Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary information

Oxidation reduces spin-orbital coupling to achieve robust fluorescent emission in halogen substituted dithieno[3,2-b:2′,3′-d]thiophene

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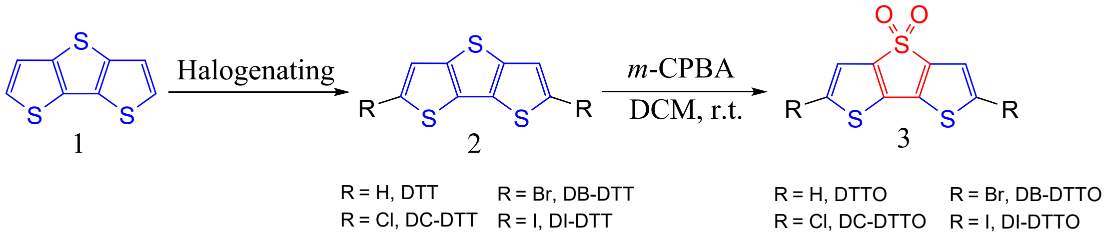
General information and methods

Materials and Measurements

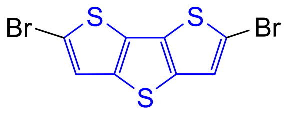
All chemicals and reagents were commercially available and used as received without further purification. ^{1}H and ^{13}C NMR spectra were acquired using the Bruker ARX 500 NMR spectrometer utilizing dichloromethane-d_2 as solvents with tetramethylsilane (TMS; $\delta = 0$ ppm) acting as the internal reference. UV-vis were obtained by PerkinElmer Lambda 365 Spectrophotometer. The fluorescence spectrum was acquired using FluoroMax-4 Spectrophotometer. Single crystal data were measured on R-AXIS RAPID with Mo-Kα ($\lambda = 0.71073$). The quantum yield (QY) was determined using a QE-2100 (Otsuka Electronics) device for measuring quantum efficiency, with a 150 W xenon lamp as the source of excitation. The fluorescent lifetime was measured by Horiba fluorescence spectrometer FL3-111. The excited-state geometry were optimized using time-dependent density function theory (TD-DFT) method with ωb97XD hybrid functional at the basis set level of def2-SVP, using Gaussian 16 package, Revision B.01. No symmetry constraint was applied for optimization. The energy levels and spin-orbit coupling (SOC) values calculated at the level of ωb97X-D3/def2-TZVP based on the optimized excited-state geometry by using ORCA 5.0.1.[1]

Experimental procedures

Synthesis and characterization.

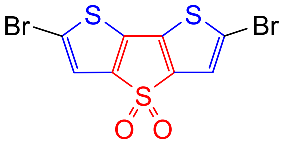


Scheme S1. Synthetic routes of molecules based on DTT and DTTO.



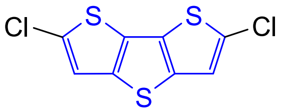
DB-DTT

2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (DB-DTT). Dithieno [2,3-b:2',3'-d] thiophene (0.35 g, 1.8 mmol) and N-Bromosuccinimide (0.64 g, 3.6 mmol) were added in a 100 mL flask with 15 mL DMF. And then the mixture was stirred overnight at room temperature. After the reaction, the mixture was poured into brine and extracted twice with dichloromethane. The organic layers were dried by anhydrous magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using petroleum ether as eluent. Obtaining a white solid of DB-DTT in 65% yield. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.28 (s, 2H); ^{13}C NMR (125 MHz, Chloroform-d), δ (ppm): 139.21, 130.96, 123.33, 112.50.



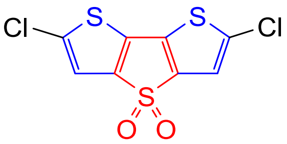
DB-DTTO

2,6-dibromodithieno[3,2-b:2',3'-d]thiophene 4,4-dioxide (DB-DTTO). DB-DTT (0.212 g, 0.6 mmol) was added in a 100 mL flask with 5 mL dichloromethane. A solution of *m*-CPBA (0.517 g, 3 mmol) in CH_2Cl_2 was added dropwise into the flask through constant pressure dropping funnel. The reaction was stirred for 10 hours at room temperature. After that, aqueous solution of sodium bicarbonate was added to quenching the reaction, and then extracted with excess CH_2Cl_2. The organic layers were dried by anhydrous magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using petroleum ether/CH_2Cl_2. Obtaining a yellow green solid of DB-DTTO in 59%. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.23 (s, 2H). ^{13}C NMR (125 MHz, Chloroform-d), δ (ppm): 141.34, 135.41, 122.88, 117.18.



DC-DTT

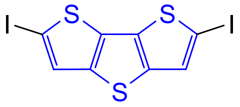
2,6-dichlorodithieno[3,2-b:2',3'-d]thiophene (DC-DTT). Dithieno [2,3-b:2',3'-d] thiophene (0.215 g, 1.1 mmol) and N-Chlorosuccinimide (0.323 g, 2.42 mmol) were added in a 100 mL flask with 15 mL DMF. The procedure was analogous to that described for DB-DTT. Obtaining a white solid of DC-DTT in 75% yield. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.15 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-d), δ (ppm): 137.89, 130.16, 128.35, 120.00.



DC-DTTO

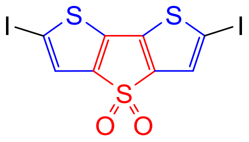
2,6-dichlorodithieno[3,2-b:2',3'-d]thiophene 4,4-dioxide

(DC-DTTO). The procedure was analogous to that described for DB-DTTO. Obtaining a yellow green solid of DC-DTTO in 41%. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.11 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ (ppm): 140.04, 135.15, 132.47, 119.54.



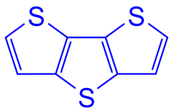
DI-DTT

2,6-diiododithieno[3,2-b:2',3'-d]thiophene (DI-DTT). Dithieno [2,3-b:2',3'-d] thiophene (0.530 g, 2.7 mmol) was added in a 100 mL flask with 15 mL CH_2Cl_2. At 0 ^{o}C, iodine (0.767 g, 3.02 mmol) and (Diacetoxyiodo)benzene (1.06 g, 3.29 mmol) were added in flask. The mixture was stirred 30 min at 0^{o}C, and then overnight at room temperature. After the reaction, aqueous solution of sodium thiosulfate was added to quenching the reaction. The procedure was analogous to that described for DB-DTT. Obtaining a faint yellow solid of DI-DTT in 62%. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.41 (s, 2H). ^{13}C NMR (125 MHz, Chloroform-d), δ (ppm): 141.03, 135.15, 129.57, 73.55.



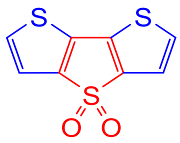
DI-DTTO

2,6-diiododithieno[3,2-b:2',3'-d]thiophene 4,4-dioxide (DI-DTTO). The procedure was analogous to that described for DB-DTTO. Obtaining a yellow solid of DI-DTTO in 15%. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.36 (s, 2H). ^{13}C NMR (125 MHz, Chloroform-d), δ (ppm): 142.97, 140.05, 128.99, 77.89.



DTT

dithieno[3,2-b:2',3'-d]thiophene (DTT). The compound was purchased from LeYan, and further purified through recrystallization. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.36 (d, J = 5.2 Hz, 2H), 7.29 (d, J = 5.2 Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-d), δ (ppm): 141.69, 130.96, 125.94, 120.90.



DTTO

dithieno[3,2-b:2',3'-d]thiophene 4,4-dioxide (DTTO). The procedure was analogous to that described for DB-DTTO. Obtaining a yellow green solid of DTTO in 47%. ^{1}H NMR (500 MHz, Chloroform-d), δ (ppm): 7.36 (d, J = 5.2 Hz, 2H), 7.23 (d, J = 5.1 Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-d), δ (ppm): 143.56, 136.21, 129.70, 120.47.

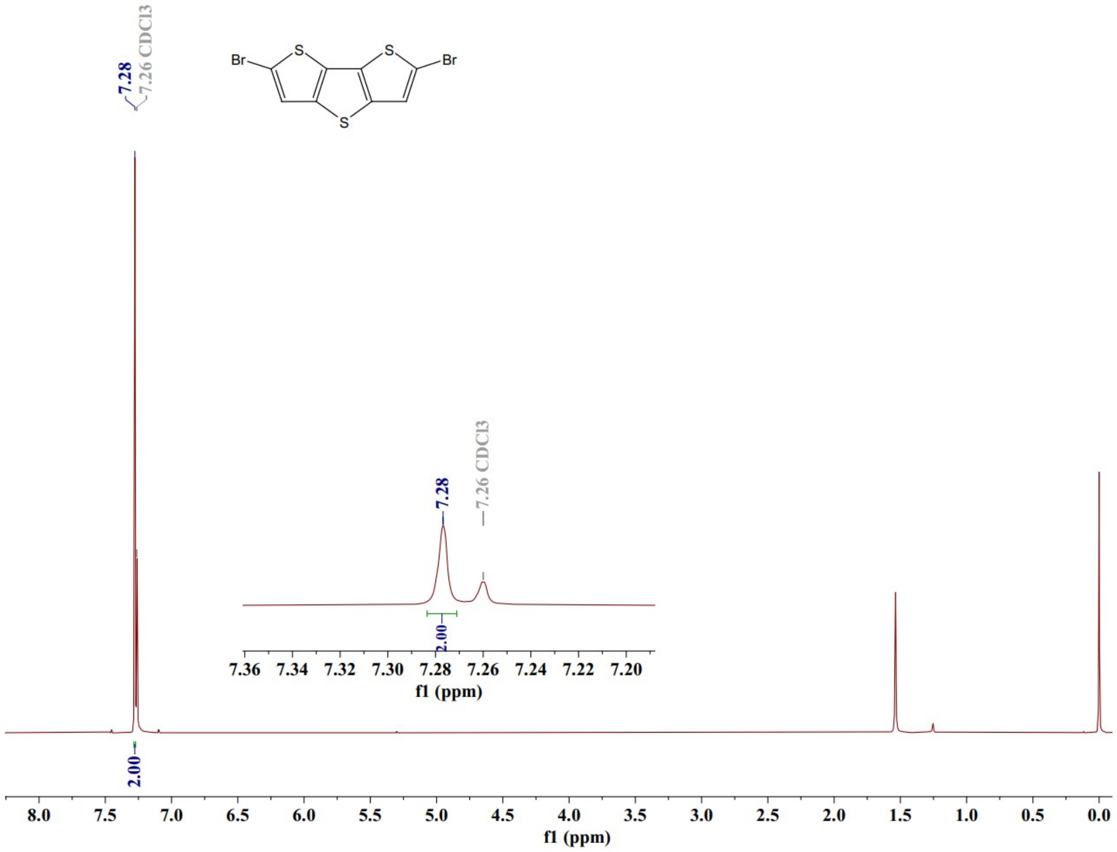


Figure S1. ^{1}H NMR spectrum of **DB-DTT**.

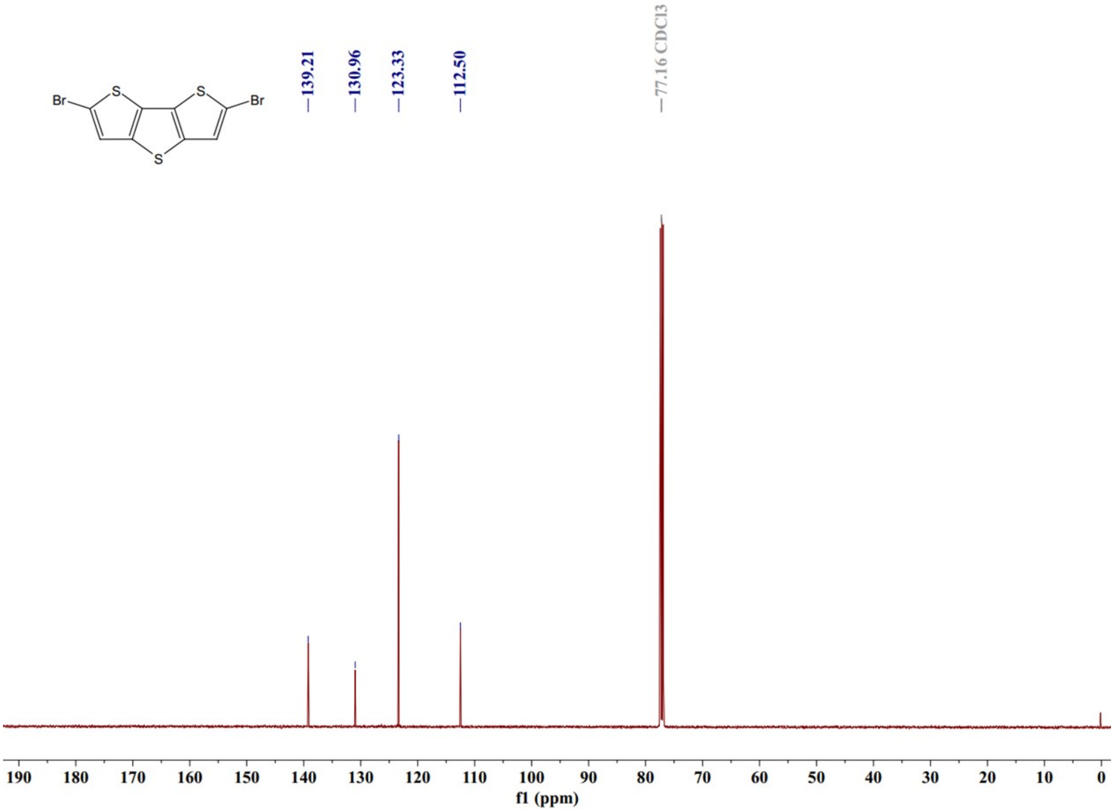


Figure S2. ^{13}C NMR spectrum of **DB-DTT**.

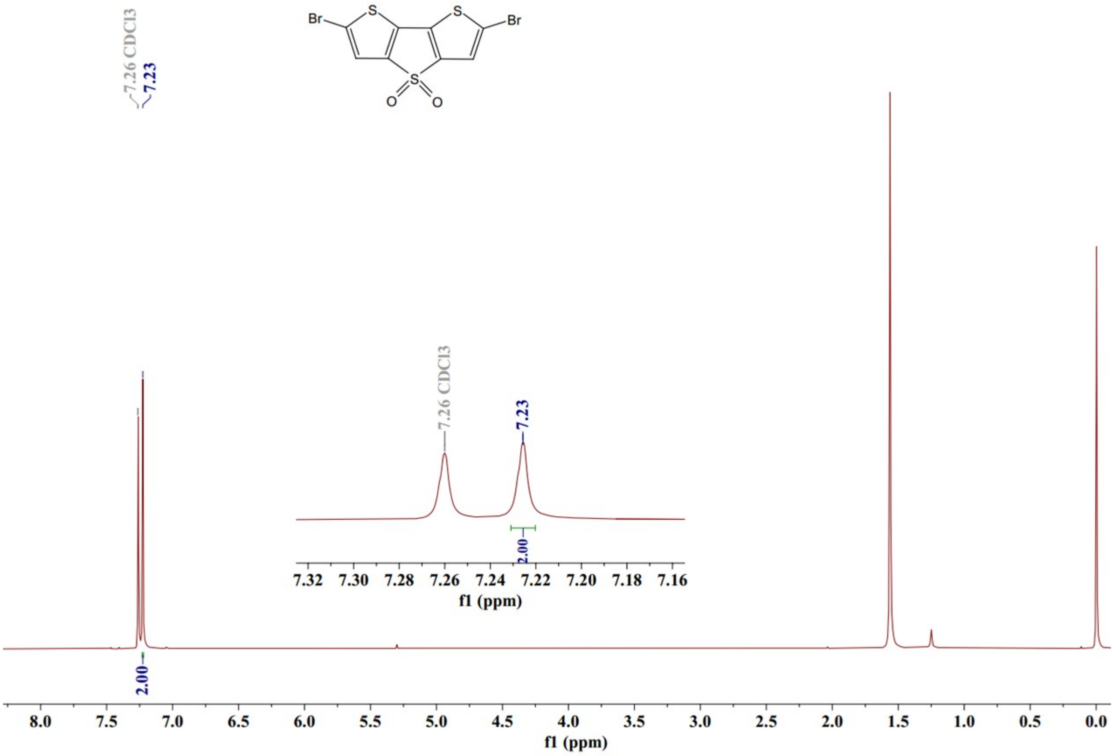


Figure S3. ^{1}H NMR spectrum of **DB-DTTO**.

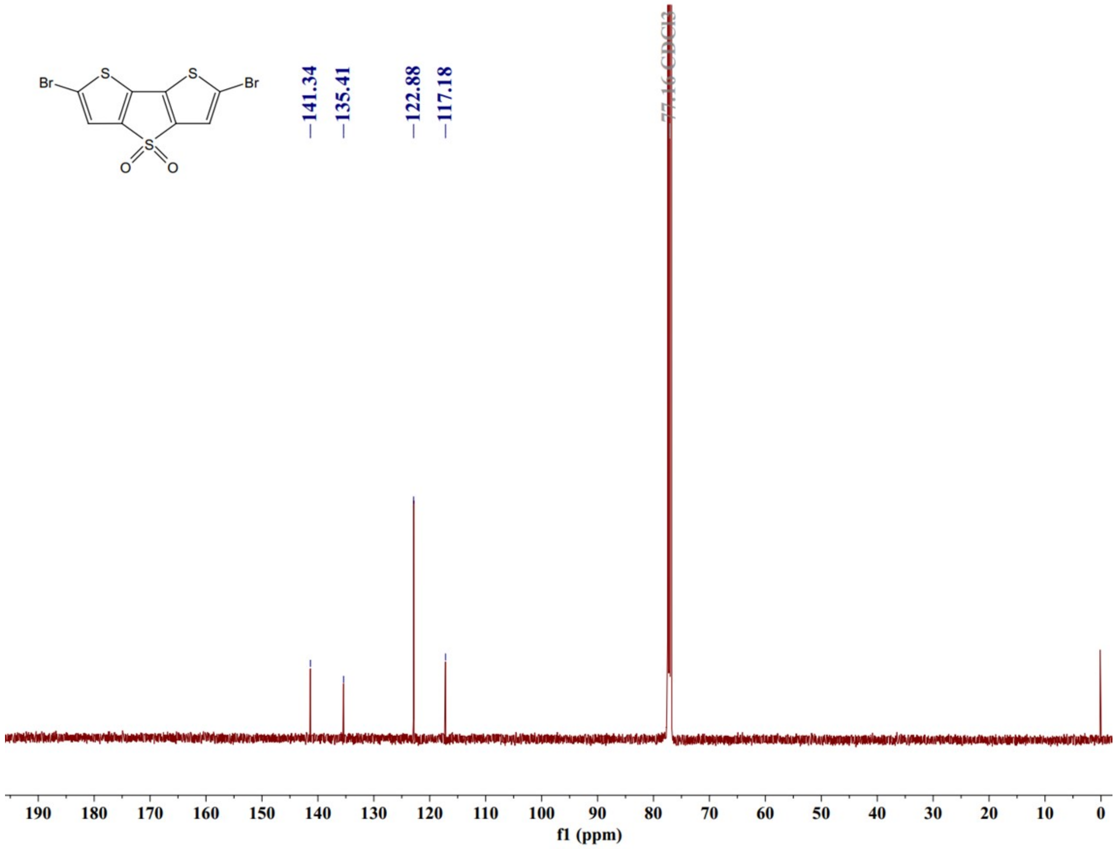


Figure S4. ^{13}C NMR spectrum of **DB-DTTO**.

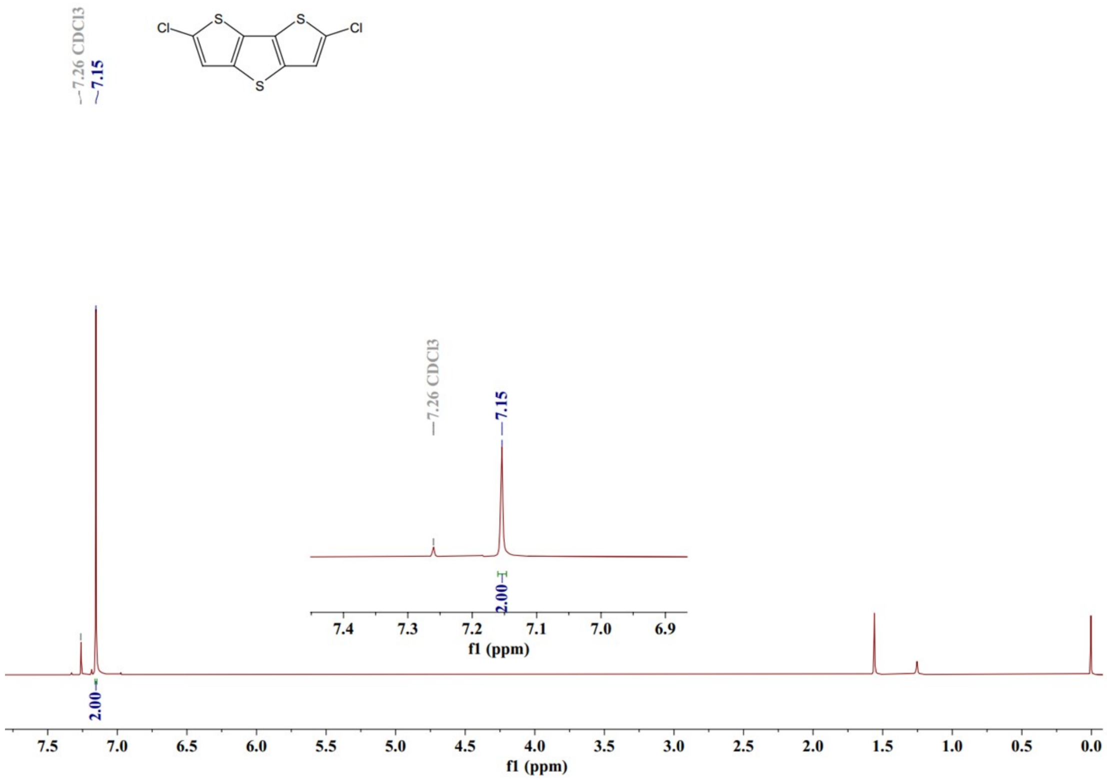


Figure S5. ^{1}H NMR spectrum of **DC-DTT**.

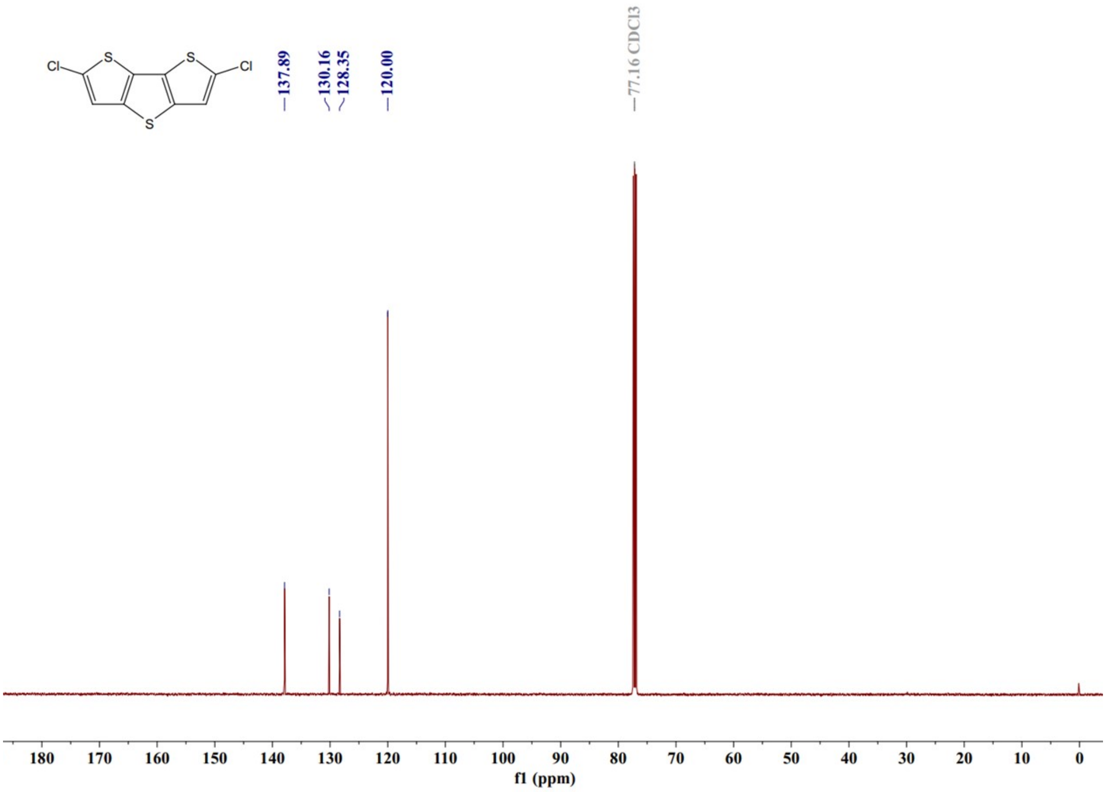


Figure S6. ^{13}C NMR spectrum of **DC-DTT**.

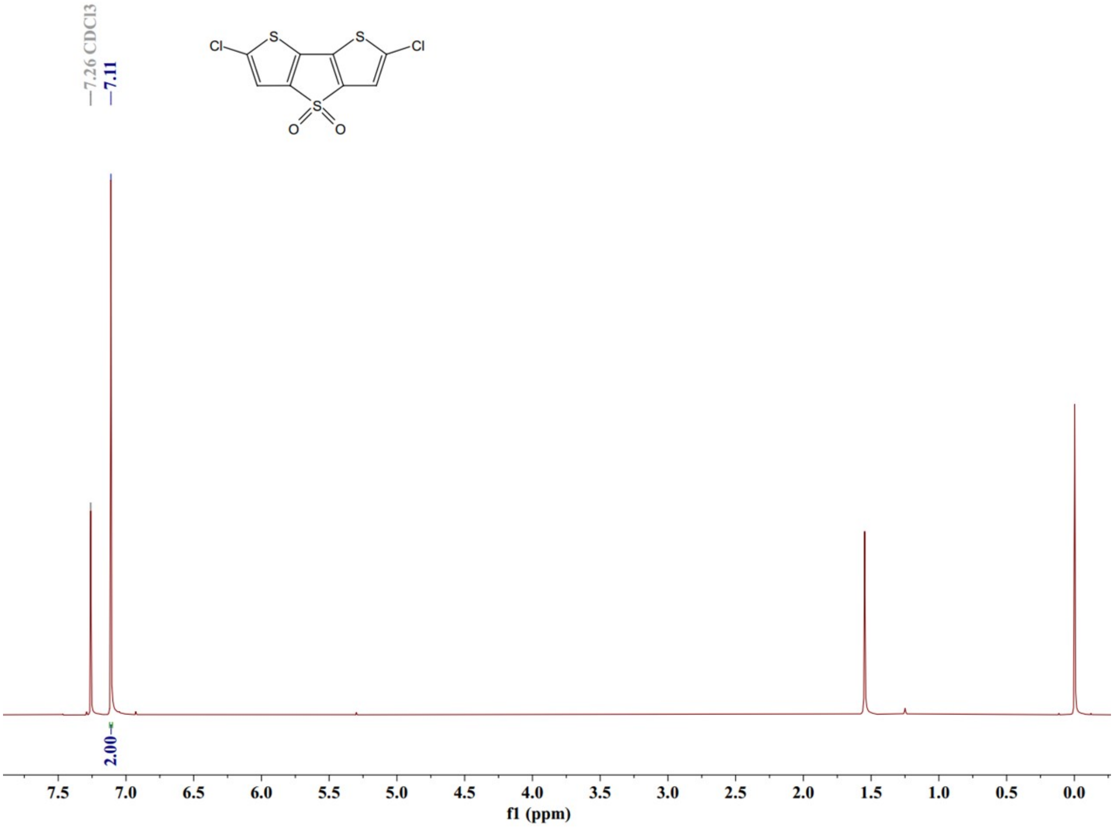


Figure S7. ^{1}H NMR spectrum of **DC-DTTO**.

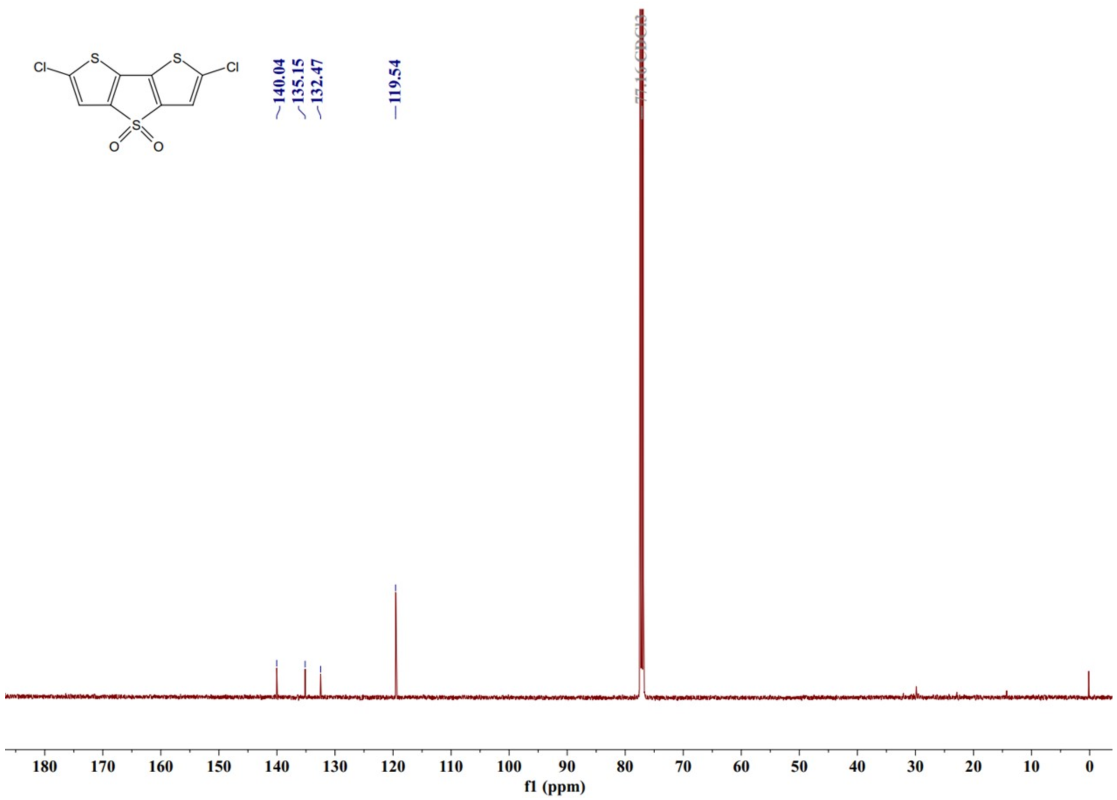


Figure S8. ^{13}C NMR spectrum of **DC-DTTO**.

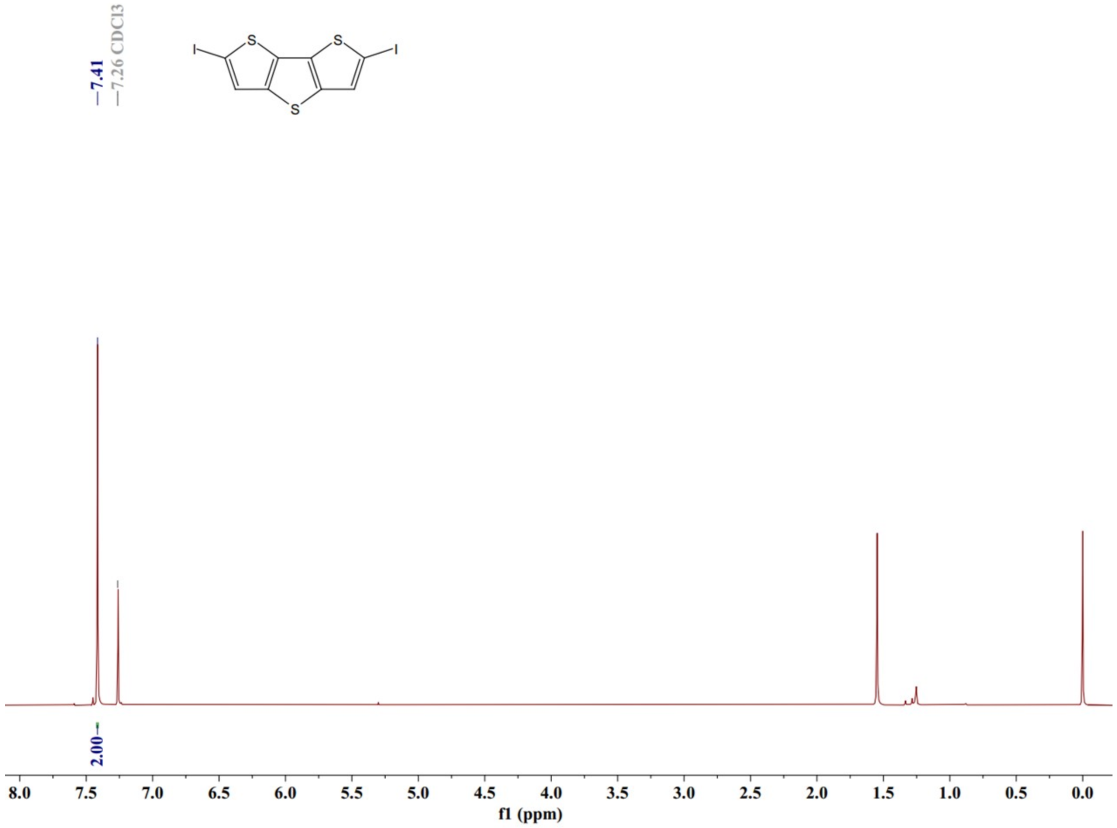


Figure S9. ^{1}H NMR spectrum of **DI-DTT**.

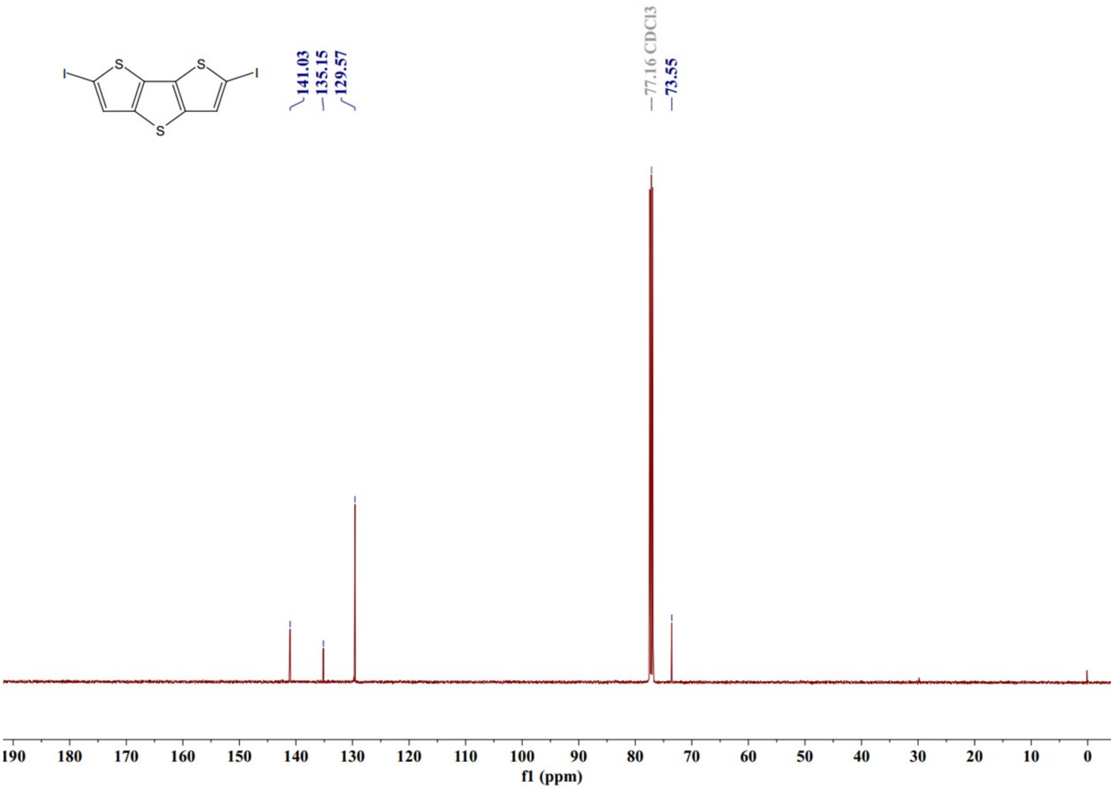


Figure S10. ^{13}C NMR spectrum of **DI-DTT**.

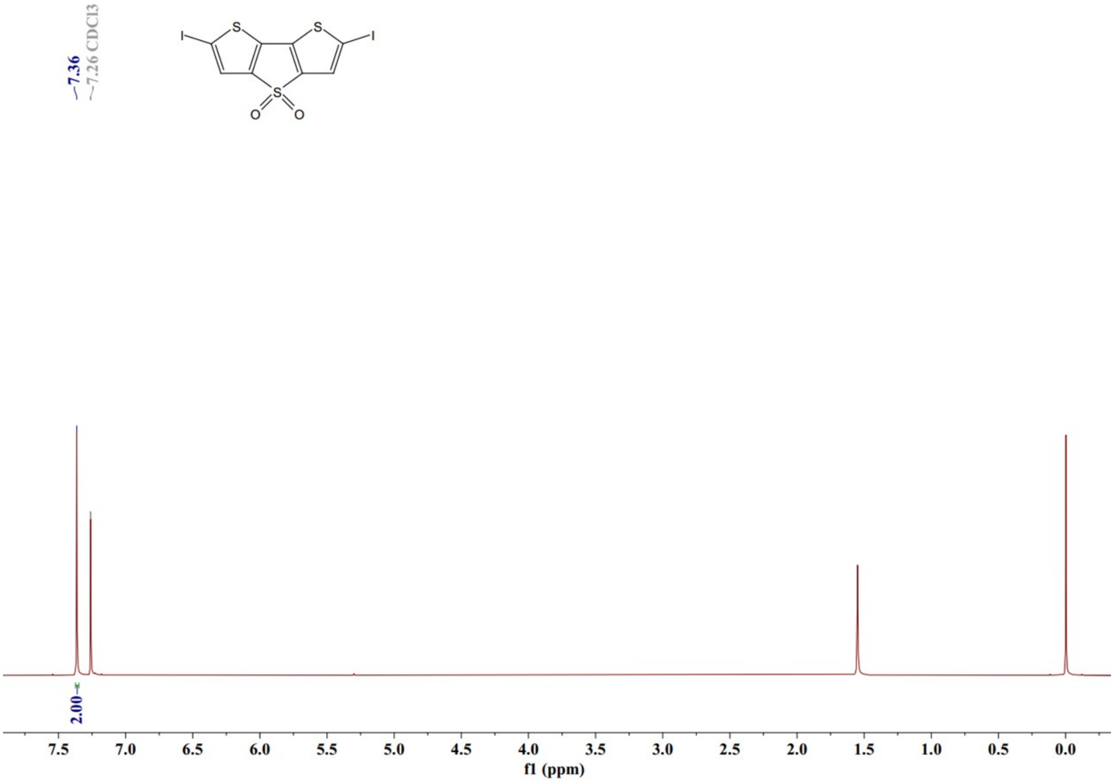


Figure S11. ^{1}H NMR spectrum of **DI-DTTO**.

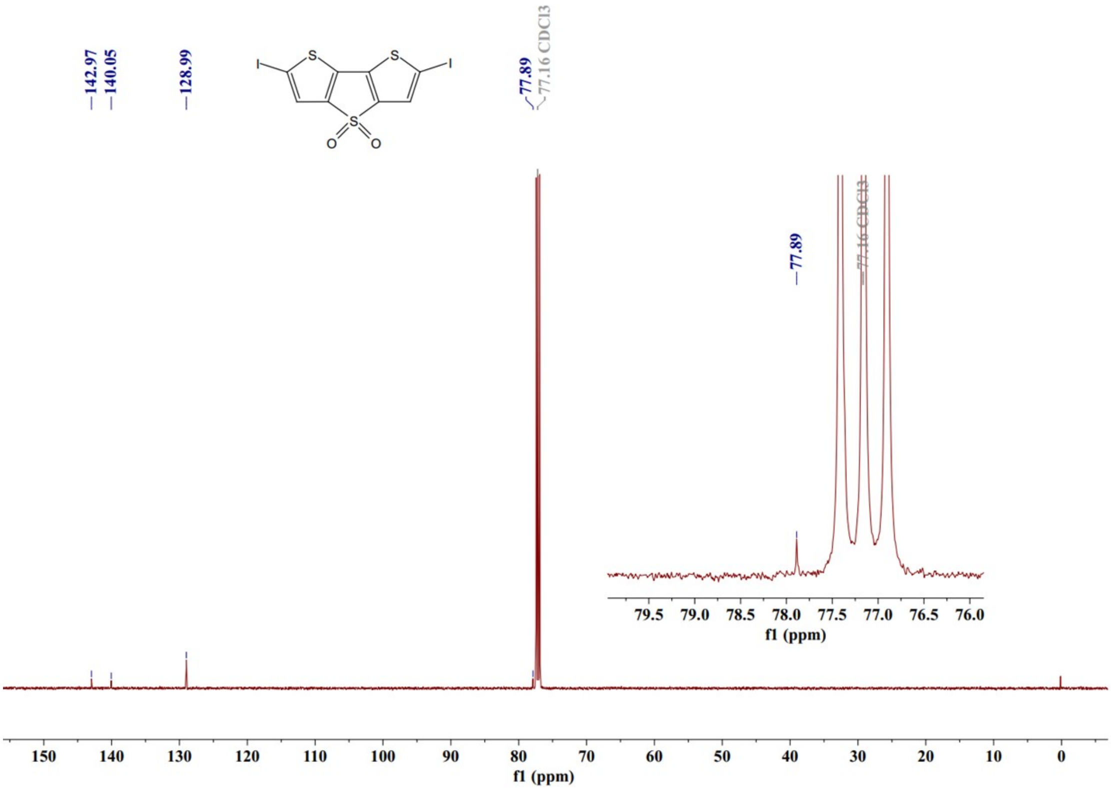


Figure S12. ^{13}C NMR spectrum of **DI-DTTO**.

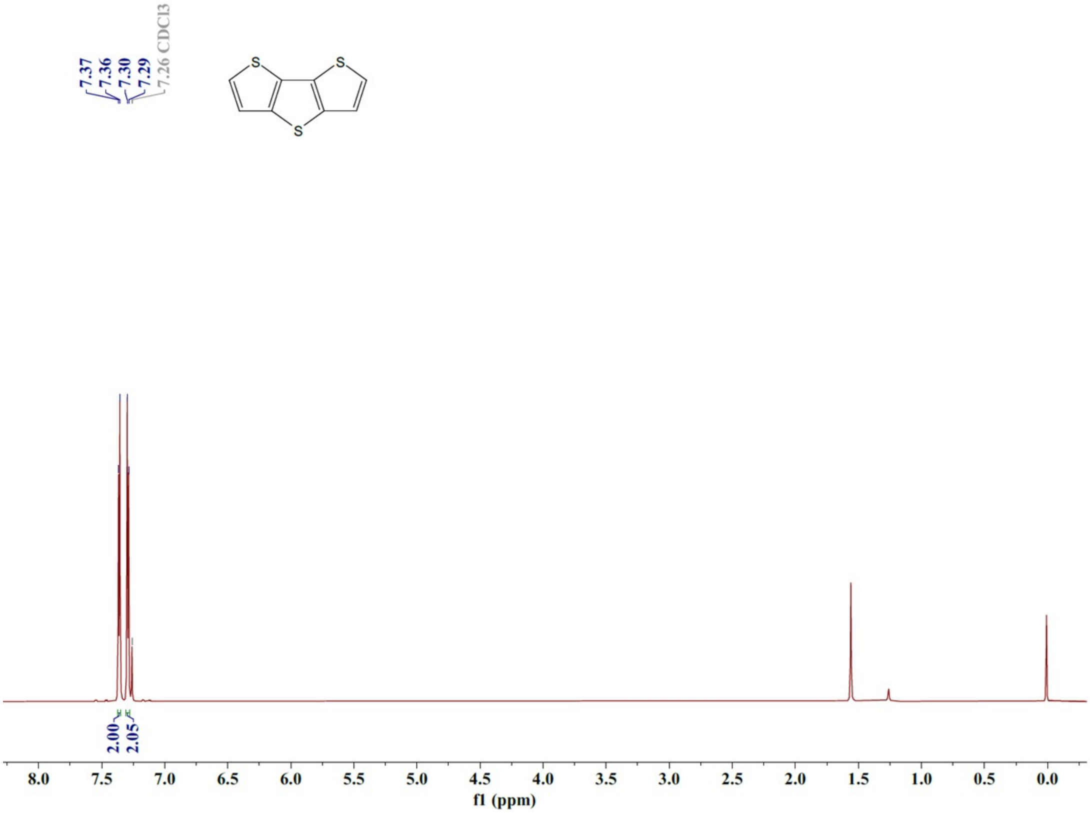


Figure S13. ^{1}H NMR spectrum of **DTT**.

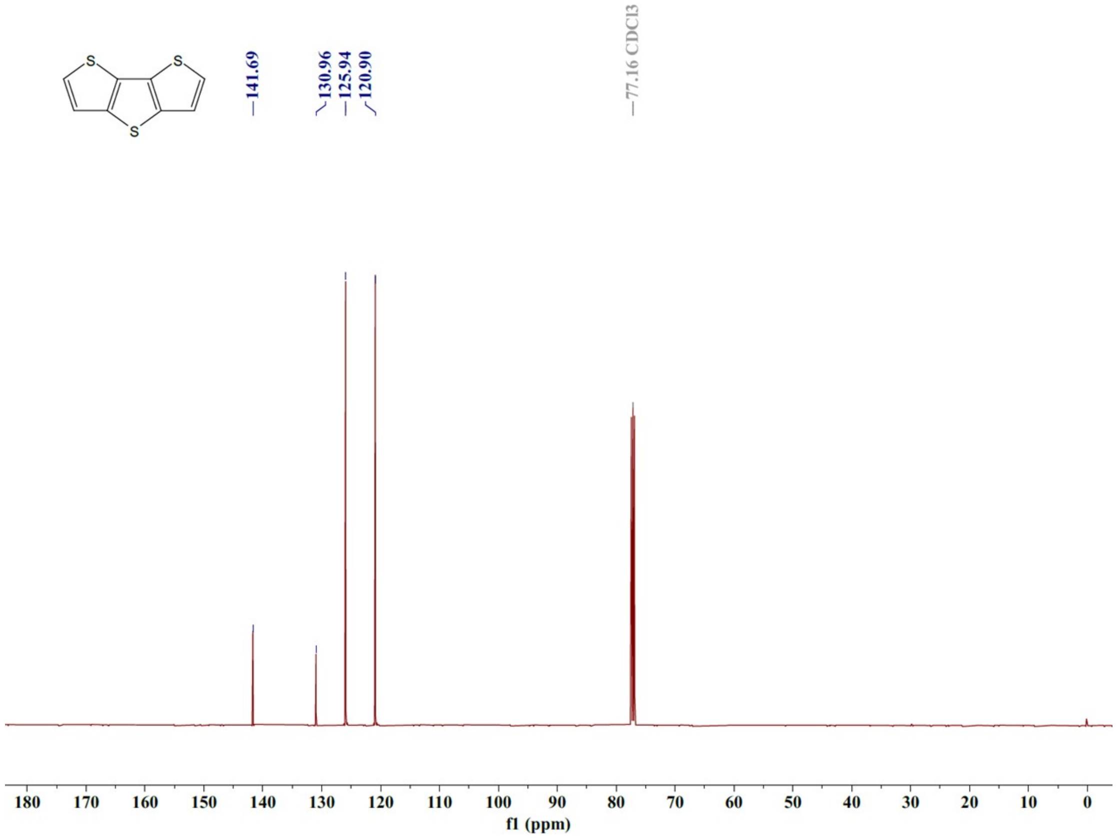


Figure S14. ^{13}C NMR spectrum of **DTT**.

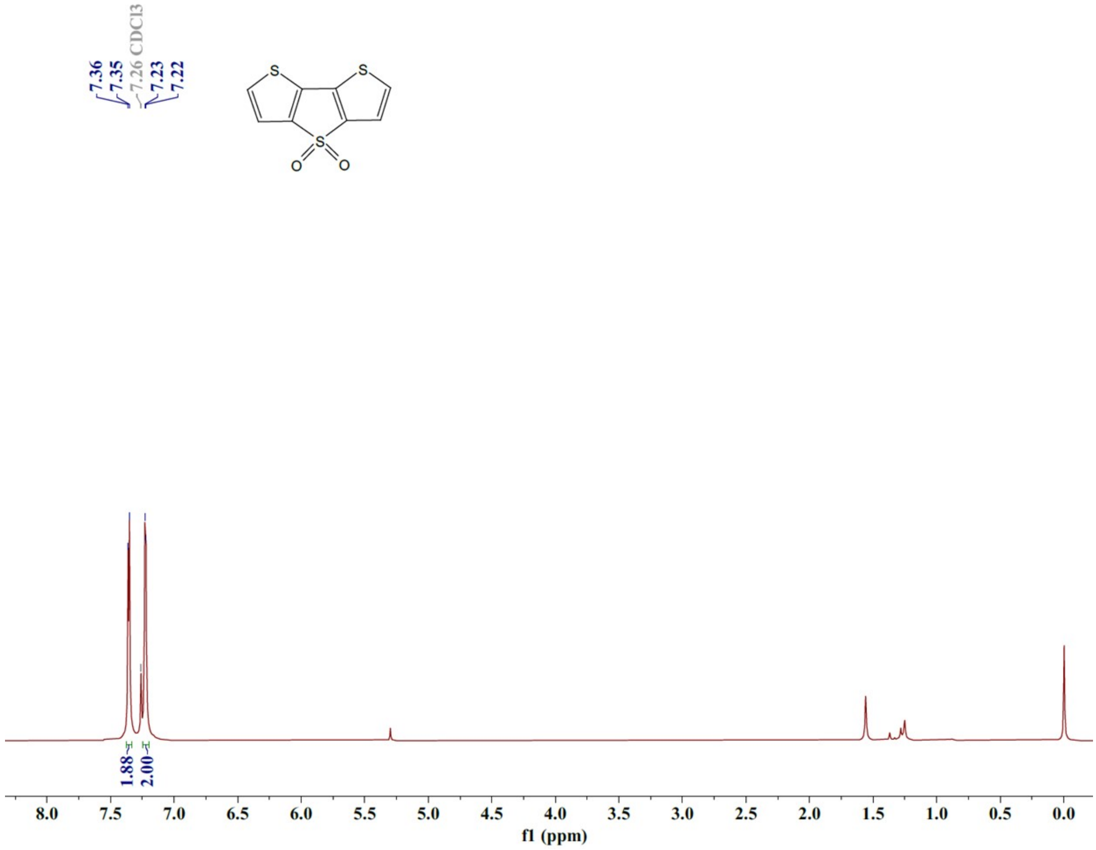


Figure S15. ^{1}H NMR spectrum of **DTTO**.

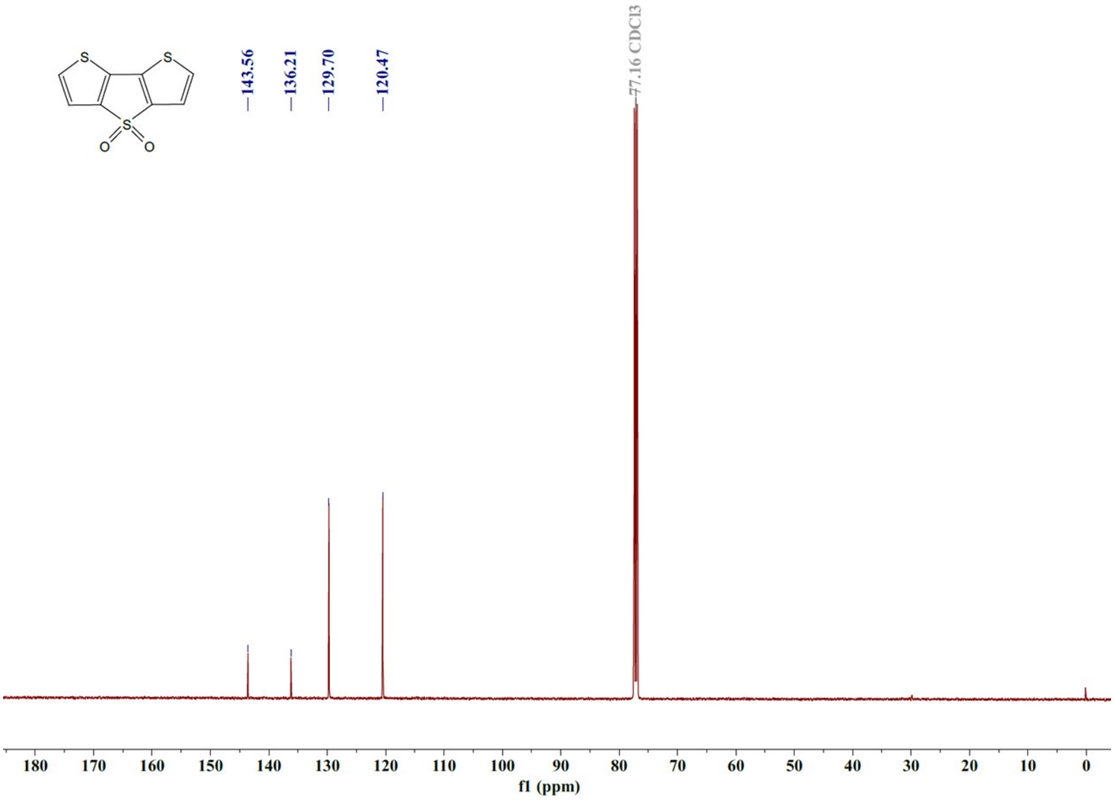


Figure S16. ^{13}C NMR spectrum of **DTTO**.

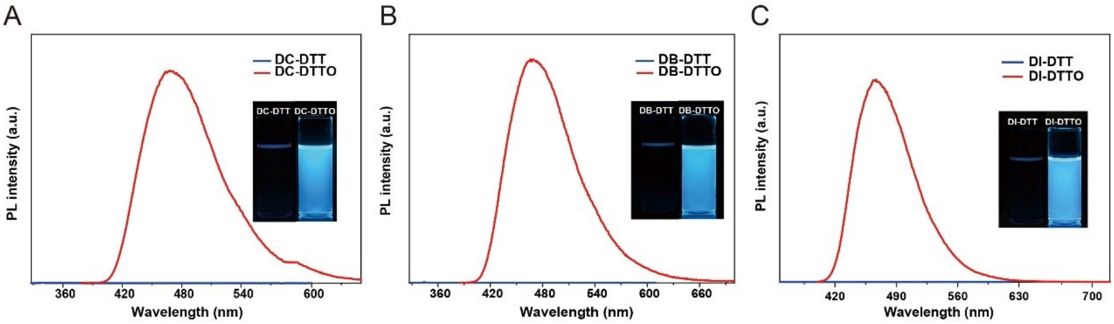


Figure S17. PL spectra of halogens substituted DTT and DTTO in THF. Inset: fluorescence photograph of halogens substituted DTT and DTTO in THF, respectively, taken under 365 nm UV irradiation.

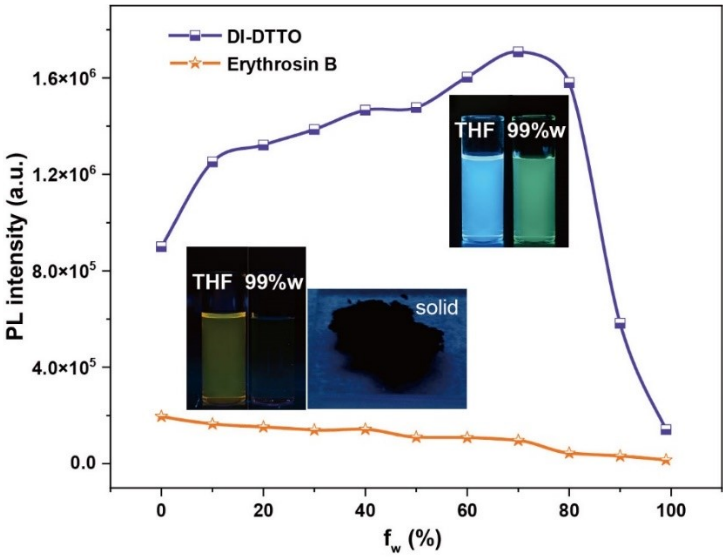


Figure S18. Plots of DI-DTTO and Erythrosin B in H_2O/THF mixtures. Inset: fluorescence photograph of DI-DTTO and Erythrosin B in pure THF and in 99% H_2O/THF mixtures, and Erythrosin B in solid state taken under 365 nm UV irradiation.

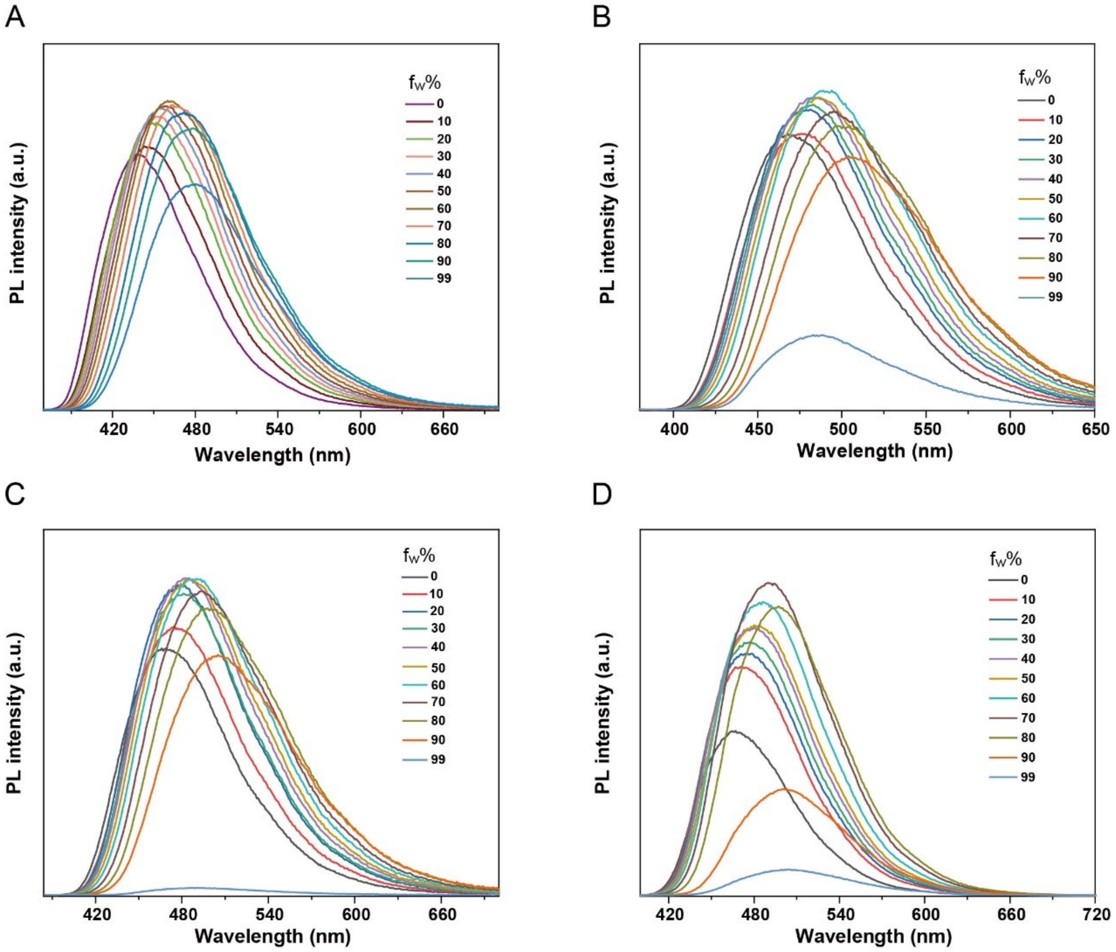


Figure S19. PL spectra of (A) DTTO, (B) DC-DTTO, (C) DB-DTTO and (D) DI-DTTO in THF/H_2O mixtures.

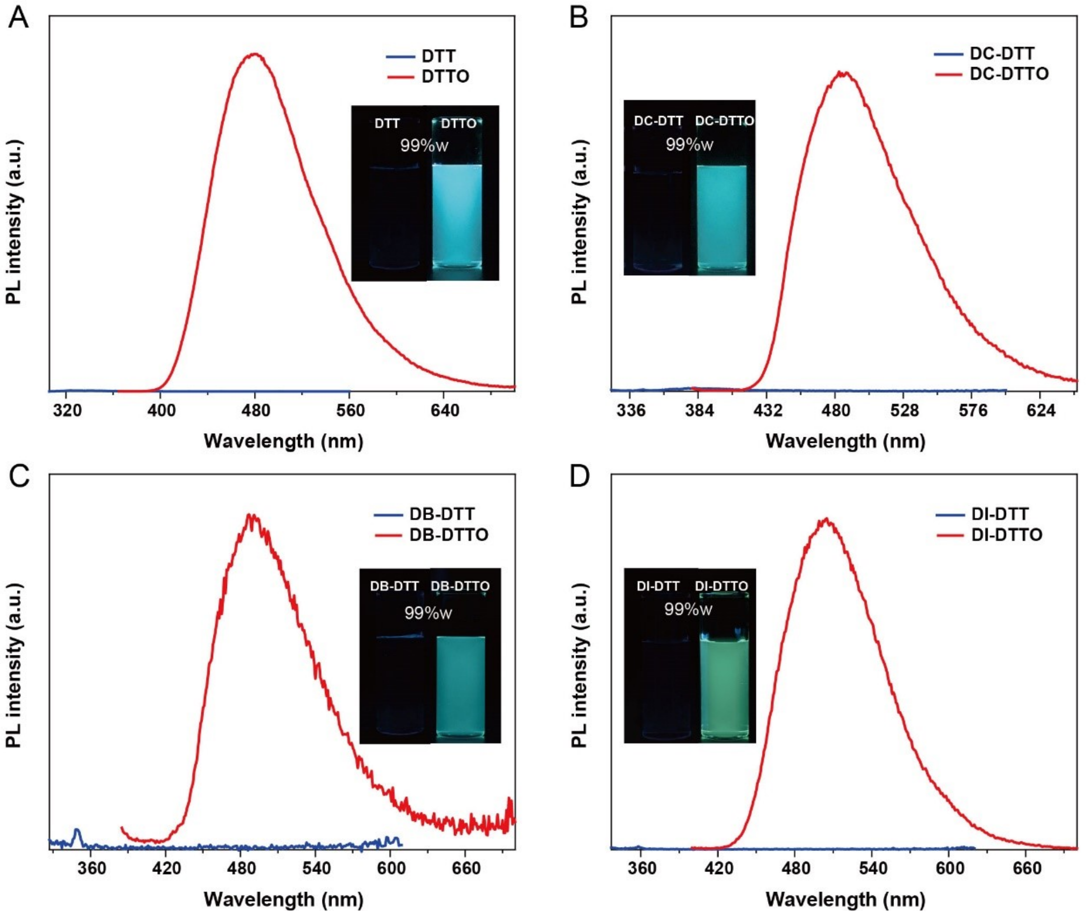


Figure S20. PL spectra of DTTs and DTTOs in 99% H_2O/THF mixtures. Inset: fluorescence photograph of DTTs and DTTOs in 99% H_2O/THF mixtures, respectively, taken under 365 nm UV irradiation.

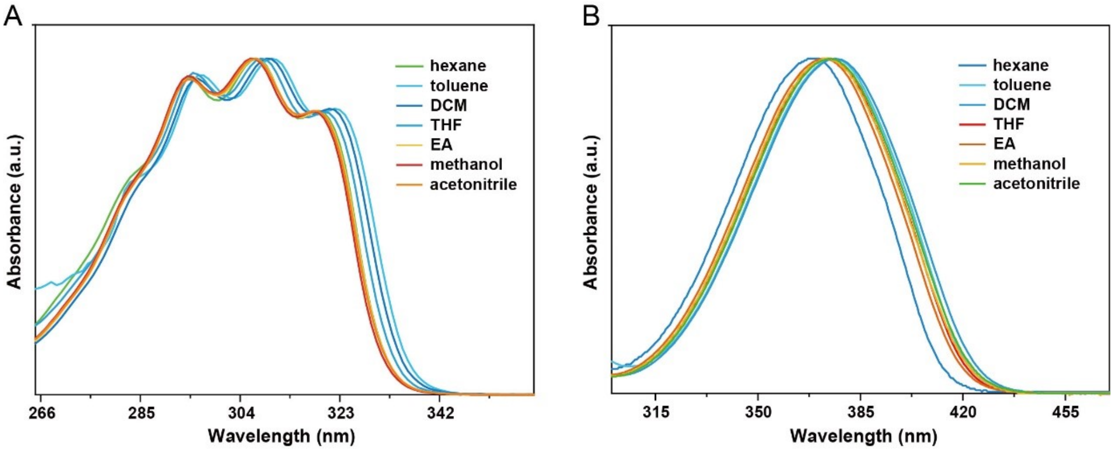


Figure S21 The UV-vis spectrums of DC-DTT (A) and DC-DTTO (B) in different polarity solvents.

Supplementary Table S1 Crystallographic and structural refinement data of DTTO, DC-DTTO, DB-DTTO, DI-DTTO, DTT and DI-DTT.

	DTTO	DC-DTTO
CCDC	2378966	2378911
Empirical formula	$C_8H_4O_2S_3$	$C_8H_2O_2S_3Cl_2$
Formula weight	228.29	297.18
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a/Å	9.756(2)	16.031(3)
b/Å	12.219(2)	6.9802(14)
c/Å	7.5175(15)	9.3455(19)
α/°	90	90
β/°	102.31(3)	101.26(3)
γ/°	90	90
Volume/Å^3	875.5(3)	1025.6(4)
Z	4	4
ρ_{calc}g/cm^3	1.732	1.925
μ/mm^{-1}	0.802	1.213
F(000)	464.0	592.0
Crystal size/mm^3	0.588 × 0.376 × 0.087	0.46 × 0.30 × 0.22
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.67 to 50.03	6.386 to 50.026
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-8 \leq l \leq 8$	$-18 \leq h \leq 18$, $-8 \leq k \leq 8$, $-11 \leq l \leq 11$
Reflections collected	3495	3862
Independent reflections	773 [R_{int} = 0.0569, R_{sigma} = 0.0506]	902 [R_{int} = 0.0722, R_{sigma} = 0.1067]
Data/restraints/parameters	773/0/61	902/0/70

Goodness-of-fit on F^2	1.090	1.086
Final R indexes [I>=2σ (I)]	$R_1 = 0.0334$, $wR_2 = 0.0936$	$R_1 = 0.0353$, $wR_2 = 0.0855$
Final R indexes [all data]	$R_1 = 0.0354$, $wR_2 = 0.0966$	$R_1 = 0.0386$, $wR_2 = 0.0874$
Largest diff. peak/hole / e Å^{-3}	0.38/-0.34	0.60/-0.44

	DB-DTTO	DI-DTTO
CCDC	2378965	2378958
Empirical formula	$C_8H_2Br_2O_2S_3$	$C_8H_2I_2O_2S_3$
Formula weight	386.10	480.08
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	C2/c	$Pca2_1$
a/Å	16.412(3)	18.519(4)
b/Å	6.9676(14)	4.9155(10)
c/Å	9.5683(19)	12.812(3)
α/°	90	90
β/°	99.34(3)	90
γ/°	90	90
Volume/Å^3	1079.6(4)	1166.2(4)
Z	4	4
ρ_{calc}g/cm^3	2.375	2.734
μ/mm^{-1}	8.060	5.904
F(000)	736.0	880.0
Crystal size/mm^3	0.27 × 0.23 × 0.11	0.417 × 0.079 × 0.070
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.366 to 49.716	6.36 to 50.026

Index ranges	$-19 \le h \le 19$, $-8 \le k \le 8$, $-11 \le l \le 11$	$-21 \le h \le 22$, $-5 \le k \le 5$, $-15 \le l \le 15$
Reflections collected	4131	8041
Independent reflections	933 [R_{int} = 0.0898, R_{sigma} = 0.0709]	2043 [R_{int} = 0.1098, R_{sigma} = 0.1255]
Data/restraints/parameters	933/0/70	2043/1/137
Goodness-of-fit on F^2	1.168	1.030
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0525, wR_2 = 0.1169	R_1 = 0.0524, wR_2 = 0.1010
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1686	R_1 = 0.0615, wR_2 = 0.1135
Largest diff. peak/hole / e Å^{-3}	0.91/-1.12	1.28/-1.08

	DTT [2]	DI-DTT [3]
Empirical formula	$C_8H_4S_3$	$C_8H_2I_2S_3$
Formula weight	196.29	448.08
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	10.277(4)	13.223(9)
b/Å	3.9383(14)	4.161(3)
c/Å	19.313(7)	19.785(14)
α/°	90.00	90.00
β/°	102.528(5)	96.339(10)
γ/°	90.00	90.00
Volume/Å^3	763.1(5)	1081.9(13)
Z	4	4
ρ_{calc}g/cm^3	1.709	2.751
μ/mm^{-1}	0.886	6.341

F(000)	400.0	816.0
Crystal size/mm^3	0.2 × 0.15 × 0.1	0.5 × 0.07 × 0.04
Radiation	MoKα ($\lambda = 0.71073$)	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.06 to 60.08	4.14 to 58
Index ranges	$-14 \leq h \leq 14$, $-5 \leq k \leq 5$, $-26 \leq l \leq 26$	$-18 \leq h \leq 17$, $-5 \leq k \leq 5$, $-26 \leq l \leq 26$
Reflections collected	11077	9493
Independent reflections	2245 [R_{int}= 0.0601, R_{sigma} = 0.0474]	2872 [R_{int} = 0.0843, R_{sigma} = 0.0966]
Data/restraints/parameters	2245/0/100	2872/0/118
Goodness-of-fit on F^2	1.017	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0350, wR_2 = 0.0729	R_1 = 0.0635, wR_2 = 0.1397
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.0817	R_1 = 0.0939, wR_2 = 0.1521
Largest diff. peak/hole / e Å^{-3}	0.46/-0.38	2.06/-1.26

References:

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