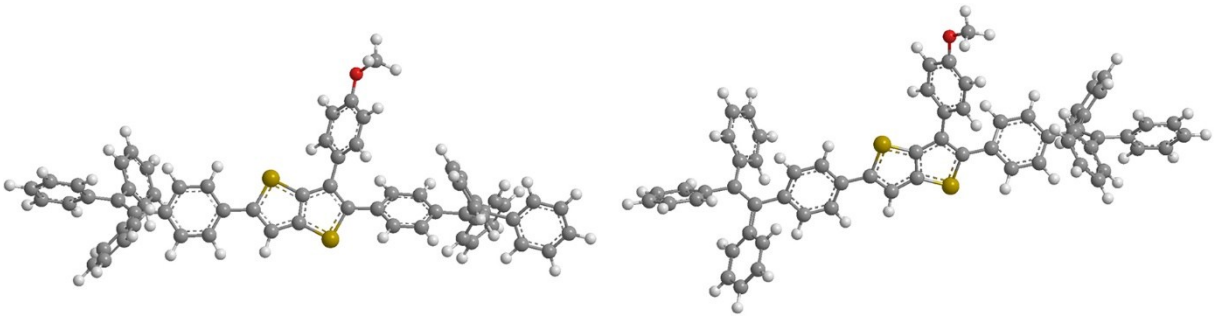


Figure S2. Front (left) and side (right) view of the optimized structure of **TPE2-TT**.

Thermal correction to Gibbs Free Energy= 0.807705

Sum of electronic and thermal Free Energies =-3375.490732

C	-4.9655	3.4078	-1.5485
C	-3.6845	3.1148	-1.2713
C	-3.225	1.85	-1.197
C	-4.1598	0.9017	-1.4153
C	-5.441	1.1954	-1.6903
C	-5.8965	2.4611	-1.7774
C	-7.1997	2.7436	-2.0457
C	-7.5693	3.9101	-2.6408
C	-8.159	1.8344	-1.7103
C	-9.1942	1.6169	-2.5663
C	-8.0563	1.1665	-0.5292
C	-8.794	4.446	-2.4429
C	-9.184	5.5894	-3.0283
C	-8.3526	6.2426	-3.8506
C	-7.1349	5.7326	-4.0773
C	-6.7597	4.5893	-3.482
C	-10.4139	1.2136	-2.1491
C	-11.4361	1.0146	-2.9964
C	-11.2721	1.2173	-4.3103
C	-10.0771	1.6257	-4.7568
C	-9.0661	1.8225	-3.8958
C	-7.404	1.698	0.5282
C	-7.2789	1.0512	1.6978

C	-7.8037	-0.1717	1.8506
C	-8.4478	-0.732	0.8184
C	-8.5659	-0.0706	-0.3438
C	5.052	-0.5818	1.5964
C	3.8124	-0.429	1.1038
C	4.2826	1.7011	0.539
C	5.5283	1.5531	1.0188
C	5.9691	0.4032	1.5653
C	7.2409	0.2622	2.0257
C	7.5482	-0.6151	3.0189
C	8.2308	1.0144	1.4658
C	9.2009	1.5377	2.2637
C	8.2218	1.2243	0.1212
C	6.6633	-0.9736	3.9743
C	6.9752	-1.8293	4.9605
C	8.2024	-2.3619	5.0279
C	9.107	-2.0204	4.101
C	8.7797	-1.1614	3.1227
C	10.4504	1.7944	1.8196
C	11.4086	2.297	2.6143
C	11.147	2.562	3.901
C	9.92	2.3112	4.3759
C	8.9738	1.8062	3.5684
C	8.7489	2.33	-0.448
C	8.7215	2.5411	-1.7735
C	8.1551	1.6413	-2.5882
C	7.6162	0.5366	-2.0559
C	7.6506	0.3417	-0.7281
C	-1.9294	1.5693	-0.9203
S	-1.3736	0.1995	-0.8232
C	0.0164	0.5062	-0.4843
C	0.1949	1.822	-0.4701
C	-0.9448	2.4679	-0.7145
C	1.1855	-0.1241	-0.2795
C	2.1139	0.8302	0.014
S	1.5734	2.1944	-0.2131
C	1.3442	-1.4618	-0.4068
C	3.3672	0.7064	0.5286
C	0.3807	-2.3675	-0.1534
C	0.5774	-3.6833	-0.3297
C	1.7337	-4.194	-0.7909
C	2.6813	-3.2855	-1.0896
C	2.4882	-1.9692	-0.9089
O	1.8481	-5.5543	-0.9477
C	3.0317	-6.0729	-1.509
H	-5.237	4.4771	-1.5219
H	-3.0298	3.9804	-1.0852
H	-3.9143	-0.1736	-1.3907
H	-6.106	0.3368	-1.8869
H	-9.521	3.9854	-1.7528

H	-10.1882	6.0001	-2.8279
H	-8.668	7.1796	-4.3385
H	-6.449	6.247	-4.7717
H	-5.7668	4.202	-3.766
H	-10.6438	1.0843	-1.0781
H	-12.4218	0.7019	-2.612
H	-12.1081	1.0583	-5.0111
H	-9.9254	1.7916	-5.8369
H	-8.1042	2.1249	-4.3432
H	-6.9752	2.7137	0.4909
H	-6.75	1.5275	2.5407
H	-7.7003	-0.7108	2.8067
H	-8.8633	-1.7488	0.9222
H	-9.0555	-0.622	-1.1641
H	5.2988	-1.5806	1.9949
H	3.1504	-1.2956	1.2494
H	4.0722	2.6994	0.1187
H	6.1792	2.4436	0.9743
H	5.654	-0.5311	4.0211
H	6.2277	-2.0825	5.7316
H	8.4658	-3.0631	5.8369
H	10.1202	-2.4551	4.1407
H	9.5669	-0.9562	2.3777
H	10.7593	1.5468	0.7901
H	12.4218	2.4757	2.2158
H	11.9302	2.9722	4.5596
H	9.6883	2.5295	5.4322
H	7.9798	1.6593	4.0236
H	9.1769	3.1441	0.1608
H	9.1473	3.467	-2.1961
H	8.1262	1.8103	-3.6772
H	7.151	-0.2163	-2.7146
H	7.2174	-0.6075	-0.3699
H	-1.0121	3.5632	-0.74
H	-0.5954	-2.0736	0.2613
H	-0.241	-4.3807	-0.0783
H	3.6501	-3.5973	-1.5117
H	3.3022	-1.3013	-1.2414
H	2.9251	-7.1796	-1.565
H	3.1724	-5.6841	-2.5422
H	3.9031	-5.8414	-0.8567

TPE3-TT

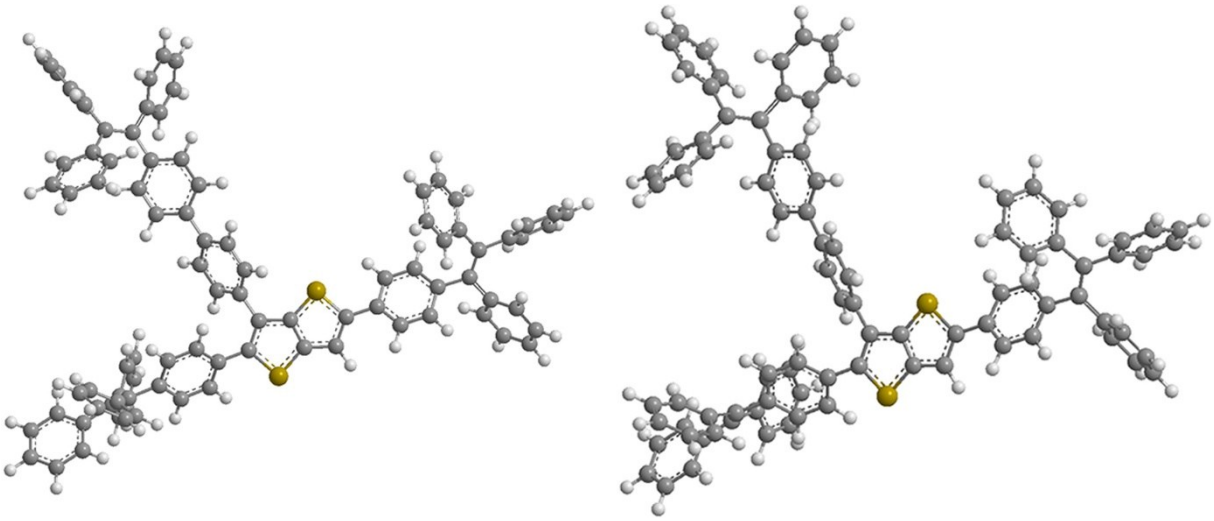


Figure S3. Front (left) and side (right) view of the optimized structure of **TPE3-TT**.

Thermal correction to Gibbs Free Energy= 1.103359

Sum of electronic and thermal Free Energies= -4262.316384

C	-4.9627	7.1732	-2.2482
C	-3.6774	6.9212	-1.9512
C	-3.2235	5.6851	-1.6639
C	-4.168	4.722	-1.6935
C	-5.4534	4.975	-1.989
C	-5.9042	6.2101	-2.2862
C	-7.212	6.4551	-2.5691
C	-7.5885	7.5054	-3.348
C	-8.169	5.6292	-2.0578
C	-9.2293	5.281	-2.8364
C	-8.0403	5.1732	-0.7822
C	-8.8031	8.0827	-3.2151
C	-9.1996	9.1125	-3.9797
C	-8.3855	9.6033	-4.9233
C	-7.1785	9.0465	-5.0889
C	-6.7966	8.0187	-4.3143
C	-10.4404	4.9718	-2.3243
C	-11.4875	4.6438	-3.0978
C	-11.3586	4.6157	-4.4308
C	-10.173	4.925	-4.9719
C	-9.1366	5.2531	-4.1843
C	-7.3565	5.871	0.1515
C	-7.2051	5.4333	1.4114
C	-7.7347	4.2612	1.7853
C	-8.4104	3.5395	0.8814

C	-8.5544	3.9927	-0.3741
C	5.048	3.7391	1.4672
C	3.8089	3.8139	0.9564
C	4.3018	5.7958	0.0047
C	5.5471	5.7242	0.5035
C	5.9767	4.6896	1.2523
C	7.2486	4.6168	1.7278
C	7.5487	3.9278	2.8618
C	8.2469	5.2395	1.0387
C	9.2294	5.8816	1.7271
C	8.2347	5.203	-0.3216
C	6.6651	3.7627	3.8698
C	6.9694	3.0913	4.9919
C	8.1876	2.5566	5.1481
C	9.0911	2.7105	4.1713
C	8.7715	3.3867	3.0565
C	10.4806	6.0331	1.2414
C	11.4509	6.654	1.9309
C	11.2002	7.1502	3.1495
C	9.9717	7.0098	3.6643
C	9.0133	6.3841	2.9627
C	8.7763	6.179	-1.0822
C	8.746	6.1472	-2.424
C	8.1619	5.124	-3.0614
C	7.6087	4.1424	-2.3371
C	7.6463	4.1904	-0.9961
C	-1.9243	5.4465	-1.3651
S	-1.3733	4.1112	-1.0348
C	0.0215	4.4655	-0.7711
C	0.2077	5.7609	-0.9964
C	-0.9324	6.3601	-1.3385
C	1.1897	3.8763	-0.4655
C	2.1236	4.8632	-0.3523
S	1.591	6.1654	-0.8263
C	1.349	2.5387	-0.3427
C	3.3758	4.8264	0.1781
C	0.3973	1.685	0.0728
C	0.6071	0.3607	0.1667
C	1.7688	-0.2407	-0.1697
C	2.6922	0.621	-0.6466
C	2.4912	1.9455	-0.7368
C	1.2919	-3.7626	0.5726
C	1.0703	-2.4448	0.4328
C	3.1552	-2.1733	-0.3753
C	3.3852	-3.4889	-0.2332
C	2.4614	-4.3438	0.2458
C	2.7167	-5.6694	0.4115
C	1.7223	-6.5973	0.3773
C	4.0017	-6.0736	0.6242
C	4.4486	-7.2116	0.0269

C	4.807	-5.3265	1.4275
C	1.8296	-7.772	1.0366
C	0.8657	-8.7059	1.0075
C	-0.2529	-8.4972	0.301
C	-0.3867	-7.3473	-0.3729
C	0.5857	-6.4226	-0.3312
C	5.4265	-7.9778	0.5572
C	5.8546	-9.1075	-0.0284
C	5.3091	-9.5177	-1.181
C	4.3307	-8.7856	-1.7296
C	3.9126	-7.6597	-1.1298
C	4.3003	-4.5554	2.415
C	5.0743	-3.7977	3.208
C	6.4023	-3.7795	3.0342
C	6.9365	-4.5258	2.0585
C	6.1483	-5.2796	1.2755
C	1.9883	-1.5788	-0.0471
H	-5.227	8.2333	-2.4034
H	-3.0143	7.8002	-1.9337
H	-3.9278	3.6656	-1.4847
H	-6.1277	4.1017	-2.0172
H	-9.5148	7.7578	-2.4374
H	-10.1946	9.5643	-3.8281
H	-8.7064	10.4458	-5.5578
H	-6.5074	9.4246	-5.8788
H	-5.8148	7.5757	-4.5517
H	-10.6415	5.0317	-1.2415
H	-12.4649	4.4152	-2.6397
H	-12.2153	4.3502	-5.0718
H	-10.0501	4.9009	-6.068
H	-8.1849	5.4611	-4.7019
H	-6.9216	6.8601	-0.0708
H	-6.6505	6.0411	2.1463
H	-7.61	3.8932	2.817
H	-8.8309	2.5609	1.169
H	-9.0699	3.3146	-1.0747
H	5.2831	2.8279	2.043
H	3.1372	2.9983	1.2633
H	4.1006	6.7006	-0.5939
H	6.2087	6.5826	0.294
H	5.664	4.2248	3.8407
H	6.2234	2.9937	5.7988
H	8.4447	2.0061	6.068
H	10.0968	2.2711	4.2837
H	9.5564	3.4406	2.2833
H	10.7802	5.5992	0.2727
H	12.4649	6.741	1.5047
H	11.9934	7.6586	3.7222
H	9.7489	7.418	4.6647
H	8.0193	6.3384	3.4389

H	9.2198	7.0827	-0.6313
H	9.1843	6.9743	-3.0079
H	8.1306	5.0937	-4.163
H	7.129	3.2902	-2.8478
H	7.2005	3.3285	-0.4712
H	-0.9947	7.4339	-1.5574
H	-0.582	2.053	0.4173
H	-0.2542	-0.1972	0.5629
H	3.6797	0.299	-1.0081
H	3.3004	2.5426	-1.1938
H	0.4815	-4.3489	1.0393
H	0.0745	-2.1237	0.7723
H	4.0109	-1.6182	-0.7867
H	4.3732	-3.8528	-0.5651
H	2.7045	-8.002	1.6679
H	0.9876	-9.6458	1.5722
H	-1.0465	-9.2618	0.2688
H	-1.2922	-7.1724	-0.9785
H	0.4287	-5.5298	-0.9594
H	5.8819	-7.7389	1.5329
H	6.6444	-9.7134	0.4473
H	5.6541	-10.4458	-1.6657
H	3.8757	-9.1083	-2.6814
H	3.128	-7.0939	-1.6598
H	3.2208	-4.5438	2.6419
H	4.6204	-3.1925	4.011
H	7.0436	-3.1553	3.6781
H	8.0263	-4.5016	1.8883
H	6.6553	-5.8167	0.4564

TPE2-DTT

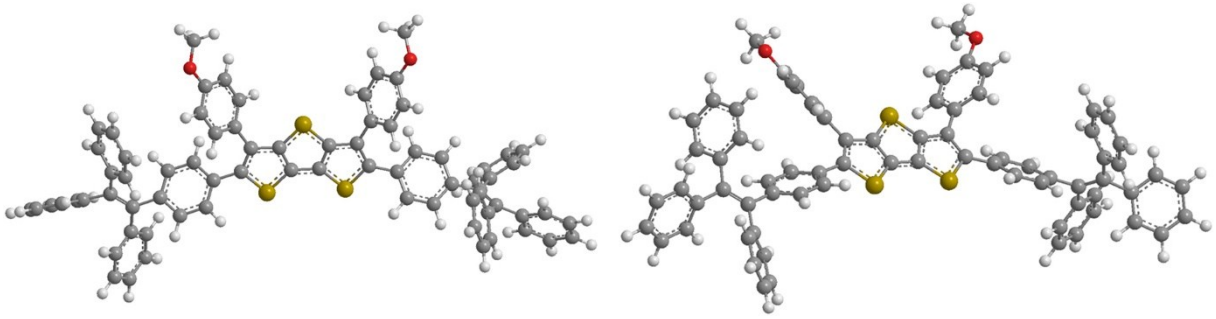


Figure S4. Front (left) and side (right) view of the optimized structure of **TPE2-DTT**.

Thermal correction to Gibbs Free Energy= 0.918776

Sum of electronic and thermal Free Energies= -4195.368217

C	3.26534	-0.08879	-0.28829
S	2.02626	-1.42504	-0.20922
C	0.7356	-0.19413	-0.26406
C	1.2573	1.04823	-0.33685
C	2.69242	1.1292	-0.34609
C	-0.68106	-0.22189	-0.2312
C	-1.25417	0.99867	-0.27874
S	-0.02493	2.3198	-0.35559
S	-1.91799	-1.50162	-0.11746
C	-3.21327	-0.21512	-0.13554
C	-2.69012	1.02469	-0.22098
C	-3.45423	2.29709	-0.22459
C	3.4134	2.42591	-0.37618
C	4.69107	-0.44811	-0.28504
C	-4.61914	-0.63905	-0.064
C	-4.33023	2.61265	0.81241
C	-5.02074	3.79995	0.8102
C	-4.85414	4.70957	-0.22706
C	-3.98781	4.4093	-1.25963
C	-3.2944	3.20833	-1.25338
C	4.32196	2.76335	0.62563
C	4.97156	3.97366	0.60408
C	4.73221	4.8835	-0.4189
C	3.8334	4.56098	-1.41652
C	3.17989	3.33814	-1.38974
C	5.19688	-1.32917	0.66287
C	6.53781	-1.66407	0.6676
C	7.40247	-1.13321	-0.27842
C	6.88978	-0.27256	-1.24291
C	5.55445	0.07314	-1.24353
C	-5.01452	-1.62834	0.83179
C	-6.32951	-2.04427	0.8852

C	-7.28988	-1.47005	0.06136
C	-6.89309	-0.48899	-0.83775
C	-5.57524	-0.08219	-0.9059
C	-8.70829	-1.9495	0.11572
C	8.85339	-1.50538	-0.30197
C	9.65484	-1.35731	0.75535
C	11.06511	-1.86285	0.79345
C	9.31633	-2.05171	-1.61855
C	9.22363	-0.66587	2.01377
C	-9.74636	-1.12718	0.28485
C	-8.85033	-3.43395	-0.03621
C	-11.17324	-1.57456	0.18547
C	-9.58835	0.3307	0.59551
O	-5.58368	5.86501	-0.13842
O	5.4272	6.06109	-0.35242
C	5.24242	7.08254	-1.3455
C	-5.47929	6.88011	-1.14925
C	8.71813	0.62693	1.98565
C	8.35228	1.26309	3.15906
C	8.48308	0.61349	4.37338
C	8.99224	-0.67397	4.41043
C	9.3691	-1.3053	3.23985
C	11.36156	-3.18979	0.51236
C	12.66557	-3.64775	0.58224
C	13.68908	-2.78447	0.92996
C	13.40117	-1.46069	1.21736
C	12.09727	-1.00554	1.15879
C	8.62269	-3.09889	-2.21522
C	9.02418	-3.60068	-3.43913
C	10.11416	-3.05029	-4.09235
C	10.79953	-1.99743	-3.513
C	10.40448	-1.50179	-2.28289
C	-8.2496	-4.08022	-1.11105
C	-8.35383	-5.45117	-1.25413
C	-9.04492	-6.19764	-0.31445
C	-9.63148	-5.56407	0.76644
C	-9.53646	-4.1904	0.90435
C	-12.06484	-1.27462	1.20965
C	-13.38878	-1.66294	1.125
C	-13.84461	-2.33997	0.00623
C	-12.9678	-2.627	-1.0246
C	-11.63974	-2.24858	-0.9352
C	-10.22165	1.2812	-0.19746
C	-10.09731	2.62807	0.08674
C	-9.35562	3.04289	1.18046
C	-8.73998	2.102	1.98603
C	-8.85283	0.75382	1.69398
H	-4.46559	1.91806	1.61562
H	-5.69911	4.05145	1.59715
H	-3.84159	5.0896	-2.07151

H	-2.62855	2.98309	-2.06282
H	4.51253	2.06924	1.41824
H	5.66706	4.2474	1.36897
H	3.63072	5.24136	-2.21611
H	2.48694	3.09672	-2.17133
H	4.54245	-1.74236	1.40442
H	6.91711	-2.32952	1.41532
H	7.54109	0.11819	-1.99869
H	5.17365	0.74214	-1.98689
H	-4.29088	-2.06808	1.48892
H	-6.61505	-2.8204	1.56649
H	-7.61913	-0.04351	-1.48578
H	-5.28408	0.66626	-1.61253
H	5.89122	7.89106	-1.05175
H	5.52399	6.72991	-2.32998
H	4.21654	7.42871	-1.36737
H	-6.14156	7.66981	-0.83485
H	-4.46809	7.26098	-1.22149
H	-5.79257	6.50647	-2.11625
H	8.60668	1.12911	1.04662
H	7.96816	2.2634	3.1231
H	8.19707	1.10574	5.28166
H	9.10066	-1.18186	5.3483
H	9.78356	-2.29321	3.27124
H	10.57286	-3.85773	0.23318
H	12.87969	-4.67547	0.36521
H	14.69927	-3.13938	0.9817
H	14.18859	-0.78694	1.49195
H	11.87232	0.01355	1.40255
H	7.76626	-3.51184	-1.72056
H	8.48526	-4.41367	-3.884
H	10.42194	-3.43495	-5.04441
H	11.64007	-1.56175	-4.01585
H	10.94264	-0.69335	-1.83237
H	-7.6965	-3.50611	-1.82743
H	-7.89254	-5.93576	-2.0918
H	-9.1203	-7.26157	-0.42151
H	-10.16213	-6.13606	1.50156
H	-9.99971	-3.70153	1.73659
H	-11.71794	-0.7314	2.06586
H	-14.06343	-1.43305	1.92586
H	-14.87272	-2.63556	-0.06265
H	-13.31478	-3.14461	-1.89687
H	-10.96132	-2.48108	-1.73004
H	-10.81376	0.95964	-1.03105
H	-10.58075	3.3516	-0.53939
H	-9.26148	4.08726	1.4024
H	-8.17329	2.41475	2.84076
H	-8.36671	0.0278	2.31303