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Supporting Information for

Synthesis and Structures of Unsymmetrical Bull's Horn-Shaped Heptathienoacenes with Isomeric Location of Sulfur Atoms

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1. General information

Ether and tetrahydrofuran (THF) for use on vacuum line were freshly distilled from sodium/benzophenone prior to use. *t*-BuLi (pentane) and *n*-BuLi (hexane) were obtained from Energy Chemical prior to use, and their concentrations were determined by titration with *N*-pivaloyl-*o*-toluidine.[1] Column chromatography was carried out on silica gel (300-400 mesh). Analytical thin-layer chromatography was performed on glass plates of silica gel GF-254 with detection by UV. Standard techniques for synthesis under inert atmosphere, using gasbag and Schlenk glassware equipped with an 8 mm PTFE vacuum stopcock, were employed. All starting materials and reagents were commercially available.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on 300 or 400 MHz NMR instruments using $CDCl_3$ (δH (7.26 ppm) and $CDCl_3$ δ C (77.00 ppm)) as solvent. IR spectra were obtained using an FT-IR instrument. MS analysis was carried out at 70 eV MS spectrometer using a direct insertion. HRMS analysis was carried out on mass spectrometers equipped with ESI and DART Positive. Melting point determination was taken on a Melt-Temp apparatus and was uncorrected. UV-vis spectra were obtained with a double-beam spectrophotometer at room temperature. Cyclic voltammetry (CV) was performed on an electrochemical analyzer with a three-electrode cell in the solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in CH_2Cl_2. Platinum electrode (0.6 cm^2), Pt wire and Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively. The X-ray crystallographic analyses were performed using crystals of compounds **1**-**4** with the size 0.12 × 0.10 × 0.08, 0.21 × 0.14 × 0.07, 0.21 × 0.11 × 0.06 and 0.22 × 0.18 × 0.13 mm, respectively. The intensity data were collected on a diffractometer with a CCD detector using M*o* Kα radiation (λ = 0.71073 Å) and with the ω scan mode 100 K, 298 K, 150 K and 230 K, respectively. The data were corrected for Lorentz and polarization effects, and absorption corrections were performed using SADABS program.[2] The crystal structures were solved using the SHELXTL program and refined using full-matrix least-squares.[3]

Further details are in the deposited CIF files. Slow evaporation of solutions of **1**-**4** in $CHCl_3$-CH_3OH (1:3, v/v) was employed for growing single crystals.

2. References

[1] J. Suffert, Simple Direct Titration of Organolithium Reagents Using N-Pivaloyl-*o*-toluidine and/or N-pivaloyl-*o*-benzylaniline. *J. Org. Chem*, 1989, **54**, 509-510.

[2] G. M. Sheldrick, *SADABS*, University of Gottingen: Germany, 1996.

[3] G. M. Sheldrick. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

3. NMR and HRMS spectra

NMR and HRMS spectra of **6**

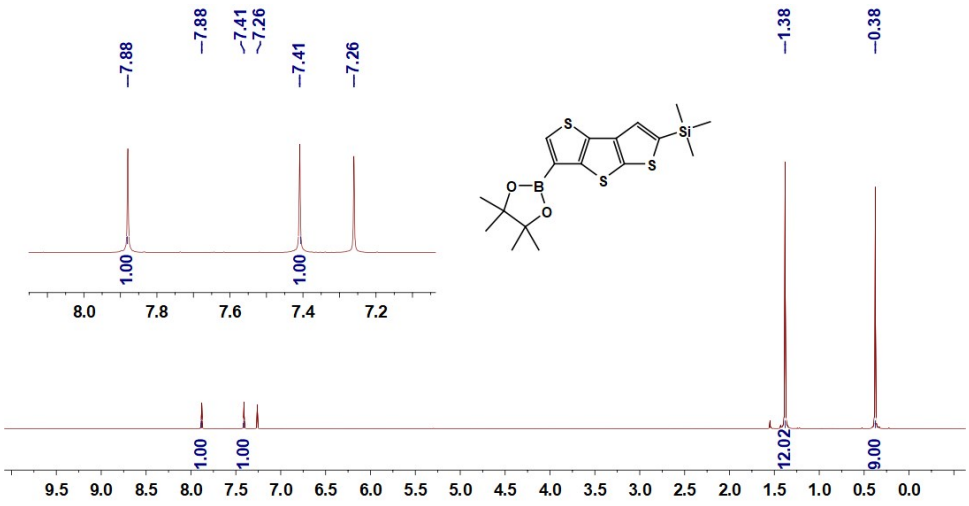


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**

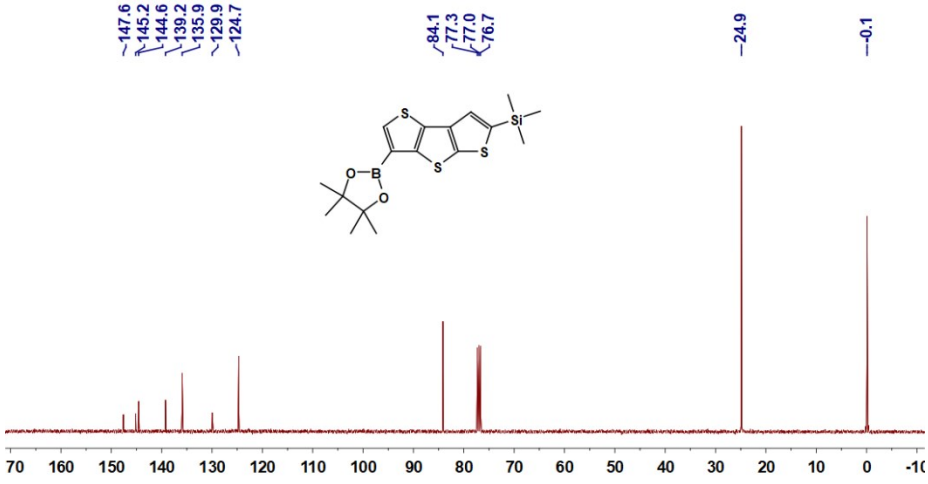


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6**

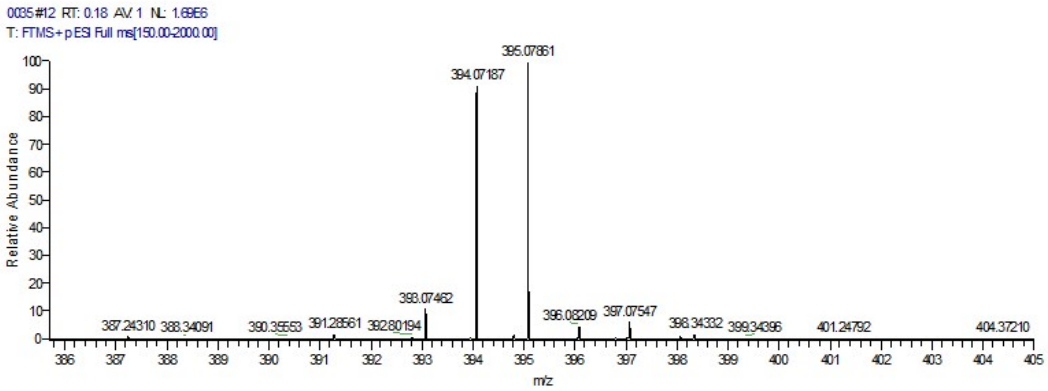


Figure S3. HRMS spectrum of **6**

NMR and HRMS spectra of **7**

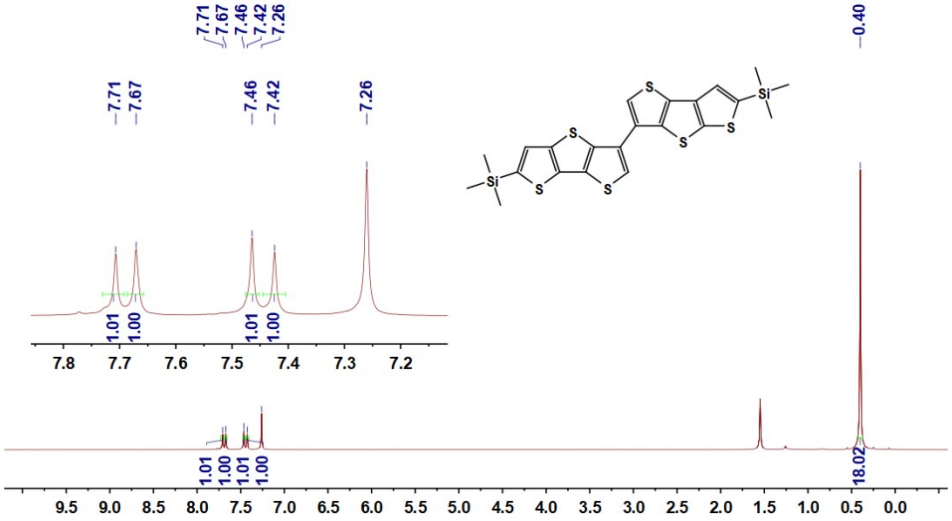


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

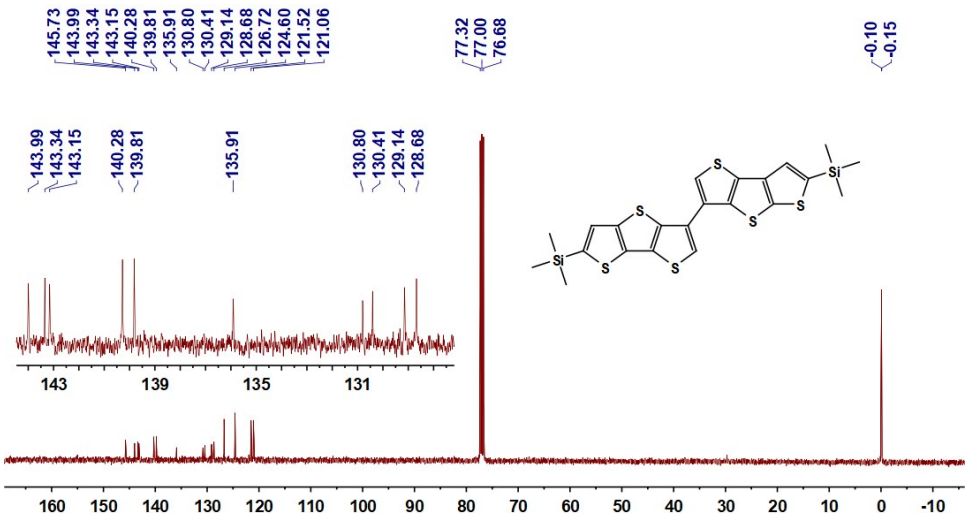


Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7**

Z-3: HRMS (ESI) m/z calcd for $C_{22}H_{22}S_6Si_2^+$ $(M)^+$ 533.95788, found 533.95788; calcd for $C_{22}H_{23}S_6Si_2^+$ $(M+H)^+$ 534.96570, found 534.96558.

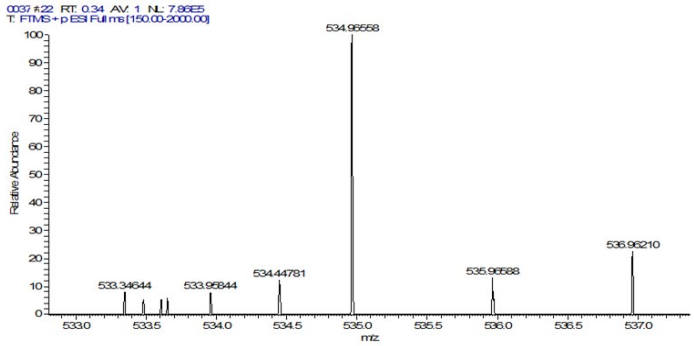


Figure S6. HRMS spectrum of **7**

NMR and HRMS spectra of **1**

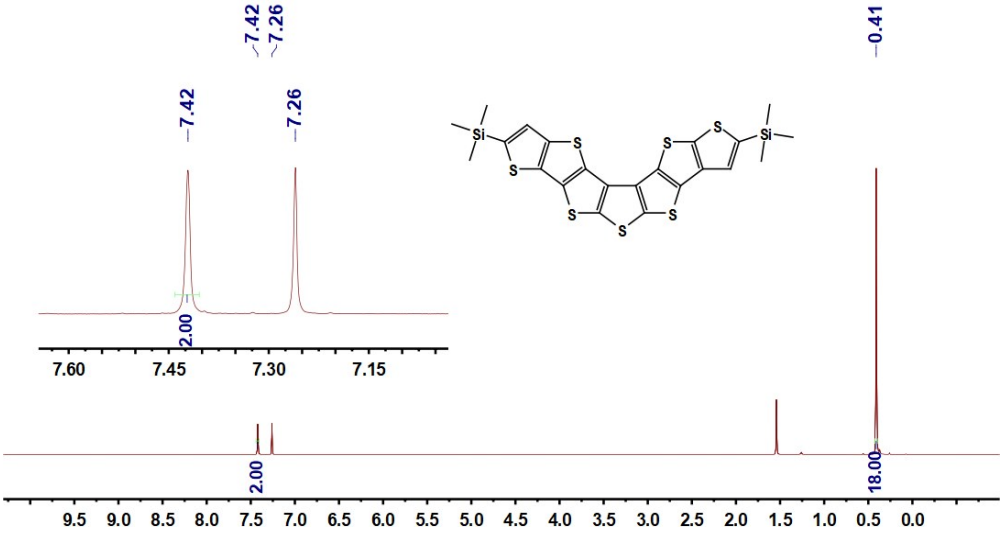


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**

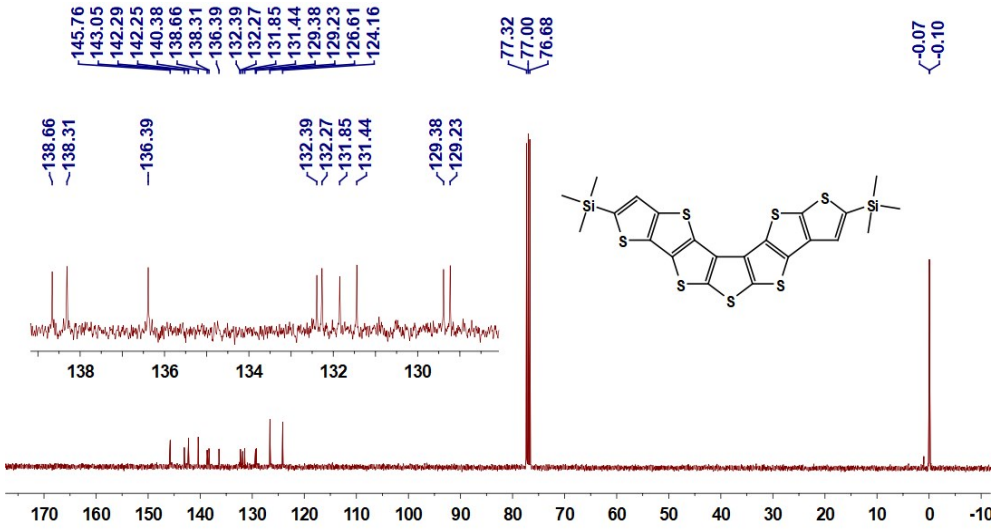


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1**

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : D20201231

Sample Serial Number: 1

Operator : DONG Date: 2020/06/01

Operation Mode: DART POSITIVE

Elemental composition search on mass 564.92

m/z= 559.92-569.92

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
564.9215	564.9221	-1.14	14.5	$C_{22}H_{21}S_7Si_2$
	564.9188	4.82	19.5	$C_{25}H_{17}S_6Si_2$

Figure S9. HRMS data of **1**

NMR and HRMS spectra of **9**

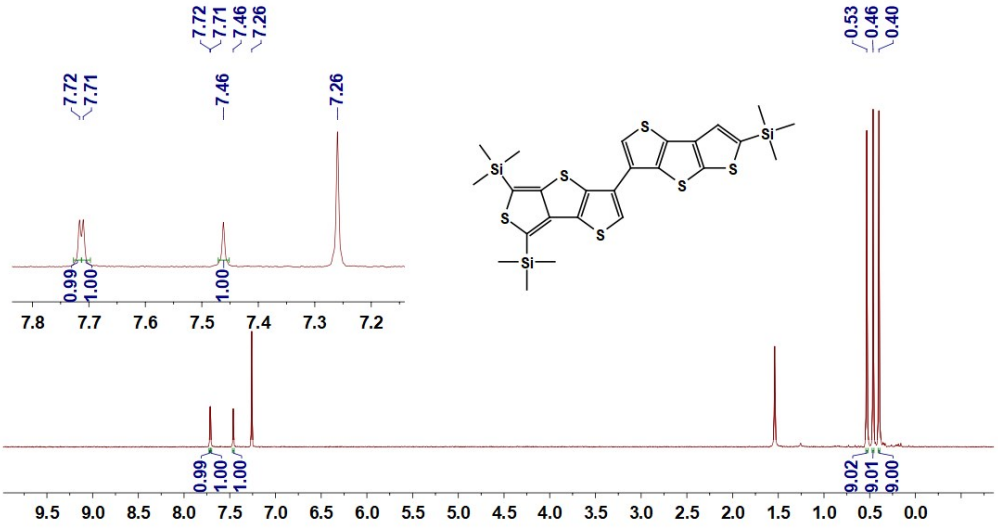


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **9**

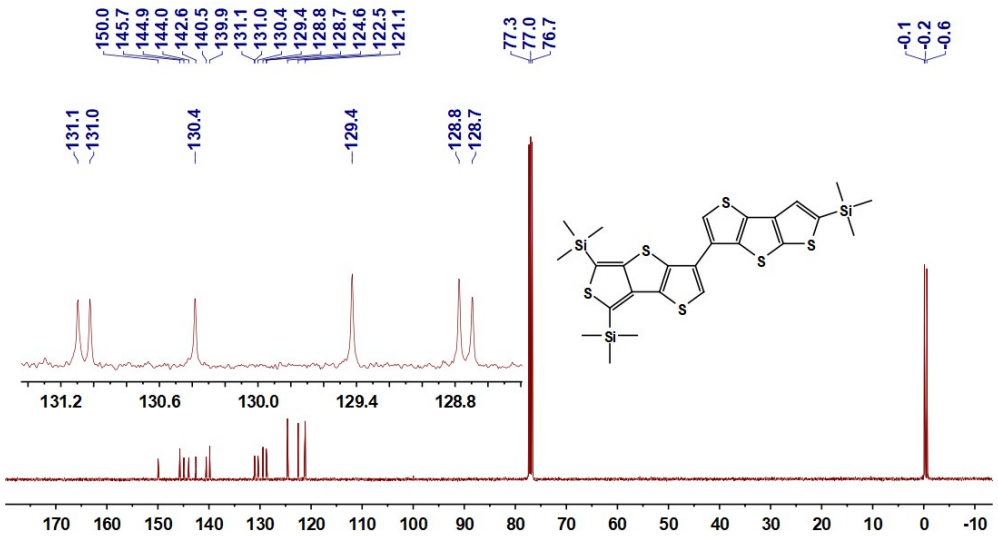


Figure S11. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9**

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: H-W200200

Sample Serial Number: 9

Operator: QHL Date: 2020/05/29

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 607.01

m/z= 602.01-612.01

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
607.0051	607.0052	-0.17	13.5	$C_{25}H_{31}S_6Si_3$
	607.0032	3.13	14.5	$C_{26}H_{28}FS_6Si_2$
	607.0028	3.80	10.5	$C_{23}H_{32}NaS_6Si_3$

Figure S12. HRMS data of **9**

NMR HRMS spectra of **2**

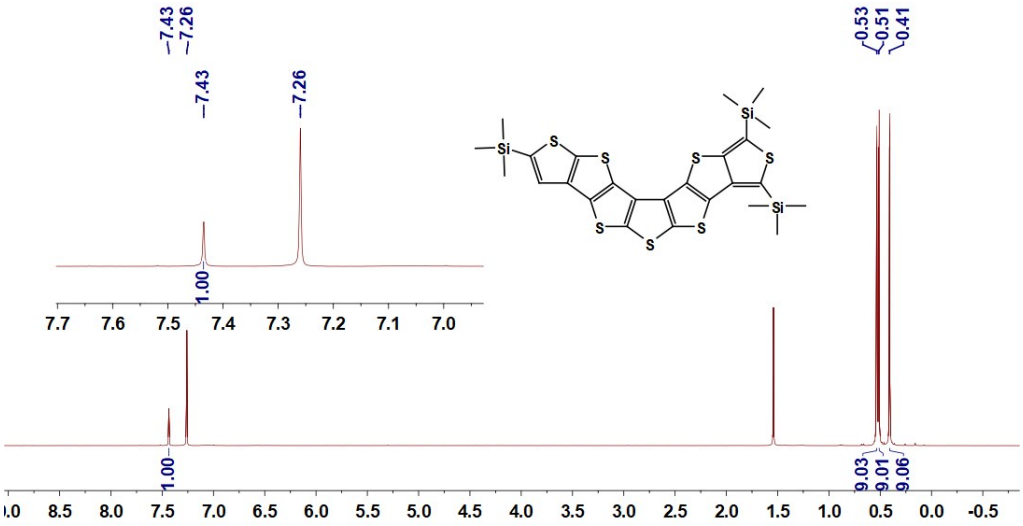


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**

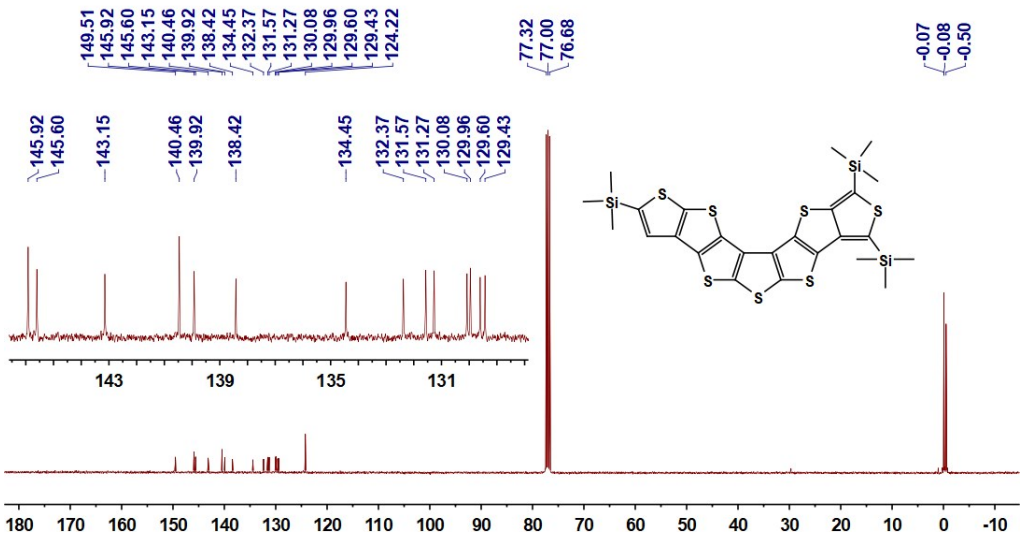


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2**

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: H-W200198

Sample Serial Number: 2

Operator: QHL Date: 2020/05/29

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 636.96

m/z= 631.96-641.96

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
636.9614	636.9617	-0.46	14.5	$C_{25}H_{29}S_7Si_3$
	636.9597	2.68	15.5	$C_{26}H_{26}FS_7Si_2$
	636.9592	3.32	11.5	$C_{23}H_{30}NaS_7Si_3$
	636.9583	4.83	19.5	$C_{28}H_{25}S_6Si_3$

Figure S15. HRMS data of **2**

NMR and HRMS spectra of **10**

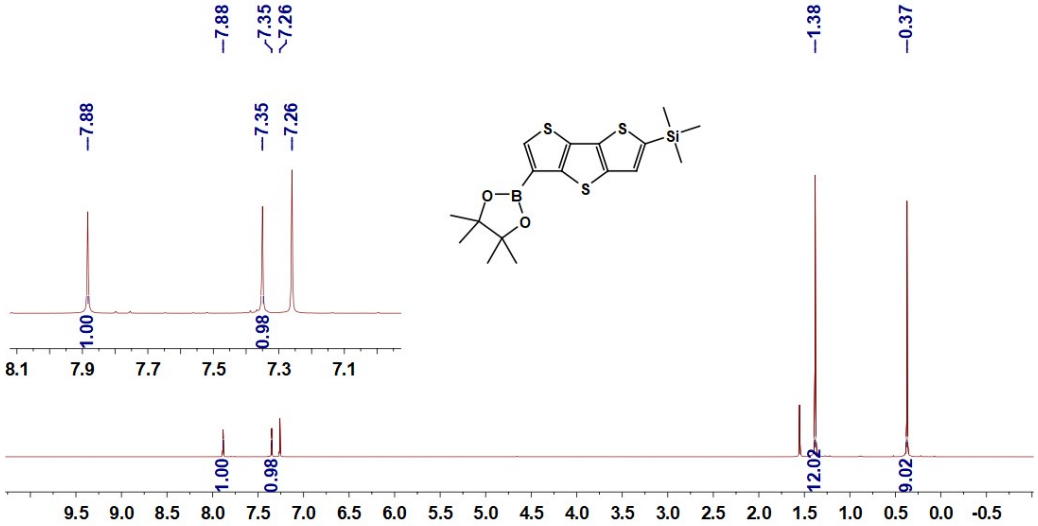


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

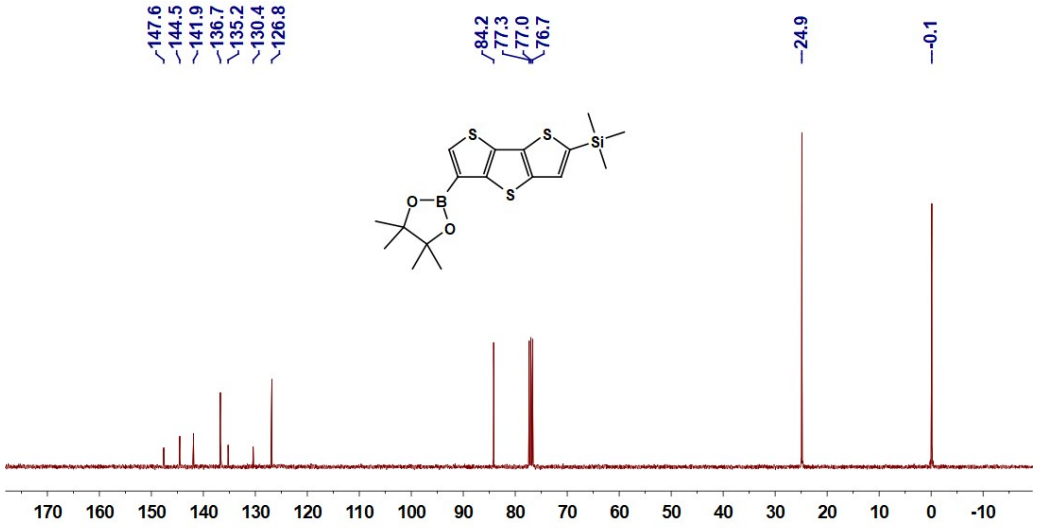


Figure S17. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number: W181547

Sample Serial Number: ZC-7-9-col-pp

Operator: Songw Date: 2018/11/01

Operation Mode: DART Positive Ion Mode

Elemental composition search on mass 394.08

m/z= 389.08-399.08

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
394.0831	394.0832	-0.20	7.0	$C_{17}H_{24}O_2{}^{10}BS_3Si$
	394.0836	-1.22	9.0	$C_{17}H_{22}O_3N_2S_2Si$
	394.0838	-1.81	9.0	$C_{18}H_{22}O_2N_2S_3$
	394.0850	-4.79	12.5	$C_{19}H_{18}O_4N{}^{10}BSSi$

Figure S18. HRMS data of **10**

NMR and HRMS spectra of **11**

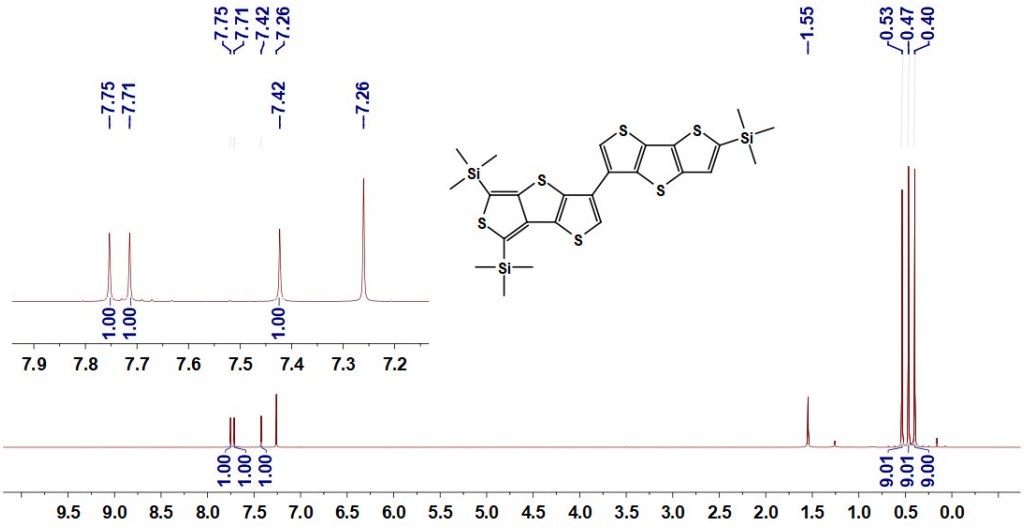


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

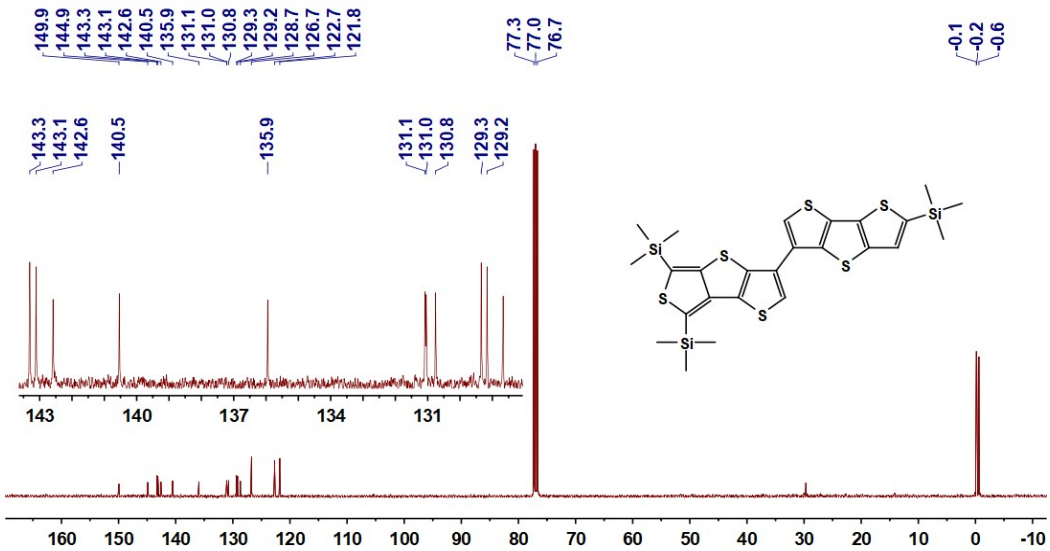


Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11**

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: H-W200201

Sample Serial Number: 11

Operator: QHL Date: 2020/05/29

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 607.00

m/z= 602.00-612.00

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
607.0046	607.0052	-0.97	13.5	$C_{25}H_{31}S_6Si_3$
	607.0032	2.32	14.5	$C_{26}H_{28}FS_6Si_2$
	607.0028	2.99	10.5	$C_{23}H_{32}NaS_6Si_3$
	607.0019	4.58	18.5	$C_{28}H_{27}S_5Si_3$

Figure S21. HRMS data of **11**

NMR and HRMS spectra of **3**

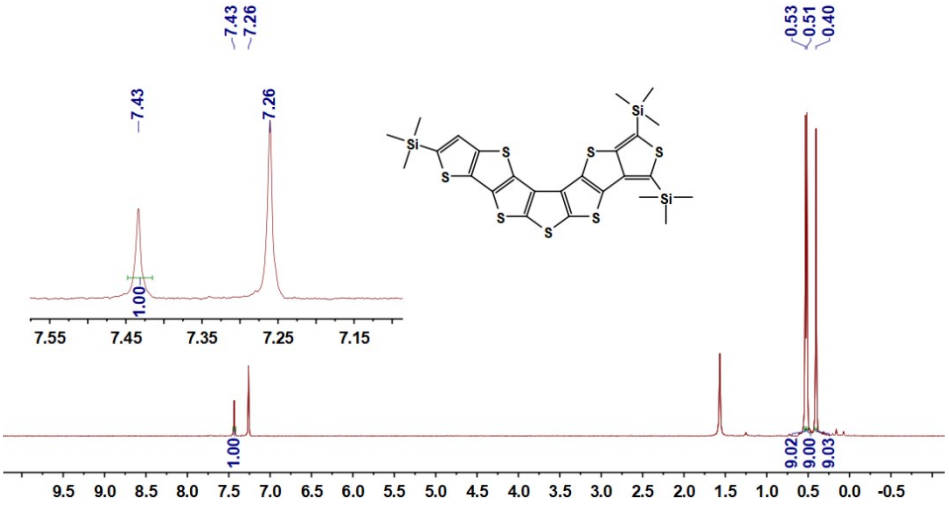


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**

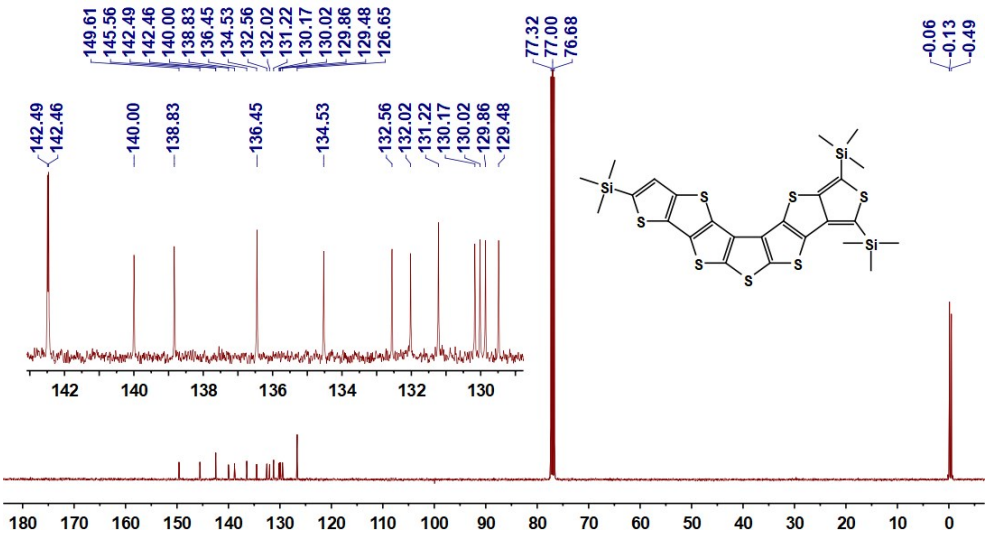


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**

Instrument: Thermo Scientific Q Exactive HF Orbitrap-FTMS

Card Serial Number: H-W200199

Sample Serial Number: 3

Operator: QHL Date: 2020/05/29

Operation Mode: ESI Positive Ion Mode

Elemental composition search on mass 636.96

m/z= 631.96-641.96

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
636.9609	636.9612	-0.47	15.5	$C_{26}H_{25}O_3S_7Si$
	636.9617	-1.12	14.5	$C_{25}H_{29}S_7Si_3$
	636.9583	4.17	19.5	$C_{28}H_{25}S_6Si_3$
	636.9581	4.46	20.5	$C_{30}H_{21}O_2S_7$
	636.9579	4.82	20.5	$C_{29}H_{21}O_3S_6Si$

Figure S24. HRMS data of **3**

^{1}H NMR spectrum of **12**

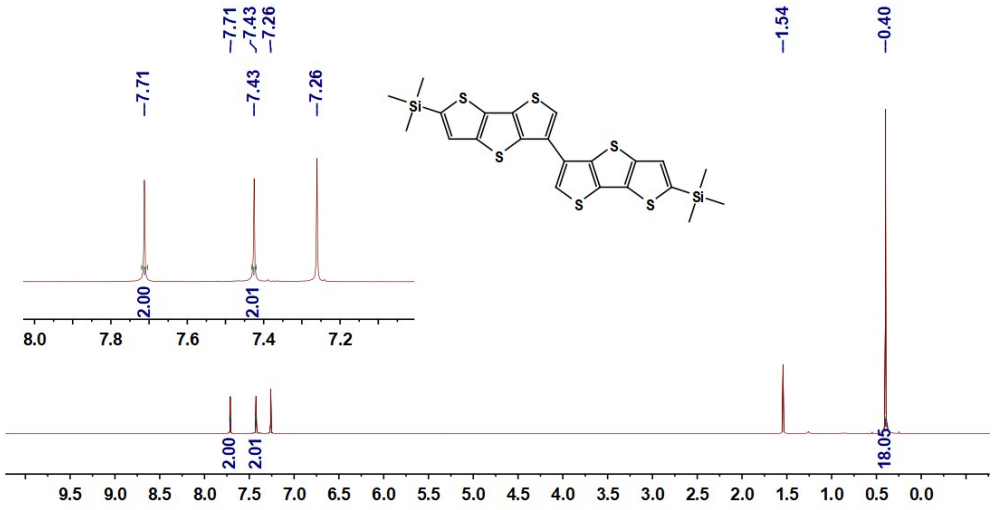


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**

NMR and HRMS spectra of **4**

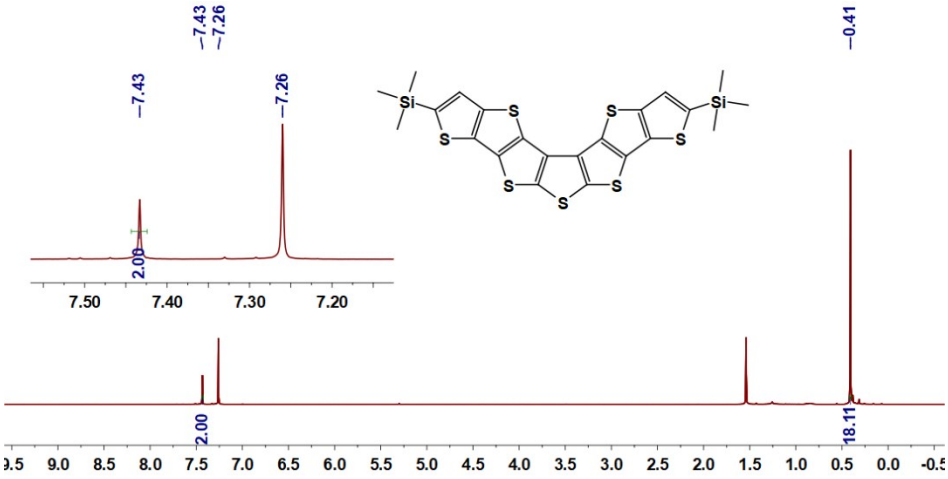


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**

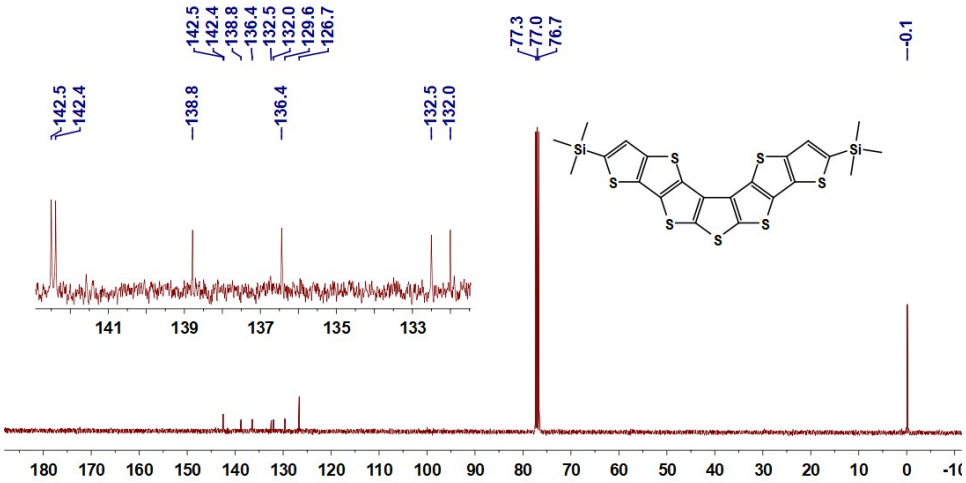


Figure S27. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4**

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : D20201233

Sample Serial Number: 4

Operator : DONG Date: 2020/06/01

Operation Mode: DART POSITIVE

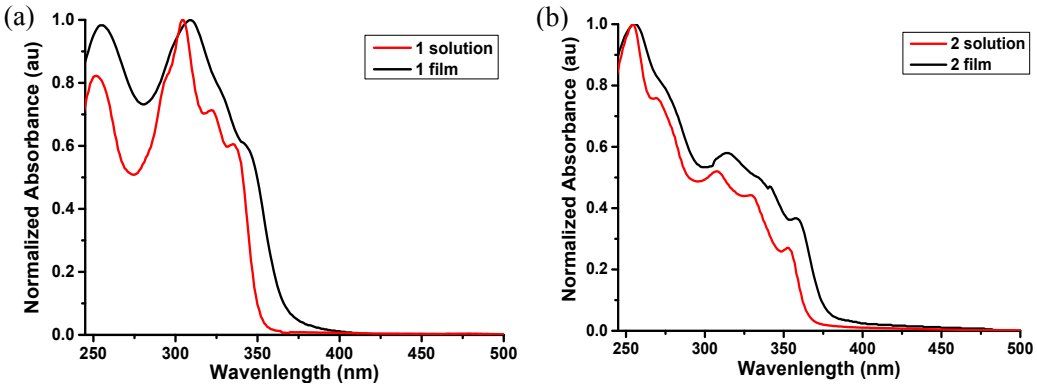
Elemental composition search on mass 564.92

m/z= 559.92-569.92

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
564.9216	564.9221	-0.98	14.5	$C_{22}H_{21}S_7Si_2$
	564.9188	4.98	19.5	$C_{25}H_{17}S_6Si_2$

Figure S28. HRMS data of **4**

4. UV-vis absorption spectra of 1-4



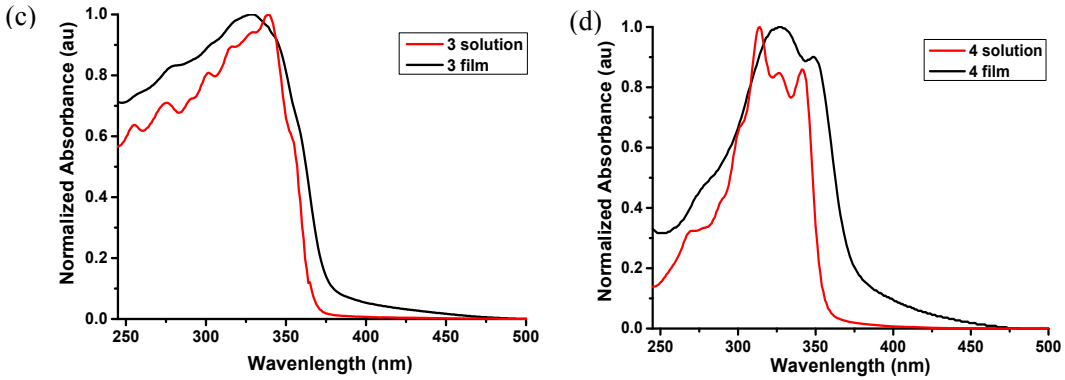


Figure S29. Normalized UV-vis absorption spectra of **1**(a), **2**(b), **3**(c) and **4**(d) in CH_2Cl_2 and thin film.

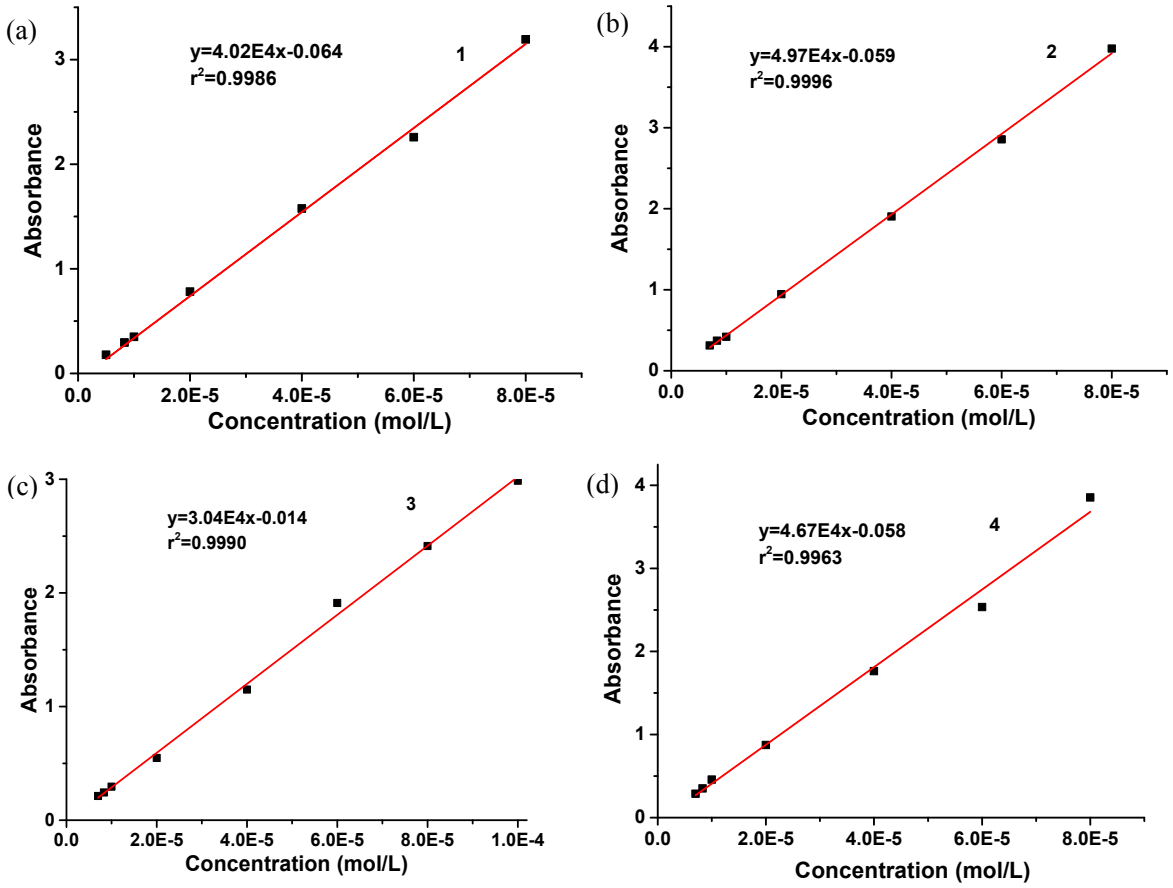


Figure S30. Beer-Lambert plots of **1**(a), **2**(b), **3**(c) and **4**(d) in CH_2Cl_2 at room temperature.

5. XRD patterns of 1-4

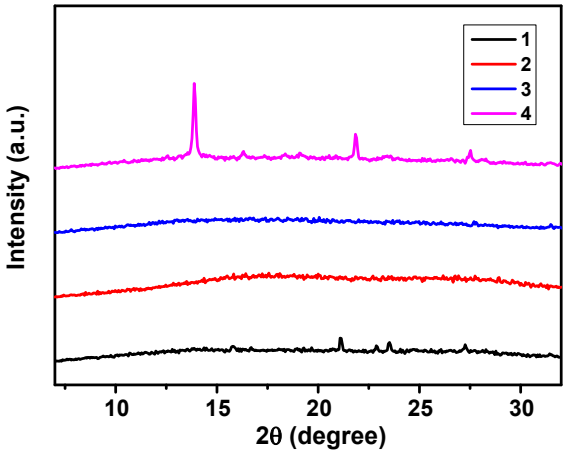


Figure S31. XRD patterns of **1-4** based on SiO_2/Si substrate at room temperature.

6. Cyclic voltammetry of 1-4

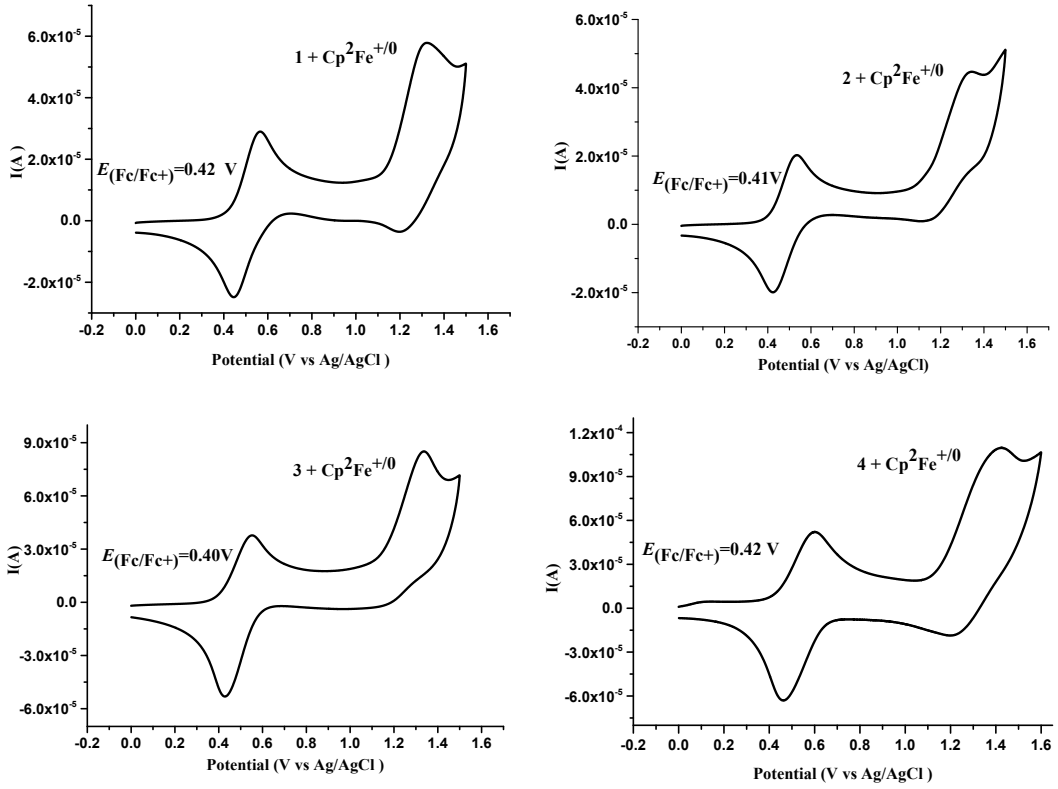


Figure S32. Cyclic voltammetry of **1-4** using Ag/AgCl as reference electrode and Fc/Fc^+ as internal standard, in CH_2Cl_2 ([C] = 1×10^{-3} M), at a scan rate of 100 mV/s with CH_2Cl_2/Bu_4F_6NP (0.1 M) as the supporting electrolyte.

7. Table S1. Photophysical and Electrochemical Data for 1-4

Table S1. Photophysical and Electrochemical Data for **1**, **2**, **3** and **4**

compound	λabs max (nm)	λabs onset (nm)	λfilm max (nm)	λfilm onset (nm)	E_g (eV)	E_{ox} (V)	HOMO (eV)	LUMO (eV)
1	304	351	308	366	3.53	1.14	-5.51	-1.98
2	254	366	256	377	3.39	1.12	-5.52	-2.13
3	339	366	330	376	3.39	1.15	-5.54	-2.15
4	314	353	327	375	3.51	1.14	-5.52	-2.01

$E_{HOMO} = -[E_{ox} - E_{(Fc/Fc+)} + 4.8]$ eV. $E_{LUMO} = E_{g\,(opt)} + E_{HOMO}$

8. DFT calculations of 1-4 at the B3LYP/6-31G** level of theory

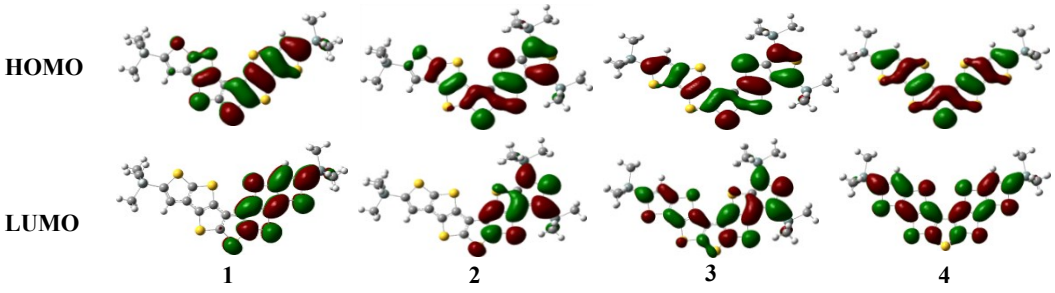


Figure S33. Isosurface map of the HOMO and LUMO for **1-4** calculated at B3LYP/6-31G** level of theory.

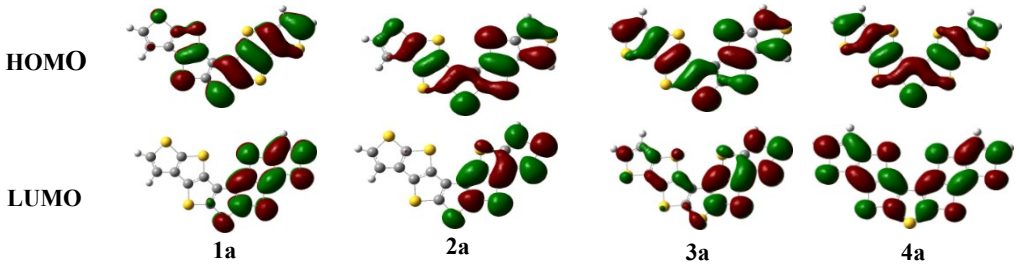


Figure S34. Isosurface map of the HOMO and LUMO for the isomeric position of sulfur atoms without TMS groups **1a-4a** calculated at B3LYP/6-31G** level of theory.

9. Table S2. Adiabatic ionization potentials, reorganization energy, and average mobility of 1-4

Table S2. Adiabatic ionization potentials, reorganization energy, and average mobility of **1-4**

Compounds	**1**	**2**	**3**	**4**
Adiabatic ionization potentials (AIP) [a] (eV)	6.47	6.34	6.30	6.51
Reorganization energy [a] (meV)	264	227	219	225
Average mobility [b] (cm^2 / V·s)	0.05	0.46	1.61	0.65

a: The adiabatic ionization potentials, reorganization energy are calculated at B3LYP/6-31G** level of theory.
b: The neutral and cation states associated with hole transfer process are optimized at B3LYP/6-31G** level of theory.
All the electronic structure calculations are using the Gaussian 09 program.

10. Table S3. Transfer integral a of 1-4

Table S3. Transfer integral[a] of **1-4**

Compounds	**1**		**2**		**3**		**4**	
	d (Å)	V(meV)	*d* (Å)	V(meV)	*d* (Å)	V(meV)	*d* (Å)	V(meV)
P1	5.10	-3.02	4.55	-49.02	6.38	46.22	6.34	20.81
P2	6.11	5.85	6.64	-17.88	6.38	46.22	6.34	20.81
P3	6.11	5.85	6.64	-17.88	7.30	-3.42	6.34	20.81
P4	8.11	0.82	7.64	-1.61	8.30	56.95	6.34	20.81
P5	8.11	0.82	7.64	-1.61	8.42	-0.23	8.09	9.02
P6	8.49	-0.22	9.70	4.69	9.42	3.21	8.09	9.02
P7	10.56	-23.69	11.54	5.57	12.17	-0.29	17.03	0.84
P8	17.03	0.19	11.54	5.57	14.34	0.19	17.03	0.84
P9	17.03	0.19	19.58	-0.02	16.88	0.77	18.34	-0.88
P10	18.83	-0.02	19.58	-0.02	17.56	0.16	18.34	-0.88
P11	19.13	-0.46	20.02	-0.04	18.96	0.97	20.11	-1.10
P12	19.13	-0.44	20.02	-0.04	18.96	0.97	20.11	-1.10
P13	20.01	-0.02	20.40	0.05	19.13	0.03	21.58	-0.43
P14	21.58	-0.22	20.67	-0.14	20.54	0.20	21.58	-0.43
P15	21.58	-0.22	20.67	-0.14	20.54	0.20		
P16			21.27	0.05				

a: The electronic structures for intermolecular transfer integral are calculated at PW91PW91/6-31G** level of theory by using the G09 program.

11. Table S4. Total energies of optimized structures of 1-4

Table S4. Cartesian coordinates, the number of imaginary frequencies, and computed total energies of optimized structures at B3LYP/6-31G** level of theory

1				
the number of imaginary frequencies = 0, E_{total} = -4216.791556 hartree				
Cartesian coordinates	S	-1.95069200	-0.94533000	0.01061900
	S	-2.90094000	3.19054400	0.00201000
	S	0.10737400	4.23620000	-0.00415800
	S	3.03667000	2.98158400	-0.00770100
	S	1.80898200	-1.07831300	0.01716900
	Si	-7.69597600	-2.00963100	-0.00734300
	Si	7.88895700	-1.54285900	-0.00575900
	C	-6.01489800	-1.15255000	-0.00091900
	C	-3.70507700	-0.80238900	0.00700200

	C	-4.12782300	0.52467100	0.00537700
	C	-3.04079700	1.43922100	0.00640500
	C	-1.80223600	0.80501300	0.00902400
	C	-0.69949800	1.71513200	0.00708300
	C	-1.15923200	3.02900500	0.00292600
	C	1.28882700	2.94374100	-0.00153300
	C	0.73959900	1.66534000	0.00521500
	C	1.78079100	0.68384200	0.00652900
	C	3.05755900	1.22461000	-0.00064100
	C	3.55770900	-1.03534800	0.01134000
	C	4.10319500	0.24643200	0.00086300
	C	6.06615600	-1.05071800	-0.00512400
	C	-7.38311500	-3.87287000	-0.03440400
	H	-6.82439800	-4.17710500	-0.92552500
	H	-8.33437200	-4.41637700	-0.04109000
	H	-6.82251100	-4.20289900	0.84632200
	C	-8.65576500	-1.52773100	1.54833800
	H	-8.11670300	-1.82483500	2.45372400
	H	-9.63846900	-2.01241700	1.56762700
	H	-8.81900400	-0.44601200	1.60063100
	C	-8.66381400	-1.48378800	-1.54366200
	H	-8.82760400	-0.40106300	-1.56474100
	H	-9.64656800	-1.96790300	-1.57145100
	H	-8.12945000	-1.75509200	-2.45985900
	C	8.21771100	-2.71661200	-1.45034700
	H	7.60685700	-3.62309400	-1.38031800
	H	9.26835600	-3.02748700	-1.46958400
	H	7.99120600	-2.23832200	-2.40871600
	C	8.31657000	-2.40012200	1.62372300
	H	8.13490100	-1.74006800	2.47807800
	H	9.37191900	-2.69474000	1.64464200
	H	7.71683300	-3.30459200	1.77089700
	C	8.90342200	0.03969300	-0.19933100
	H	8.66237700	0.56270400	-1.13038300
	H	9.97290500	-0.19717700	-0.22076400
	H	8.73789200	0.73310600	0.63173600
	S	-5.86366500	0.61183100	-0.00042200
	S	4.77597000	-2.26554500	0.00903200
	C	-4.77005000	-1.74349300	0.00336600
	H	-4.62887600	-2.81811400	0.00323800
	C	5.53316000	0.21601100	-0.00885600
	H	6.14941900	1.10826800	-0.02005400
2				
the number of imaginary frequencies = 0, E_{total} = -4625.483845 hartree				

Cartesian coordinates	S	5.68054500	1.52197300	-0.00758900
	S	1.41208600	1.10054900	0.00427700
	S	2.74860500	-2.93541400	0.00293100
	S	-0.15449400	-4.24323500	-0.00028100
	S	-3.17901400	-3.24249300	-0.00474400
	S	-2.30501600	0.90776700	0.00981600
	S	-5.36252400	1.83526100	0.00241800
	Si	3.75282300	4.06133400	0.00016100
	Si	6.46934700	-1.52324400	-0.00172000
	Si	-8.40162200	0.84880300	-0.00199500
	C	4.07175200	2.19870200	-0.00556800
	C	3.18901500	1.14246800	-0.00082800
	C	3.78259800	-0.17626500	0.00095400
	C	5.17203800	-0.14855700	-0.00204900
	C	2.74327700	-1.17571100	0.00443400
	C	1.45877800	-0.66430400	0.00623200
	C	0.43596400	-1.66221700	0.00572900
	C	1.00495100	-2.93268500	0.00388400
	C	-1.44106800	-3.05455400	0.00031600
	C	-1.00290100	-1.73399100	0.00407200
	C	-2.12479700	-0.84543200	0.00349800
	C	-3.35055900	-1.49400500	-0.00152300
	C	-4.04329600	0.71408100	0.00562600
	C	-4.47676700	-0.60980200	-0.00114300
	C	-5.90410900	-0.70226100	-0.00842200
	H	-6.44241300	-1.64364700	-0.01576900
	C	-6.54372500	0.51412400	-0.00665300
	C	5.41202500	4.95609800	-0.12300400
	H	5.94106000	4.70188300	-1.04721400
	H	5.25765000	6.04082500	-0.11842700
	H	6.07012800	4.71402100	0.71797600
	C	2.87502200	4.52499500	1.60854600
	H	3.50463100	4.30894000	2.47773400
	H	2.63193600	5.59346000	1.62617800
	H	1.94008000	3.96827700	1.73041300
	C	2.66677600	4.49842800	-1.48380600
	H	1.71843200	3.95149000	-1.46986400
	H	2.43288600	5.56911400	-1.48983300
	H	3.17191100	4.25959900	-2.42531700
	C	8.18222800	-0.72268000	-0.00398100
	H	8.34466900	-0.09811600	0.88037300
	H	8.95442800	-1.50020800	-0.00397200
	H	8.34308500	-0.09977500	-0.88980300
	C	6.27853500	-2.58294500	1.55338800

	H	5.28662700	-3.03929200	1.62784400
	H	7.01763100	-3.39238800	1.55731600
	H	6.43489000	-1.98218400	2.45532700
	C	6.27618000	-2.58659900	-1.55404800
	H	6.43153400	-1.98798500	-2.45759200
	H	7.01482700	-3.39643100	-1.55717700
	H	5.28391500	-3.04256900	-1.62613300
	C	-8.88914000	1.68845100	1.62007200
	H	-8.36443700	2.64071700	1.75146500
	H	-9.96487100	1.89616300	1.64566000
	H	-8.64827800	1.05659100	2.48110000
	C	-8.83868500	1.97247300	-1.45779900
	H	-8.57503400	1.50574800	-2.41235000
	H	-9.91285900	2.18876500	-1.47446800
	H	-8.31033500	2.93023500	-1.40074200
	C	-9.27985100	-0.81593800	-0.16939500
	H	-10.36579900	-0.67110900	-0.17763300
	H	-9.00743200	-1.32437500	-1.09989400
	H	-9.04497500	-1.48606100	0.66411400
3				
the number of imaginary frequencies = 0, E_{total} = -4625.486741 hartree				
Cartesian	S	-5.59118500	1.67396300	-0.00835600
coordinates	S	-1.34308100	1.08026600	0.00529900
	S	-2.84350500	-2.89785700	0.00234200
	S	0.00176500	-4.32454700	0.00208000
	S	3.06417200	-3.45783000	-0.00011300
	S	2.36696200	0.72832400	0.00672300
	S	6.17627700	-1.06774600	-0.00271600
	Si	-3.56305400	4.13332500	0.00377900
	Si	-6.50152900	-1.33837200	-0.00539300
	Si	8.16878000	1.43095500	-0.00484000
	C	-3.95636900	2.28511200	-0.00518100
	C	-3.11681600	1.19410300	-0.00060700
	C	-3.76352600	-0.09929400	0.00033100
	C	-5.15080400	-0.01557500	-0.00328700
	C	-2.76566800	-1.14000500	0.00370200
	C	-1.46123100	-0.68136800	0.00610700
	C	-0.48038800	-1.72078000	0.00603200
	C	-1.10167100	-2.96645600	0.00437600
	C	1.33608400	-3.19157700	0.00279400
	C	0.95461700	-1.85289700	0.00507700
	C	2.11031700	-1.01002800	0.00467400
	C	3.30837000	-1.71837700	0.00169500
	C	4.44947500	-0.87276300	0.00057500

	C	4.10906800	0.47760000	0.00318300
	C	5.23063000	1.35091800	0.00269800
	H	5.15733600	2.43228400	0.00490300
	C	6.43645300	0.68400800	-0.00066000
	C	-2.44363100	4.52556100	-1.46801900
	H	-2.94825000	4.30804900	-2.41495800
	H	-2.16587500	5.58576100	-1.47082100
	H	-1.51881000	3.94009000	-1.44452100
	C	-2.68583000	4.56345900	1.62176500
	H	-1.77399700	3.97170400	1.75346000
	H	-2.40289700	5.62202400	1.64242800
	H	-3.33251000	4.37128800	2.48401000
	C	-5.18293300	5.09477100	-0.13891700
	H	-5.85805700	4.88445800	0.69710100
	H	-4.98356800	6.17215800	-0.13794600
	H	-5.71367700	4.85820200	-1.06680300
	C	-8.18145300	-0.47105400	-0.00707900
	H	-8.31694000	0.15953300	-0.89170600
	H	-8.98398500	-1.21722700	-0.00902900
	H	-8.31946500	0.15771200	0.87845100
	C	-6.35261800	-2.40595300	1.54874200
	H	-6.49091400	-1.80071000	2.45065700
	H	-7.11923400	-3.18940100	1.54990800
	H	-5.37737900	-2.89636500	1.62612000
	C	-6.34880900	-2.40510900	-1.55976300
	H	-5.37389400	-2.89668100	-1.63400000
	H	-7.11644000	-3.18754900	-1.56414800
	H	-6.48313500	-1.79906900	-2.46174400
	H	8.55191100	1.23783100	-2.47175200
	H	10.09106300	1.32548200	-1.60029200
	C	7.98234600	3.31114900	0.04032200
	H	7.45768600	3.64598400	0.94113100
	H	8.96906400	3.78735900	0.03812000
	H	7.43489000	3.68677900	-0.83039100
	C	9.08073900	0.90172200	-1.57398600
	H	9.17672600	-0.18755700	-1.63497900
	C	9.11569200	0.82934600	1.51667200
	H	9.21181900	-0.26165900	1.52523900
	H	10.12702200	1.25084200	1.53940300
	H	8.60802100	1.12371800	2.44087900
4				
the number of imaginary frequencies = 0, E_{total} = -4216.794548 hartree				
Cartesian	S	5.84333900	0.50273000	0.00016600
coordinates	S	1.87962500	-0.92085500	-0.00050400

	S	2.97070000	3.18036200	0.00008400
	Si	7.58703000	-2.17684600	0.00012400
	C	5.93456000	-1.26578800	-0.00005800
	C	4.67040400	-1.81423100	-0.00034600
	H	4.49294700	-2.88345500	-0.00063400
	C	3.63787400	-0.83746900	-0.00033600
	C	4.10554900	0.47438700	-0.00001100
	C	3.05025100	1.42527100	0.00027500
	C	1.79073300	0.83360500	0.00007200
	C	0.72009300	1.78131300	-0.00021500
	C	1.22466300	3.07849000	-0.00025400
	C	7.21478800	-4.02934700	-0.00034900
	H	6.64617900	-4.32835000	-0.88699300
	H	8.14812000	-4.60310800	0.00053800
	H	6.64439700	-4.32855500	0.88506000
	C	8.56563900	-1.70415500	1.54680800
	H	8.02114100	-1.97480100	2.45723400
	H	9.53411200	-2.21655600	1.56919600
	H	8.76016300	-0.62705700	1.58581700
	C	8.56630600	-1.70379300	-1.54601600
	H	8.76320900	-0.62706100	-1.58348500
	H	9.53362700	-2.21830200	-1.56937800
	H	8.02097800	-1.97186500	-2.45670700
	S	-5.84333900	0.50273000	-0.00026300
	S	-1.87962500	-0.92085500	-0.00006700
	S	-2.97070000	3.18036200	-0.00000700
	Si	-7.58703000	-2.17684600	0.00014200
	C	-5.93456000	-1.26578800	0.00004200
	C	-4.67040400	-1.81423100	0.00006000
	H	-4.49294700	-2.88345500	0.00025900
	C	-3.63787400	-0.83746900	0.00000300
	C	-4.10554900	0.47438700	-0.00014600
	C	-3.05025100	1.42527100	-0.00038000
	C	-1.79073300	0.83360500	-0.00030900
	C	-0.72009300	1.78131300	0.00013300
	C	-1.22466300	3.07849000	0.00039100
	C	-7.21478800	-4.02934700	0.00054600
	H	-6.64602800	-4.32835200	0.88709300
	H	-8.14812000	-4.60310800	-0.00018300
	H	-6.64454700	-4.32855300	-0.88496000
	C	-8.56590100	-1.70415200	-1.54637500
	H	-8.02155700	-1.97479600	-2.45689500
	H	-9.53437700	-2.21655400	-1.56859900
	H	-8.76043100	-0.62705400	-1.58534900

	C	-8.56604500	-1.70379500	1.54644900
	H	-8.76294200	-0.62706400	1.58395400
	H	-9.53336300	-2.21830400	1.56997400
	H	-8.02056200	-1.97186900	2.45704600
	S	0.00000000	4.32868300	0.00017600
1a				
the number of imaginary frequencies = 0, E_{total} = -3399.398290 hartree				
Cartesian coordinates	S	1.76738200	-1.82640000	-0.00021900
	S	3.04259600	2.22077200	-0.00020600
	S	0.12762500	3.50347600	-0.00009700
	S	-2.89222600	2.48794000	0.00018600
	S	-1.99194400	-1.65658700	-0.00024800
	C	5.77478400	-2.32738600	0.00022500
	C	3.52562900	-1.82443500	0.00003200
	C	4.05212200	-0.53530300	0.00003600
	C	3.04224300	0.46417200	-0.00004300
	C	1.75769900	-0.06961500	-0.00009000
	C	0.73061500	0.92571700	-0.00010500
	C	1.29343200	2.19864400	-0.00010400
	C	-1.15304800	2.30974700	-0.00012300
	C	-0.70773200	0.99149400	-0.00013000
	C	-1.82410200	0.09647100	0.00012500
	C	-3.05359900	0.73824300	0.00029200
	C	-3.73116500	-1.47346900	-0.00025800
	C	-4.17363600	-0.15263200	0.00006600
	C	-6.19469600	-1.29370800	0.00050200
	S	5.79268200	-0.57562000	0.00028700
	S	-5.03915000	-2.61278300	-0.00024000
	C	4.51270400	-2.85160700	0.00024400
	H	4.30379100	-3.91425600	0.00025200
	C	-5.60415600	-0.06518500	0.00044200
	H	-6.16219300	0.86362100	0.00069800
	H	6.71443800	-2.86147200	0.00023900
	H	-7.25004500	-1.52755700	0.00074300
2a				
the number of imaginary frequencies = 0, E_{total} = -3399.394454 hartree				
Cartesian coordinates	S	6.11304100	-1.89905900	-0.00009600
	S	1.79848700	-1.71228000	0.00006700
	S	2.94893400	2.38890600	-0.00004400
	S	-0.00994000	3.56473600	-0.00006000
	S	-2.98787500	2.43416200	0.00001100
	S	-1.93313200	-1.67368400	-0.00010800
	S	-4.94267300	-2.74226100	-0.00025000
	C	4.53580400	-2.62821500	0.00019700

	C	3.57210100	-1.66132100	0.00009300
	C	4.09515400	-0.31135700	0.00007400
	C	5.46857800	-0.29008800	0.00013100
	C	3.01317500	0.63556300	0.00001000
	C	1.75767200	0.05957400	0.00000000
	C	0.69196100	1.01159800	0.00000700
	C	1.20578600	2.30678100	0.00002200
	C	-1.24349300	2.32128500	-0.00017200
	C	-0.74853200	1.02111200	-0.00009900
	C	-1.83046200	0.08436700	0.00014100
	C	-3.08319700	0.67984400	0.00018600
	C	-3.67791100	-1.55514400	-0.00020000
	C	-4.16941700	-0.25181800	-0.00002500
	C	-5.60221900	-0.21751100	0.00023100
	H	-6.19439000	0.68991600	0.00038600
	C	-6.14654700	-1.46715400	0.00043100
	H	-7.19246500	-1.74016000	0.00068400
	H	4.43128500	-3.70301500	0.00028400
	H	6.13537900	0.55983500	0.00017400
3a				
the number of imaginary frequencies = 0, E_{total} = -3399.397174 hartree				
Cartesian	S	-6.22639400	-1.71557400	-0.00061500
coordinates	S	-1.90760300	-1.71915700	0.00023000
	S	-2.87711500	2.42863000	0.00005700
	S	0.13003100	3.47396400	-0.00006600
	S	3.05592600	2.21879900	-0.00005800
	S	1.82292400	-1.84142500	0.00012800
	S	5.83492500	-0.54754100	0.00000500
	C	-4.68273500	-2.51346400	0.00038300
	C	-3.67726900	-1.59004600	0.00016300
	C	-4.14047600	-0.21845500	0.00013600
	C	-5.51165200	-0.13649800	0.00031600
	C	-3.01787000	0.67983300	0.00008100
	C	-1.78885700	0.04914500	0.00007500
	C	-0.68260400	0.95379200	0.00003200
	C	-1.13942300	2.27011000	0.00000500
	C	1.30750500	2.17844600	-0.00004900
	C	0.75716000	0.90041100	0.00000400
	C	1.79420800	-0.08490300	0.00001800
	C	3.07327100	0.46251900	-0.00003700
	C	4.09397800	-0.52574400	-0.00003500
	C	3.58087700	-1.82019800	0.00001200
	C	4.57883300	-2.83686100	-0.00005000
	H	4.38109600	-3.90165100	-0.00005500

	C	5.83529800	-2.29942300	-0.00029200
	H	-4.62586200	-3.59183400	0.00059000
	H	-6.14037800	0.74194400	0.00046700
	H	6.78055400	-2.82356800	-0.00049200
4a				
the number of imaginary frequencies = 0, E_{total} = -3399.401009 hartree				
Cartesian coordinates	S	5.84516500	-0.39884500	-0.00005700
	S	1.88051500	-1.83123600	-0.00009200
	S	2.97058400	2.26973900	0.00002400
	C	5.90649300	-2.14952400	-0.00011800
	C	4.66950400	-2.73038500	-0.00015900
	H	4.50909900	-3.80144600	-0.00020700
	C	3.63680100	-1.74914800	-0.00013100
	C	4.10447700	-0.43748800	-0.00007500
	C	3.05010700	0.51495100	0.00001500
	C	1.79113500	-0.07685200	0.00000500
	C	0.72002400	0.87079800	-0.00001100
	C	1.22430700	2.16790600	-0.00001100
	S	-5.84516500	-0.39884500	0.00000100
	S	-1.88051500	-1.83123600	0.00001100
	S	-2.97058400	2.26973900	0.00013000
	C	-5.90649300	-2.14952400	-0.00002800
	C	-4.66950400	-2.73038500	-0.00003000
	H	-4.50909900	-3.80144600	-0.00004600
	C	-3.63680100	-1.74914800	0.00002200
	C	-4.10447700	-0.43748800	0.00004400
	C	-3.05010700	0.51495100	0.00002600
	C	-1.79113500	-0.07685200	0.00000700
	C	-0.72002400	0.87079800	0.00007400
	C	-1.22430700	2.16790600	0.00014300
	S	0.00000000	3.41826000	0.00009500
	H	-6.86934700	-2.64070400	-0.00003200
	H	6.86934700	-2.64070400	-0.00014100

[a] The total energies of optimized structures

12. X-ray crystallographic data

Completed crystal data for **1**

Table S5. Crystal data and structure refinement for **1**

Identification code	**1**
Empirical formula	$C_{22}H_{20}S_7Si_2$
Formula weight	564.98

Temperature/K	99.97	
Crystal system, Space group	Monoclinic, $P2_1/c$	
	a = 17.0321(11) Å	α = 90 °
	b = 8.1148(5) Å	β = 103.715(2) °
	c = 19.0432(12) Å	γ = 90 °
Volume	2557.0(3) $Å^3$	
Z	4	
ρ_{calc}	1.468 g/cm^3	
μ	0.721 mm^{-1}	
F(000)	1168.0	
Crystal size	0.12 × 0.1 × 0.08 mm^3	
Radiation	MoKα (λ = 0.71073)	
2θ range for data collection	4.404 to 55.554°	
Index ranges	$-22 \leq h \leq 22$, $-10 \leq k \leq 10$, $-24 \leq l \leq 24$	
Reflections collected	30270	
Independent reflections	5981[R_{int} = 0.0494], 5981[R_{sigma} = 0.0422]	
Data/restraints/parameters	5981 / 19 / 299	
Goodness-of-fit on F^2	1.059	
Final R indexes [I ≥ 2sigma(I)]	R_1 = 0.0501, wR_2 = 0.1184	
Final R indexes (all data)	R_1 = 0.0734, wR_2 = 0.1298	
Largest diff. peak / hole	1.44 / -0.59 e $Å^{-3}$	

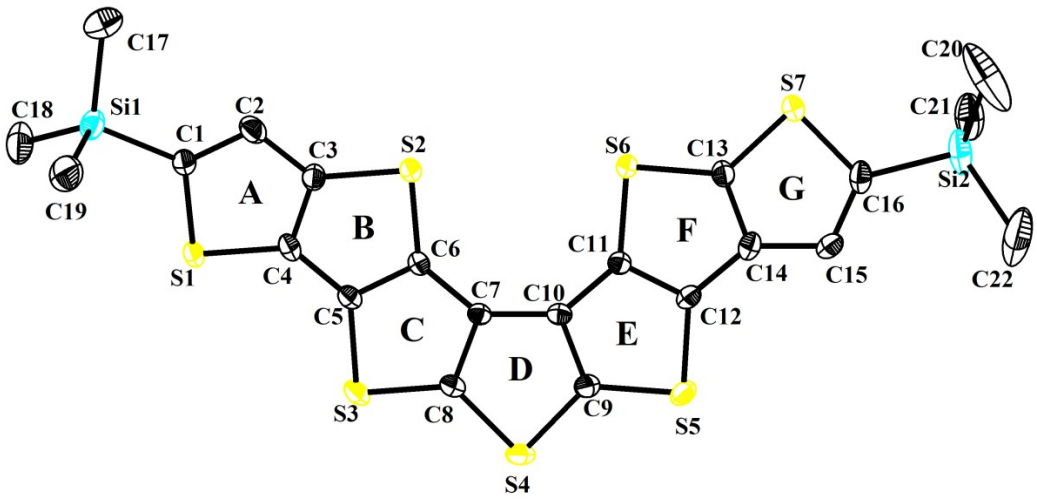


Figure S35. The crystal structures for compound **1**. Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 50% probability level, and all hydrogen atoms are omitted for clarity.

Completed crystal data for **2**

Table S6. Crystal data and structure refinement for **2**

Identification code	**2**

Empirical formula	$C_{25}H_{28}S_7Si_3$	
Formula weight	637.16	
Temperature	150.01 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.581(3) Å	$\alpha = 90°$
	b = 11.5417(15) Å	$\beta = 93.100(5)°$
	c = 13.894(2) Å	$\gamma = 90°$
Volume	3135.6(7) $Å^3$	
Z	4	
Density (calculated)	1.350 mg/m^3	
Absorption coefficient	0.633 mm^{-1}	
F(000)	1328	
Crystal size	0.21 x 0.14 x 0.07 mm^3	
θ range for data collection	2.295 to 26.000°	
Index ranges	$-24 \leq h \leq 24$, $-12 \leq k \leq 14$, $-17 \leq l \leq 13$	
Reflections collected	23591	
Independent reflections	6145 [$R_{(int)} = 0.0697$]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.5563	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6145 / 24 / 356	
Goodness-of-fit on F^2	1.039	
Final R indices [I > 2sigma(I)]	$R_1 = 0.0618$, $wR_2 = 0.1378$	
R indices (all data)	$R_1 = 0.1062$, $wR_2 = 0.1626$	
Extinction coefficient	n / a	
Largest diff. peak and hole	0.794 and -0.441 e $Å^{-3}$	

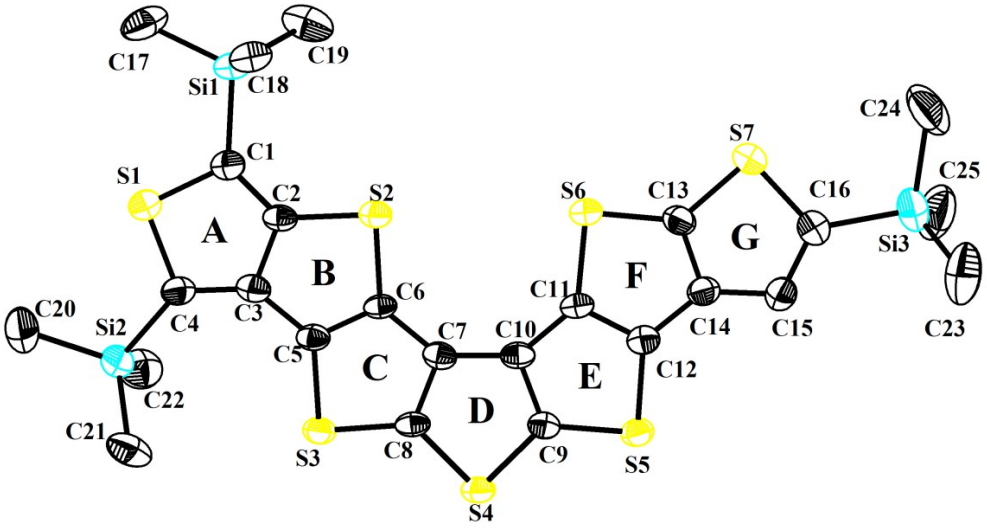


Figure S36. The crystal structures for compound **2**. Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 50% probability level, and all hydrogen atoms are omitted for clarity.

Completed crystal data for **3**

Table S7. Crystal data and structure refinement for **3**

Identification code	**3**	
Empirical formula	$C_{25}H_{28}S_7Si_3$	
Formula weight	637.16	
Temperature	298.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P_{-1}	
Unit cell dimensions	a = 6.3763(10) Å	α = 82.974(4)°
	b = 13.611(2) Å	β = 87.780(4)°
	c = 18.956(3) Å	γ = 78.881(5)°
Volume	1598.2(5) $Å^3$	
Z	2	
Density (calculated)	1.324 mg / m^3	
Absorption coefficient	0.621 mm^{-1}	
F(000)	664	
Crystal size	0.21 x 0.11 x 0.06 mm^3	
θ range for data collection	2.520 to 25.499°	
Index ranges	$-7 \le h \le 6$, $-16 \le k \le 16$, $-22 \le l \le 22$	
Reflections collected	25184	
Independent reflections	5944 [R(int) = 0.0986]	
Completeness to theta = 25.242°	99.8%	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7457 and 0.7009
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5944 / 30 / 356
Goodness-of-fit on F^2	1.027
Final R indices [I > 2sigma(I)]	$R_1 = 0.0594$, $wR_2 = 0.1226$
R indices (all data)	$R_1 = 0.1307$, $wR_2 = 0.1604$
Extinction coefficient	n / a
Largest diff. peak and hole	0.435 and -0.276 e $Å^{-3}$

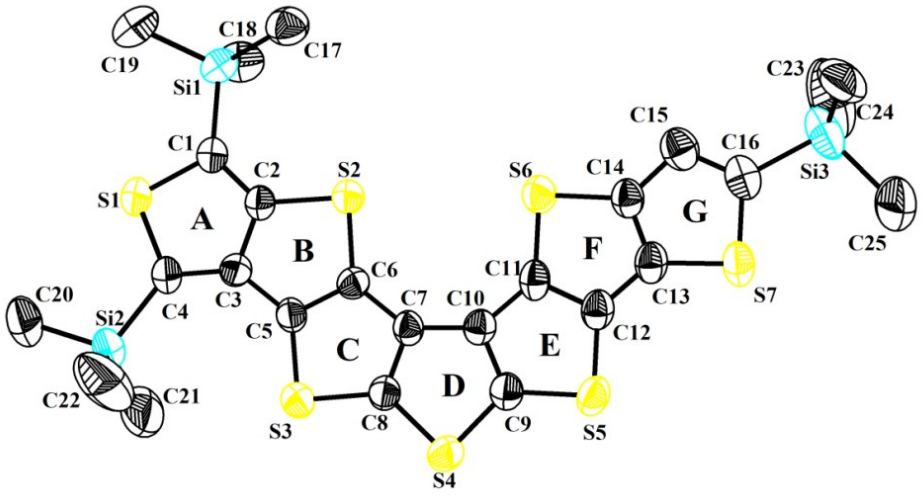


Figure S37. The crystal structures for compound **3**. Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 50% probability level, and all hydrogen atoms are omitted for clarity.

Completed crystal data for **4**

Table S8. Crystal data and structure refinement for **4**

Identification code	**4**	
Empirical formula	$C_{22}H_{20}S_7Si_2$	
Formula weight	564.98	
Temperature	230.39 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 9.767(2) Å	α = 90°.
	b = 8.0917(19) Å	β = 92.755(5)°.
	c = 31.991(8) Å	γ = 90°.
Volume	2525.5(10) $Å^3$	
Z	4	
Density (calculated)	1.486 mg/m^3	
Absorption coefficient	0.730 mm^{-1}	

F(000)	1168
Crystal size	0.22 x 0.18 x 0.13 mm^3
θ range for data collection	2.550 to 28.454°
Index ranges	$-11 \leq h \leq 12$, $-10 \leq k \leq 9$, $-42 \leq l \leq 42$
Reflections collected	9273
Independent reflections	3140 [$R_{(int)} = 0.0536$]
Completeness to theta = 25.242°	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4202
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3140 / 0 / 144
Goodness-of-fit on F^2	1.084
Final R indices [I > 2sigma(I)]	$R_1 = 0.0453$, $wR_2 = 0.1173$
R indices (all data)	$R_1 = 0.0474$, $wR_2 = 0.1188$
Extinction coefficient	n / a
Largest diff. peak and hole	0.501 and -0.533 e $Å^{-3}$

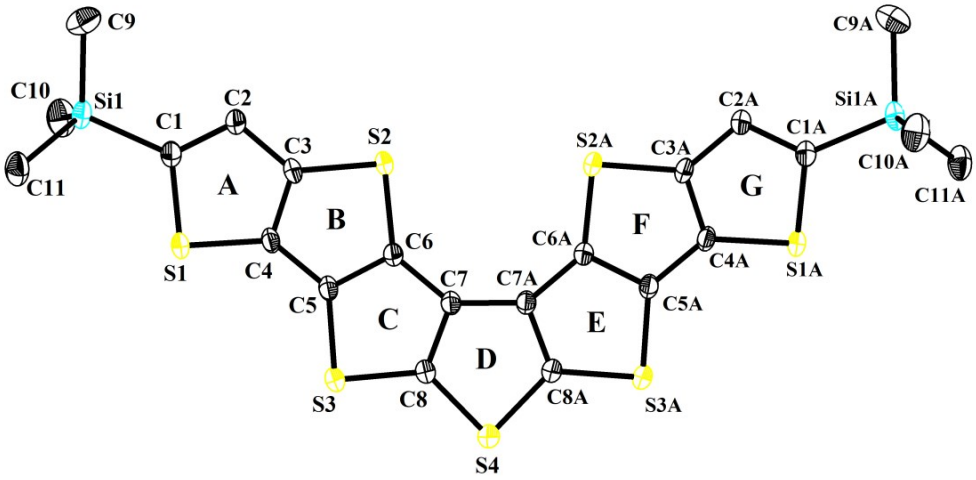


Figure S38. The crystal structures for compound **4**. Carbon, selenium, sulfur, and silicon atoms are depicted with thermal ellipsoids set at 50% probability level, and all hydrogen atoms are omitted for clarity.