Supporting Information

Flexible and Transparent Oligothiophene-*o*-Carborane-Containing Hybrid Films for Nonlinear Optical Limiting Based on Efficient Two-Photon Absorption

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Contents

1. Experimental Section

Materials. 2,2':5',2"-terthiophene (3T), *N*-bromosuccimimide (NBS), CuI, decarborane (United Boron, >95.0%), trimethylsilylacetylene, and *trans*-dichlorobis(triphenyl-phosphine) palladium(II) are obtained commercially. 5-Bromo-2,2':5',2"-terthiophene (3T-Br) and 5,5"-dibromo-2,2':5',2"-terthiophene (Br-3T-Br) are synthesized according to the literatures.[1-3] Unless stated otherwise, all other reagents are obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) is distilled from metallic sodium and diisopropylamine from calcium hydride under argon prior to use. Structural and optical measurements in the solid state were performed with the crystalline samples.

Measurements and Characterization. NMR (^{1}H, ^{13}C, and ^{11}B NMR) measurements are recorded on a Bruker AV NMR spectrometer. UV-Vis spectra in solution are recorded on a Hitachi U-3900/3900H spectrophotometer at room temperature. The high-resolution mass spectra (HRMS) are acquired in atmospheric pressure chemical ionization (APCI) sources using a Bruker maXis UHR-TOF mass spectrometer. Steady state fluorescence excitation and emission spectra are obtained by using a time-correlated single photon counting fluorimeter (Edinburgh FLS920) with xenon lamp as the light source at room temperature.

Quantum Chemical Calculation. Aiming to better understand the structure-property correlations, supporting theoretical calculations of the fluorophores are also performed. The geometry optimization and the transition dipole moments of compounds **1-1**, **1-2**, and **2-1** are performed at the time-dependent density functional level of theory (TD-DFT) using the B3LYP functional and a 6-31G(d) basis set, implemented by Gaussian 09 in gaseous phase (version 5.0). The initial input structure is based on the structural data obtained by single crystal X-ray.

X-ray Crystallography Analyses. Single-crystals of the fluorophores **1-1**, **1-2**, and **2-1** are obtained from layered *n*-hexane onto their CH_2Cl_2 solutions. All data are collected with a Bruker APEX II CCD detector/D8 diffractometer using Cu (Ga, Mo) $K\alpha$ radiation. The data are

corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures are solved using the direct methods programs SHELXS-97, and refinements are completed using the program SHELXL-97.[4]

General Synthesis Procedures for the Fluorophores. Synthetic approaches toward defined end-capped oligothiophenes have been studied extensively. Compounds 3T-acetylene-TMS and bis(TMS-acetylene)-3T are synthesized by reacting trimethylsilylacetylene with bromo-substituted precursors, 3T-Br and Br-3T-Br, under typical Sonogashira C-C cross-coupling conditions in the presence of triethylamine with moderate yields.[5-7] The deprecation processes are carried out under standard conditions and the intermediates of 3T-acetylene (5-ethynyl-2,2':5',2"-terthiophene) and bisacetylene-3T (5,5"-bisethynyl-2,2':5',2"-terthiophene) are used for the next step immediately.

3T-Acteylene-TMS. Yield ~ 62%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.23 (dd, J = 5.1, 1.1 Hz, 1H), 7.17 (dd, J = 3.6, 1.1 Hz, 1H), 7.12 (d, J = 3.8 Hz, 1H), 7.07 (s, 2H), 7.02 (dd, J = 5.1, 3.6 Hz, 1H), 6.99 (d, J = 3.8 Hz, 1H), 0.29-0.22 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 138.69, 137.09, 137.03, 135.52, 133.67, 128.08, 125.00, 124.91, 124.54, 124.09, 123.31, 122.03, 100.40, 97.52, 77.48, 77.37, 77.17, 76.85. HRMS (APCI-Orbitrap) *m/z*: $[M+H]^+$ calc. for $C_{17}H_{16}S_3Si$: 345.0245, found 345.0256.

Bis(TMS-Acetylene)-3T. Yield ~ 75%. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.12 (d, J = 3.8 Hz, 1H), 7.06 (s, 1H), 7.00 (d, J = 3.8 Hz, 1H), 0.25 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm): δ 138.40, 136.23, 133.68, 125.07, 123.57, 122.36, 100.62, 97.45, 77.39, 77.18, 76.96, 29.87. HRMS (APCI-Orbitrap) *m/z*: $[M+H]^+$ calc. for $C_{22}H_{24}S_3Si_2$: 441.0636, found 441.0651.

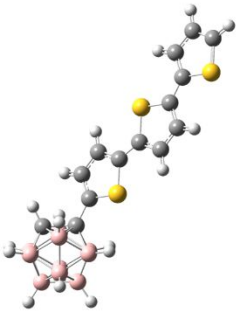
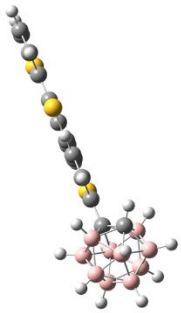
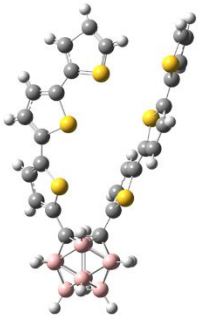
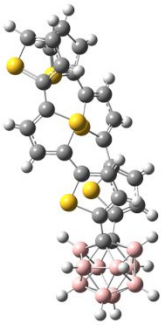
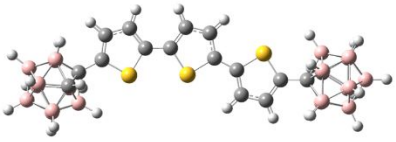
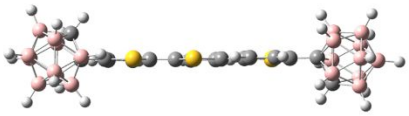
2. X-ray Crystallography Analyses

Table S1. Crystallographic data of *o*-carborane-based fluorophores

	Compound 1-1	**Compound 1-2**	**Compound 2-1**
CCDC Deposit Number	2044746	2044750	2044752
Empirical formula	$C_{14}H_{18}B_{10}S_3$	$C_{26}H_{24}B_{10}S_6$	$C_{16}H_{28}B_{20}S_3$
Formula weight	390.56	636.91	532.76
Temperature	190(2) K	190(2) K	190(2) K
Wavelength	1.34139 Å	1.34139 Å	1.34139 Å
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	P-1	$P2_1/n$	$Pna2_1$
Unit cell dimensions	a= 7.3575(8) Å	a= 11.9554(3) Å	a= 34.781(3) Å
	b= 17.184(2) Å	b= 7.5304(2) Å	b= 7.2262(7) Å
	c= 32.022(4) Å	c= 33.6629(8) Å	c= 11.1929(11) Å
	α= 74.44°	α= 90 °	α= 90 °
	β= 88.880(4) °	β= 97.8620(10) °	β= 90 °
	γ= 85.822(5) °	γ= 90 °	γ= 90 °
Volume	3889.7(8) $Å^3$	3002.15(13) $Å^3$	2813.2(5) $Å^3$
Z	8	4	4
Density (calculated)	1.334 mg/m^3	1.409 mg/m^3	1.258 mg/m^3
Absorption coefficient	2.254 mm^{-1}	2.830 mm^{-1}	1.613 mm^{-1}
F(000)	1600	1304	1088
Crystal size / mm^3	0.200 x 0.100 x 0.100	0.100 x 0.100 x 0.100	0.130 x 0.110 x 0.090
Theta range for data collection	2.328 to 53.068 °	3.293 to 53.900 °	2.210 to 53.933 °
Index ranges	-8<=h<=8	-14<=h<=9	-24<=h<=41
	20<=k<=20	-9<=k<=8	8<=k<=8
	-38<=l<=38	-40<=l<=40	-13<=l<=13
Reflections collected	51023	14870	18989
Independent reflections	13692 [R(int) = 0.0578]	5451 [R(int) = 0.0294]	5049 [R(int) = 0.0314]
Completeness to theta = 53.068°	99.2 %	99.5 %	99.1 %
Refinement method		Full-matrix least-squares on F^2	
Data / restraints / parameters	13692 / 1152 / 970	5451 / 602 / 453	5049 / 1 / 352
Goodness-of-fit on F^2	0.963	1.063	1.034
Final R indices	R_1 = 0.0688	R_1 = 0.0356	R_1 = 0.0259
[I>2sigma(I)]	wR_2 = 0.1619	wR_2 = 0.1022	wR_2 = 0.0709
R indices (all data)	R_1 = 0.0850	R_1 = 0.0434	R_v = 0.0265
	wR_2 = 0.1730	wR_2 = 0.1127	wR_2 = 0.0714
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole	1.009 and -0.884 e.$Å^{-3}$	0.840 and -0.345 e.$Å^{-3}$	0.163 and -0.185 e.$Å^{-3}$

3. Optimized Geometries of the Fluorophores

Table S2. Optimized geometries of the *o*-carborane-based fluorophores **1-1**, **1-2**, and **2-1**.

Compound	TOP View	Side View
1-1		
1-2		
2-1		

4. Summarized Optical Properties of the Fluorophores

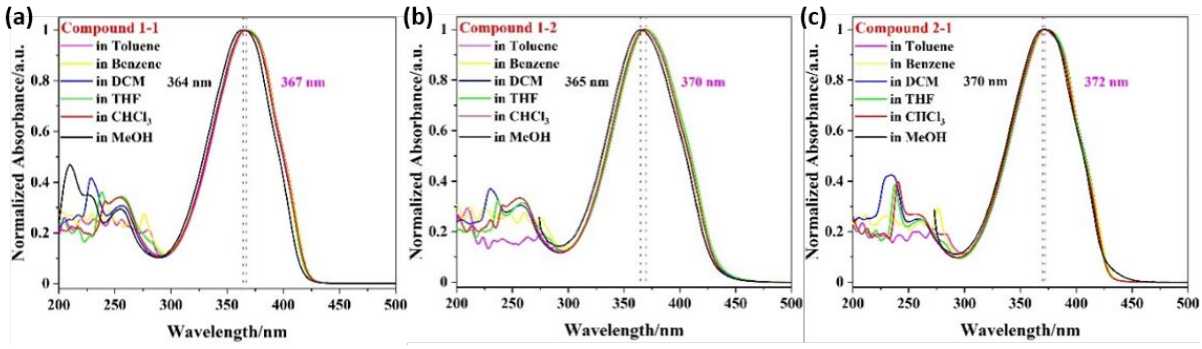


Figure S1. UV-Vis absorption spectra of compounds **1-1** (a), **1-2** (b), and **2-1** (c) in kinds of solvents with different polarities (λ_{ex} = 370 nm, c ~ 5.0 μM). *Note:* DCM for dichloromethane and THF for tetrahydrofuran.

Table S3. Photophysical properties of the *o*-carborane-based fluorophores.

Solvents	Polarity	Compound 1-1		Compound 1-2		Compound 2-1	
		λ_{max}/ nm	ε/ $M^{-1}\cdot cm^{-1}$	λ_{max}/ nm	ε/ $M^{-1}\cdot cm^{-1}$	λ_{max}/ nm	ε/ $M^{-1}\cdot cm^{-1}$
Toluene	2.4	367	2.84×10^4	370	3.89×10^4	372	3.15×10^4
Benzene	3.0	367	2.71×10^4	370	2.46×10^4	372	2.88×10^4
DCM	3.4	366	3.04×10^4	368	2.96×10^4	371	2.41×10^4
THF	4.2	367	2.66×10^4	369	3.67×10^4	371	2.69×10^4
$CHCl_3$	4.4	366	2.72×10^4	368	3.68×10^4	371	3.02×10^4
MeOH	6.6	364	2.98×10^4	365	2.97×10^4	370	2.94×10^4

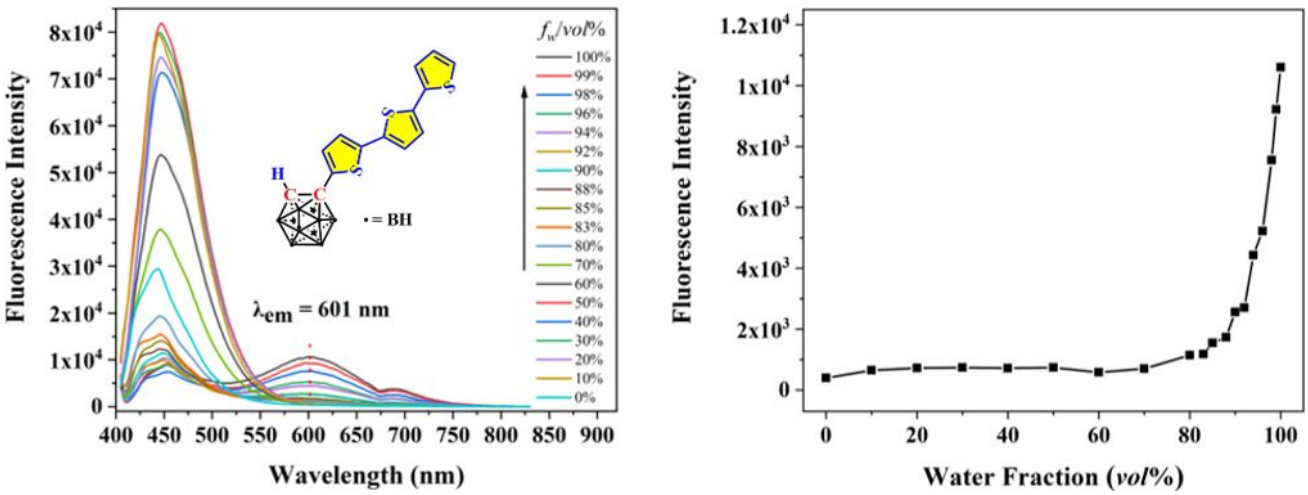


Figure S2. Emission spectra (left) and plots of emission intensity (right) of compound **1-1** in THF/H_2O versus water fractions (c ~ 5.0 μM).

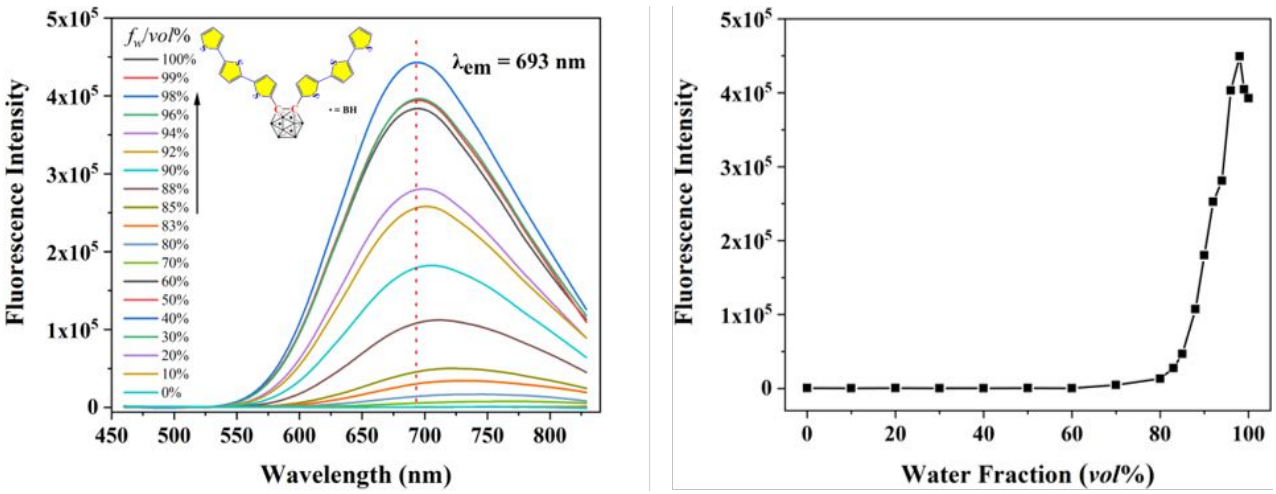


Figure S3. Emission spectra (left) and plots of emission intensity (right) of compound **1-2** in THF/H_2O versus water fractions (c ~ 5.0 μM).

5. Nonlinear Optical Properties of the Fluorophores

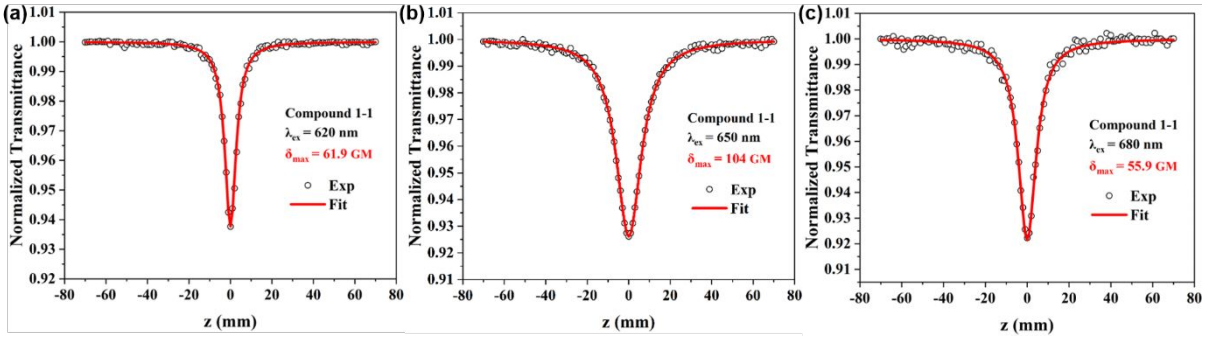


Figure S4. Open aperture Z-scan curves of compound **1-1** excited at fs-620 nm (a), fs-650 nm (b), and fs-680 nm (c), respectively (THF, $c \sim 1.0 \times 10^{-2}$ M).

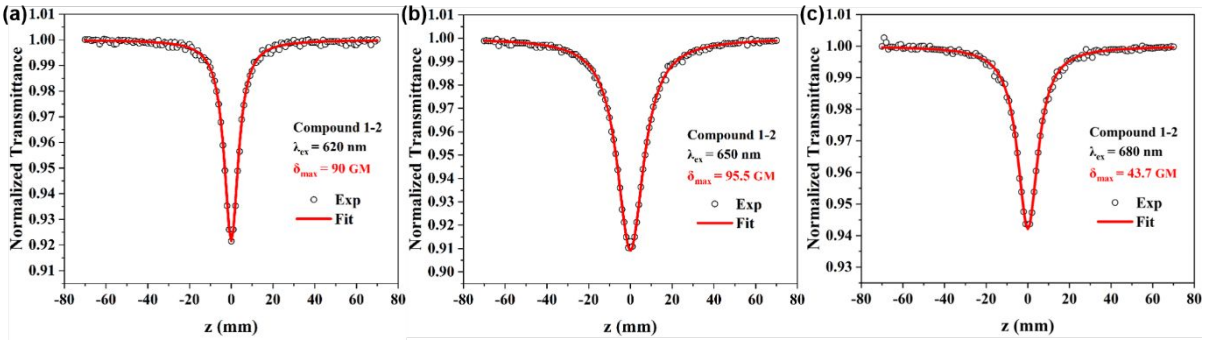


Figure S5. Open aperture Z-scan curves of compound **1-2** excited at fs-620 nm (a), fs-650 nm (b), and fs-680 nm (c), respectively (THF, $c \sim 1.0 \times 10^{-2}$ M).

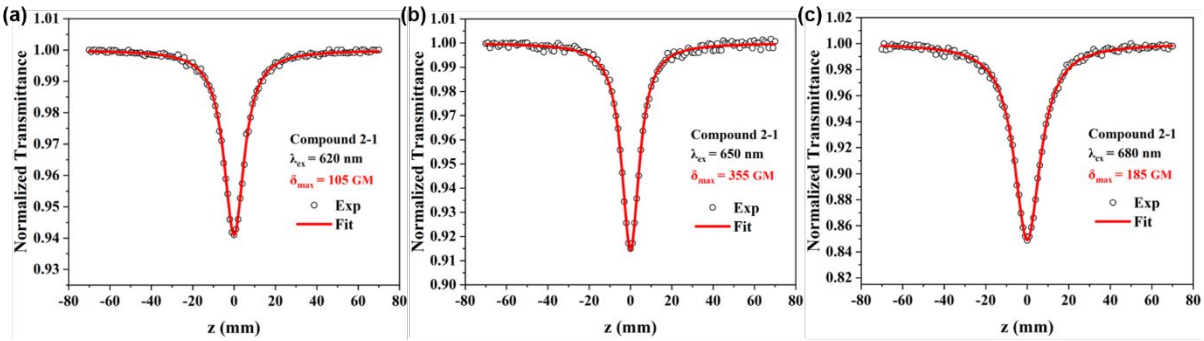


Figure S6. Open aperture Z-scan curves of compound **2-1** excited at fs-620 nm (a), fs-650 nm (b), and fs-680 nm (c), respectively (THF, $c \sim 1.0 \times 10^{-2}$ M).

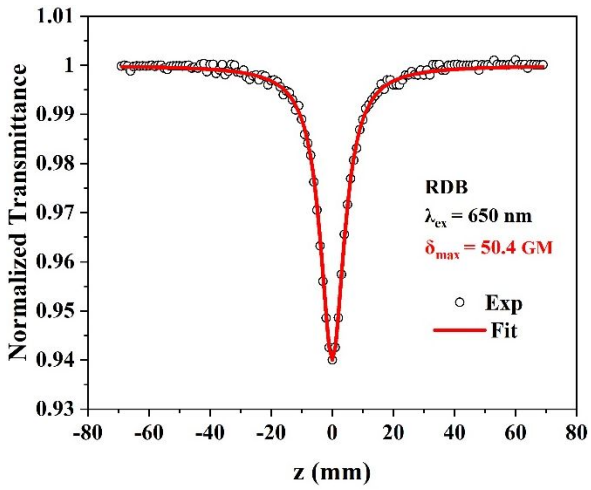


Figure S7. Open aperture Z-scan curve of rhodamine B in methanol excited at fs-650 nm (c ~ 1.0 ×10^{-2} M).

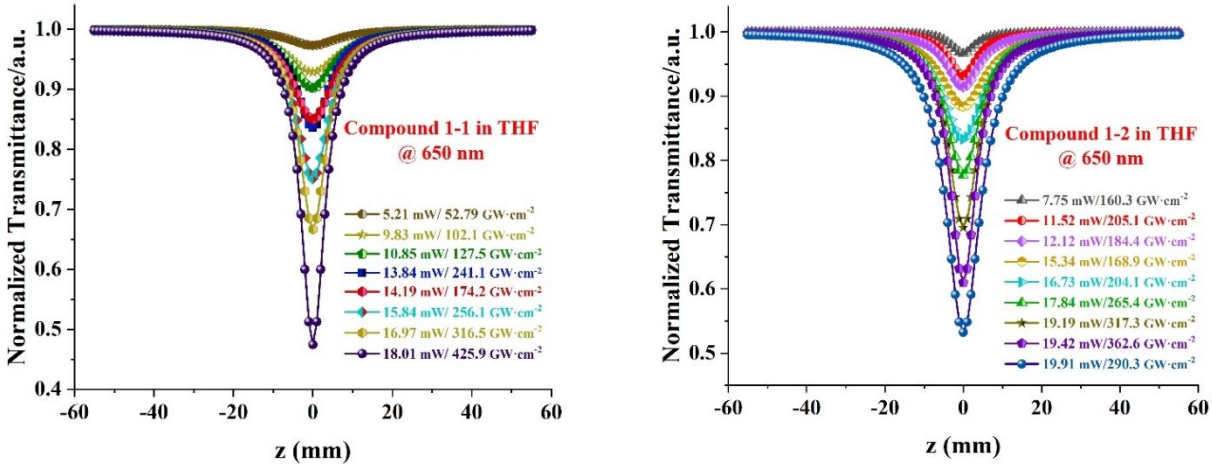


Figure S8. Normalized transmittance curves of *o*-carborane-based fluorophores **1-1** (left) and **1-2** (right) in THF excited at fs-650 nm under various laser input values (open-aperture Z-scan, c ~ 1.0 × 10^{-2} M).

Table S4. Third-order nonlinear optical parameters of the *o*-carborane-based fluorophores.

λ/ nm	Compound	Concentration/M	β/m·W^{-1}	Im($\chi^{(3)}$)/esu
620 nm	**1-1**	1.0×10^{-2}	1.2×10^{-13}	1.9×10^{-11}
	1-2	1.0×10^{-2}	1.7×10^{-13}	2.7×10^{-11}
	2-1	1.0×10^{-2}	1.9×10^{-13}	3.0×10^{-11}
650 nm	**1-1**	1.0×10^{-2}	2.0×10^{-13}	3.2×10^{-11}
	1-2	1.0×10^{-2}	2.3×10^{-13}	3.6×10^{-11}
	2-1	1.0×10^{-2}	7.0×10^{-13}	1.1×10^{-10}
680 nm	**1-1**	1.0×10^{-2}	1.2×10^{-13}	1.9×10^{-11}
	1-2	1.0×10^{-2}	9.0×10^{-13}	1.4×10^{-10}
	2-1	1.0×10^{-2}	4.6×10^{-13}	7.3×10^{-11}

6. NMR Spectra of the Compounds

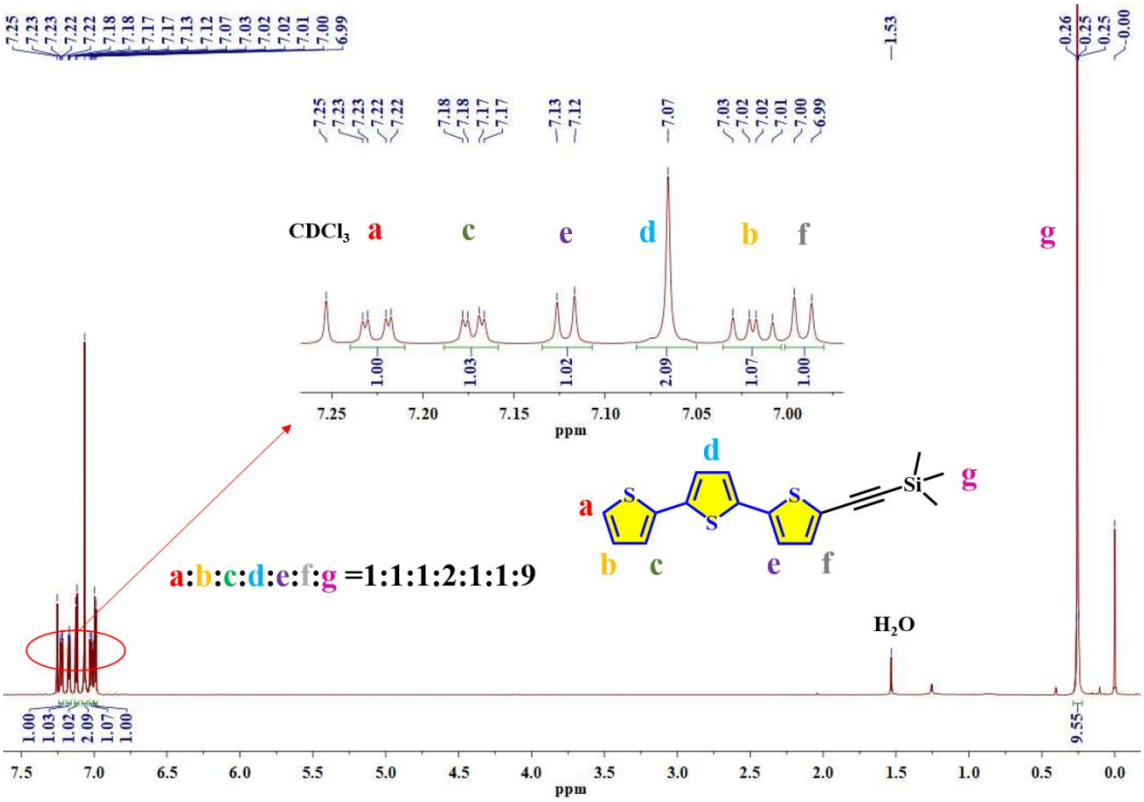


Figure S9. ^{1}H NMR spectrum of compound **3T-acetylene-TMS** in $CDCl_3$.

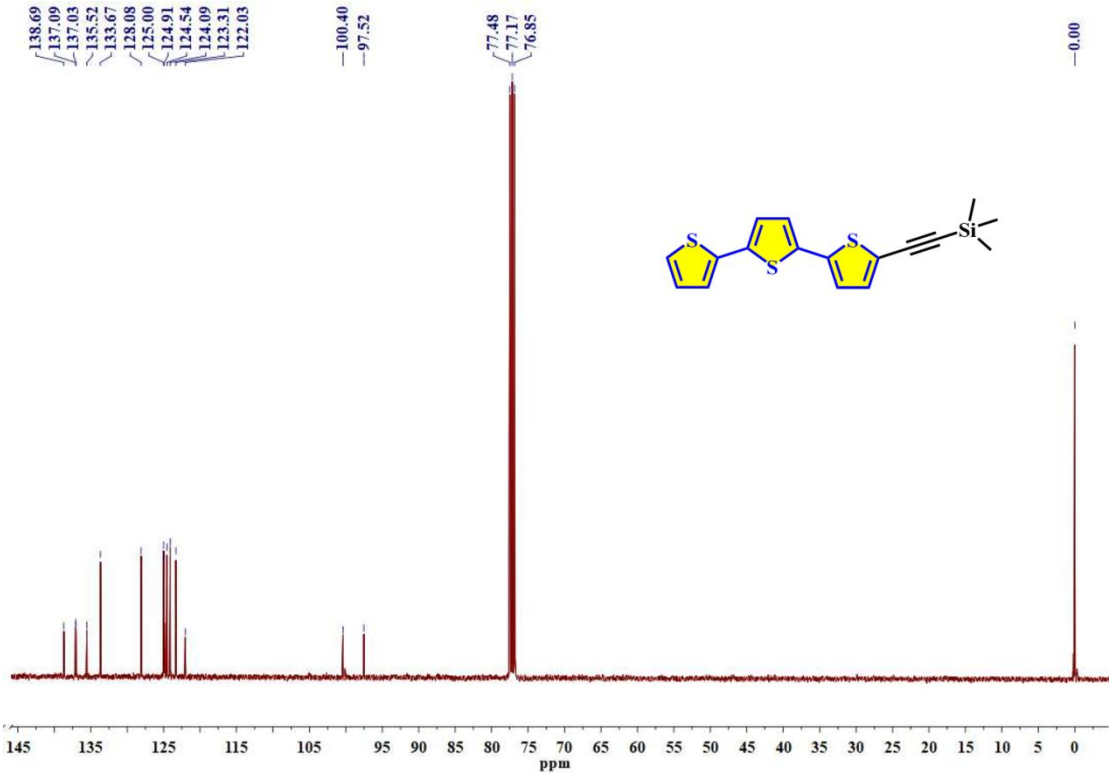


Figure S10. ^{13}C NMR spectrum of compound **3T-acetylene-TMS** in $CDCl_3$.

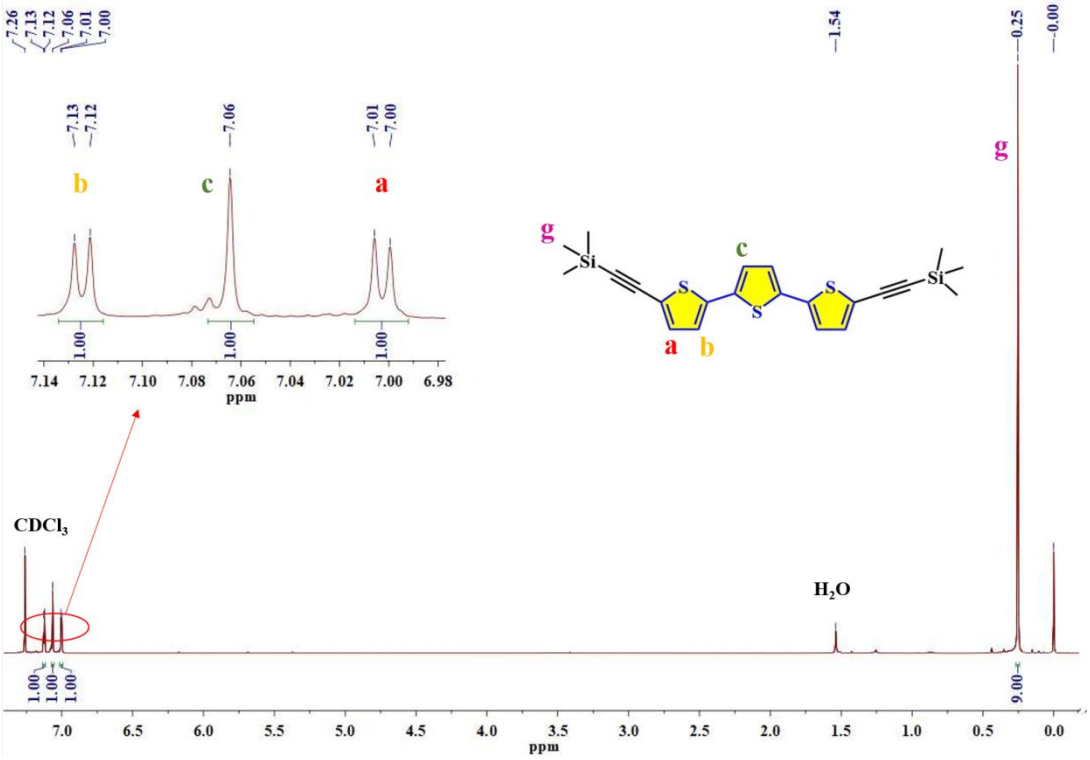


Figure S11. ^{1}H NMR spectrum of compound **bis(TMS-acetylene)-3T**.

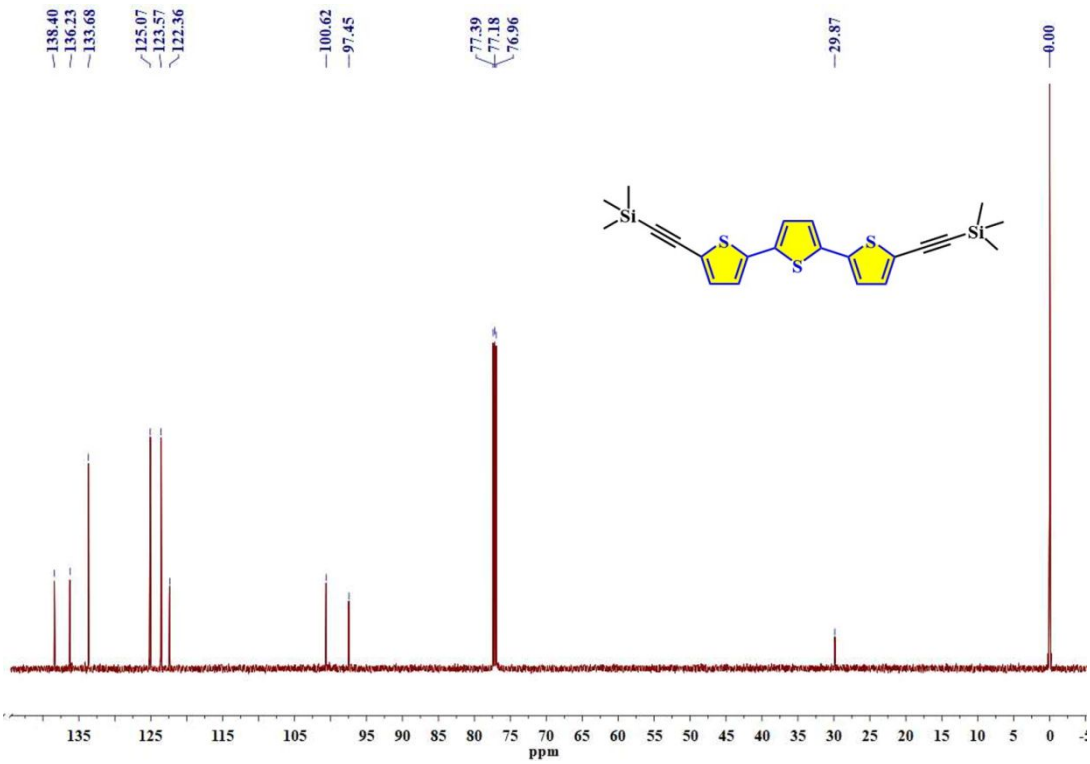


Figure S12. ^{13}C NMR spectrum of compound **bis(TMS-acetylene)-3T**.

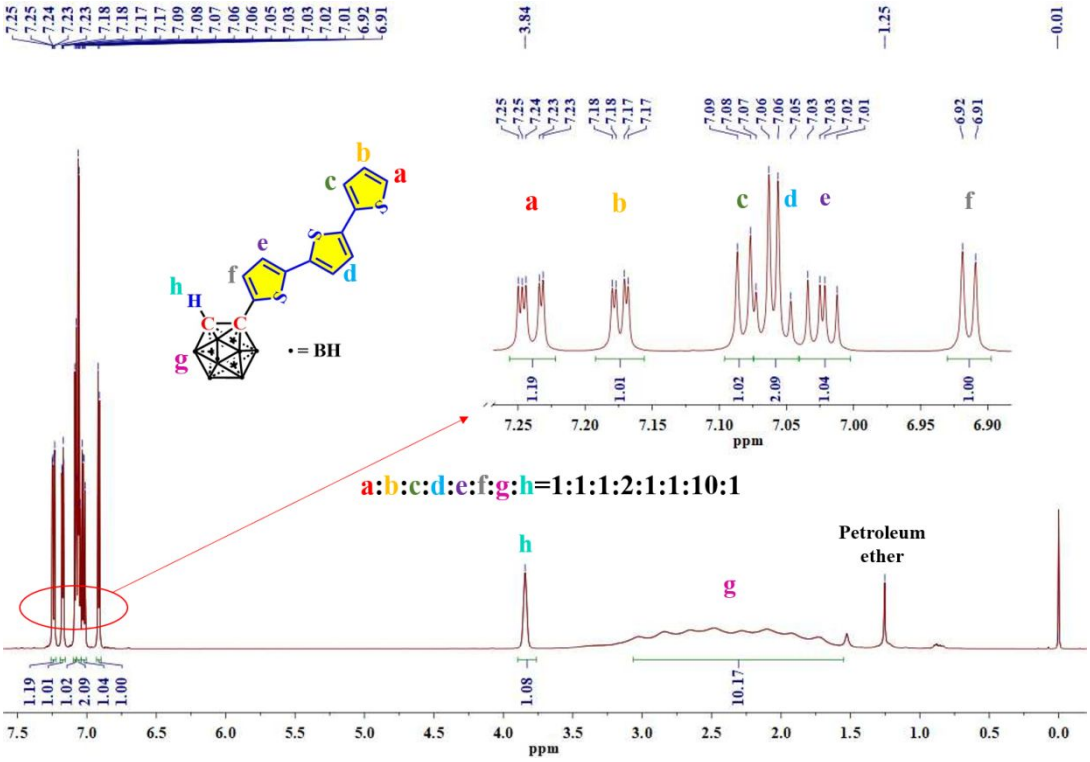


Figure S13. ^{1}H NMR spectrum of compound **1-1** in $CDCl_3$.

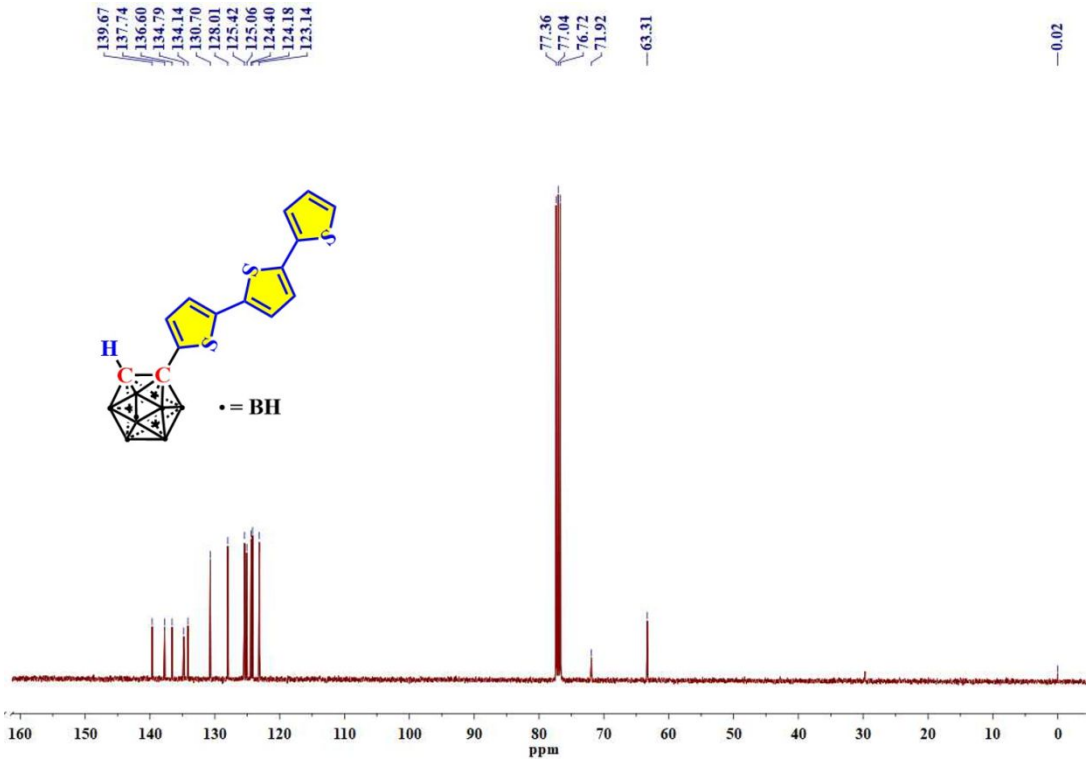


Figure S14. ^{13}C NMR spectrum of compound **1-1** in $CDCl_3$.

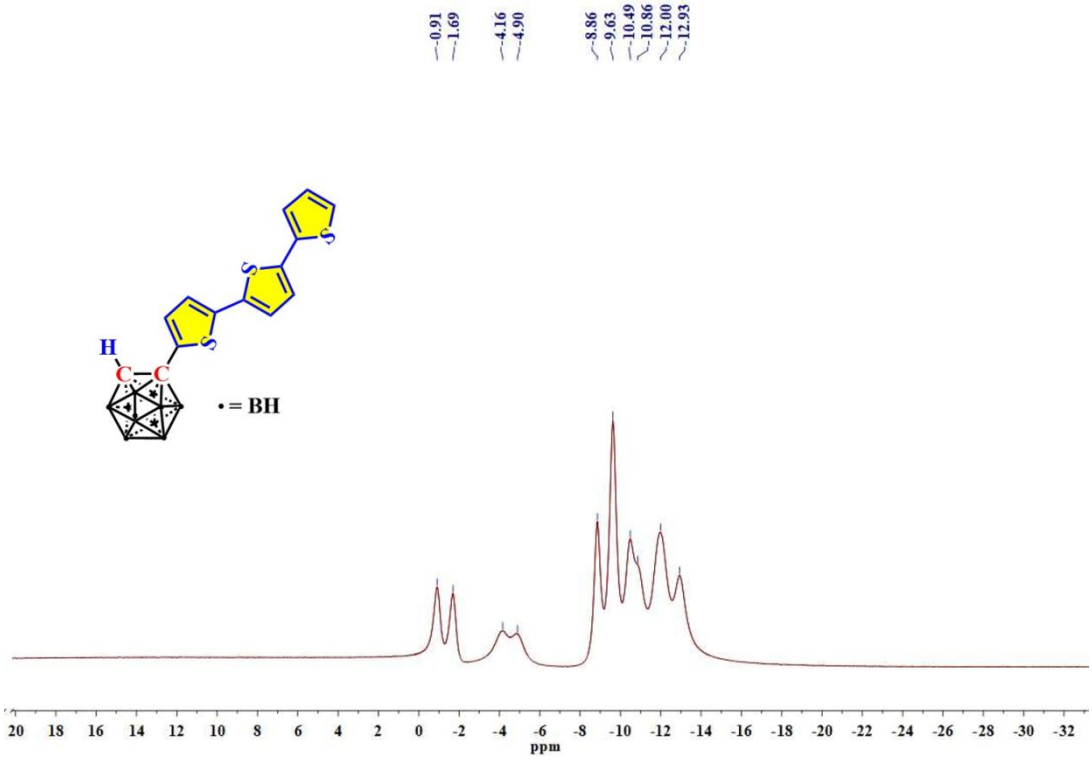


Figure S15. ^{11}B NMR spectrum of compound **1-1** in $CDCl_3$.

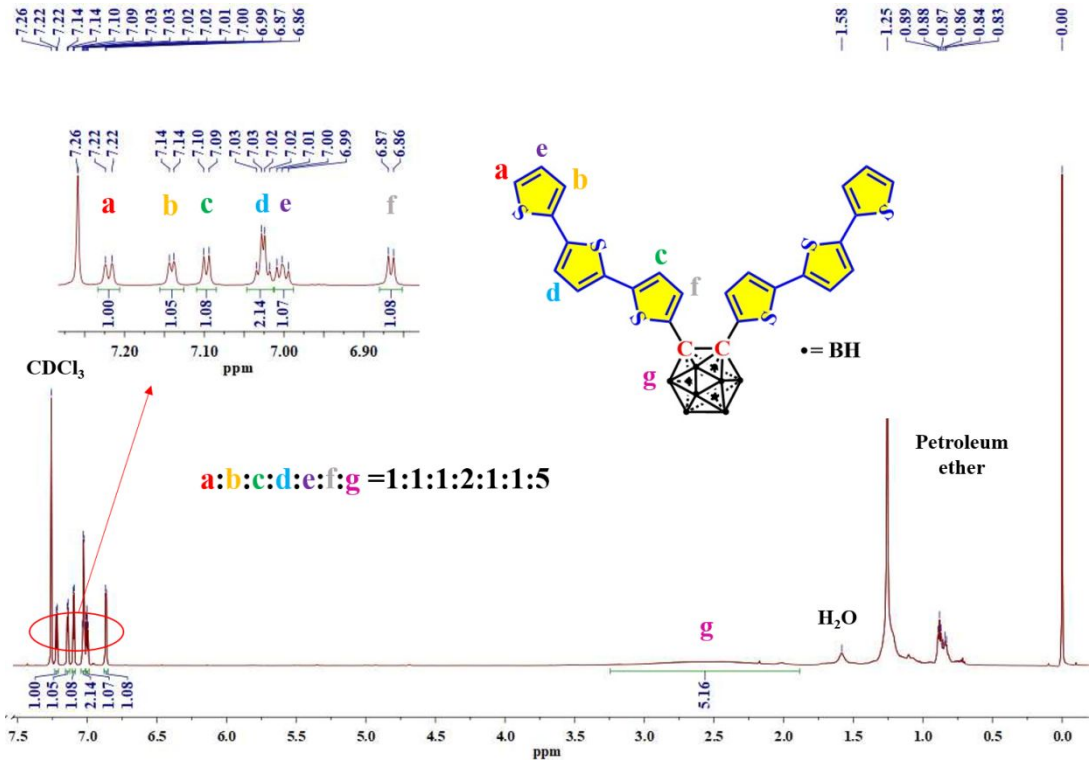


Figure S16. ^{1}H NMR spectrum of compound **1-2** in $CDCl_3$.

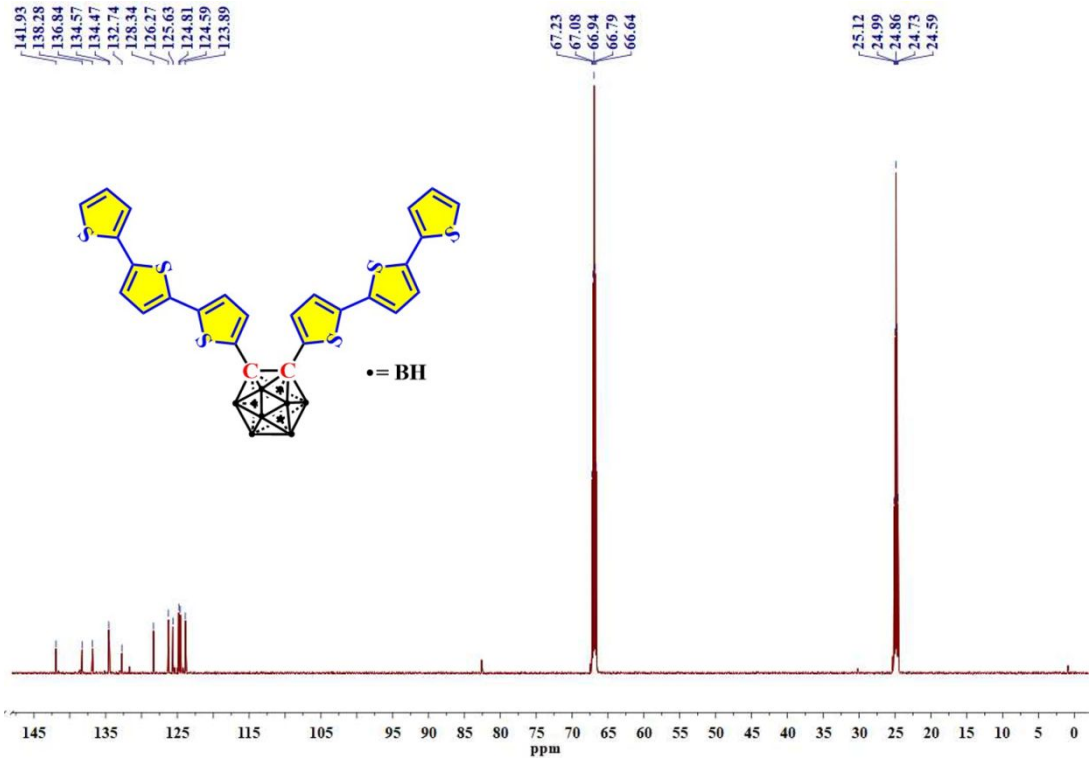


Figure S17. ^{13}C NMR spectrum of compound **1-2** in d_8-THF.

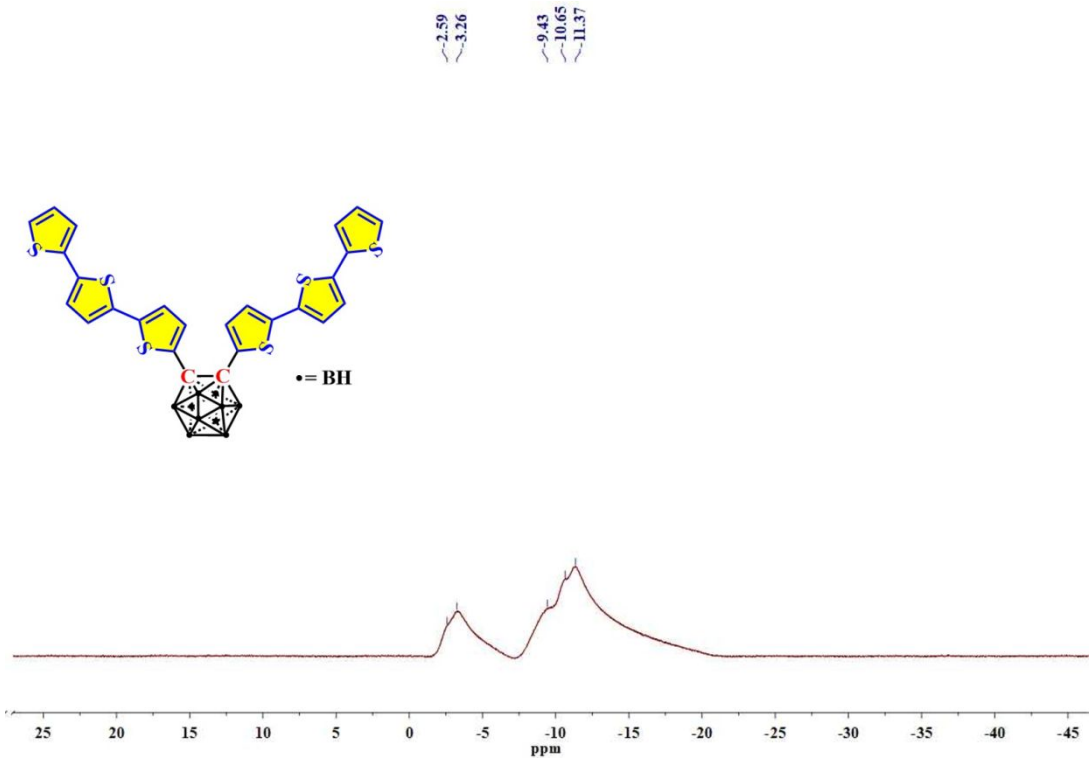


Figure S18. ^{11}B NMR spectrum of compound **1-2** in d_8-THF.

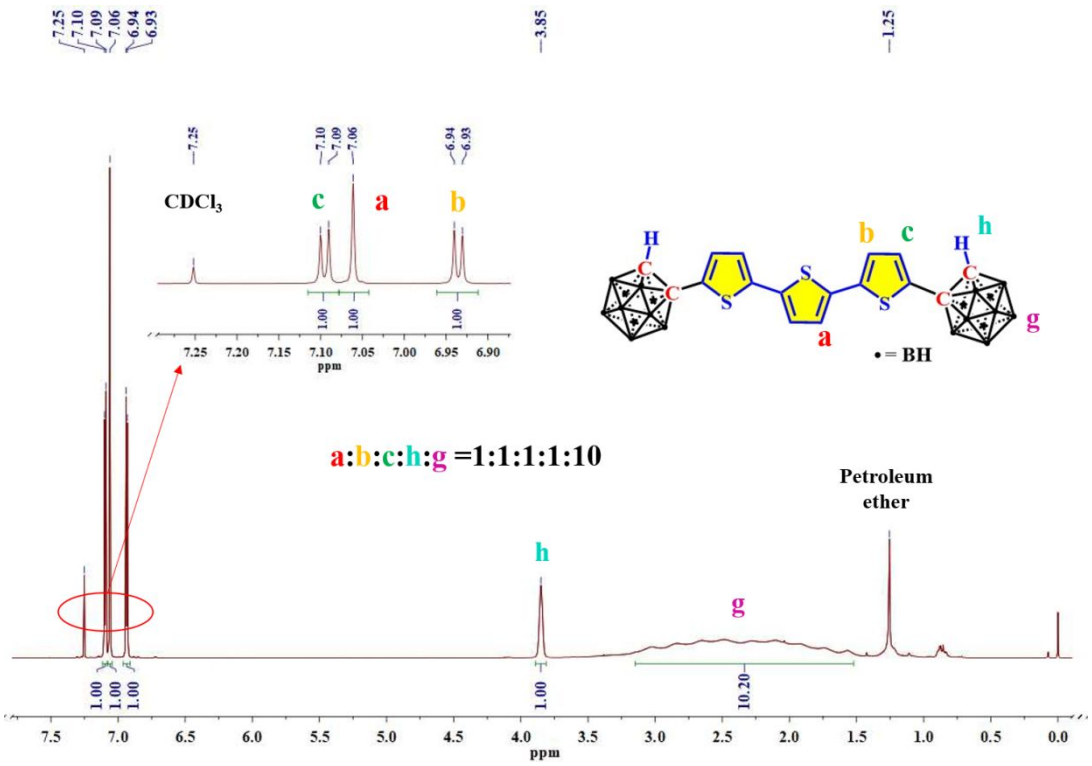


Figure S19. ^{1}H NMR spectrum of compound **2-1** in $CDCl_3$.

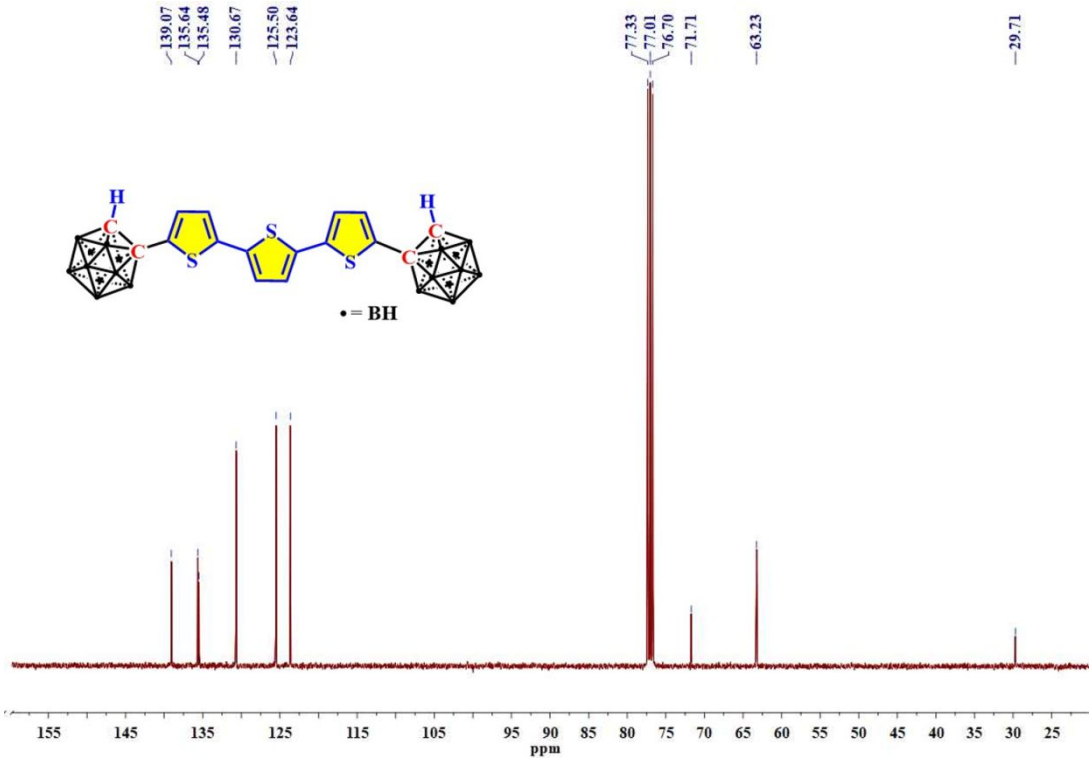


Figure S20. ^{13}C NMR spectrum of compound **2-1** in $CDCl_3$.

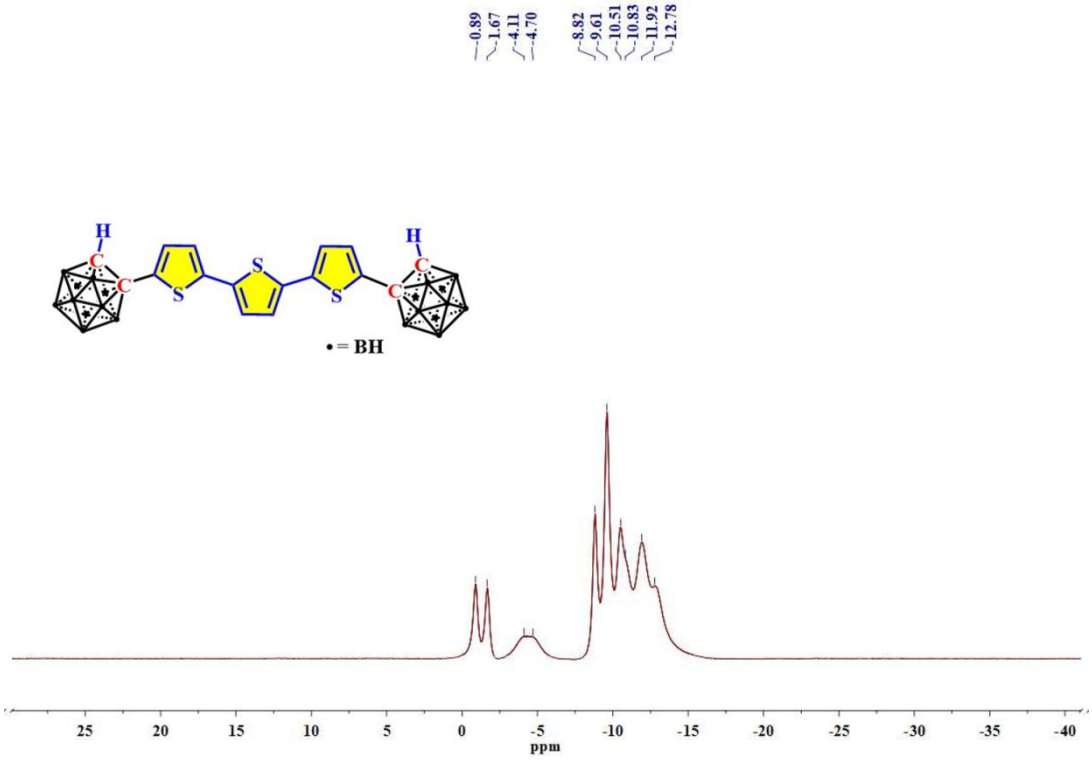


Figure S21. ^{11}B NMR spectrum of compound **2-1** in $CDCl_3$.

7. HRMS Spectra of the Compounds

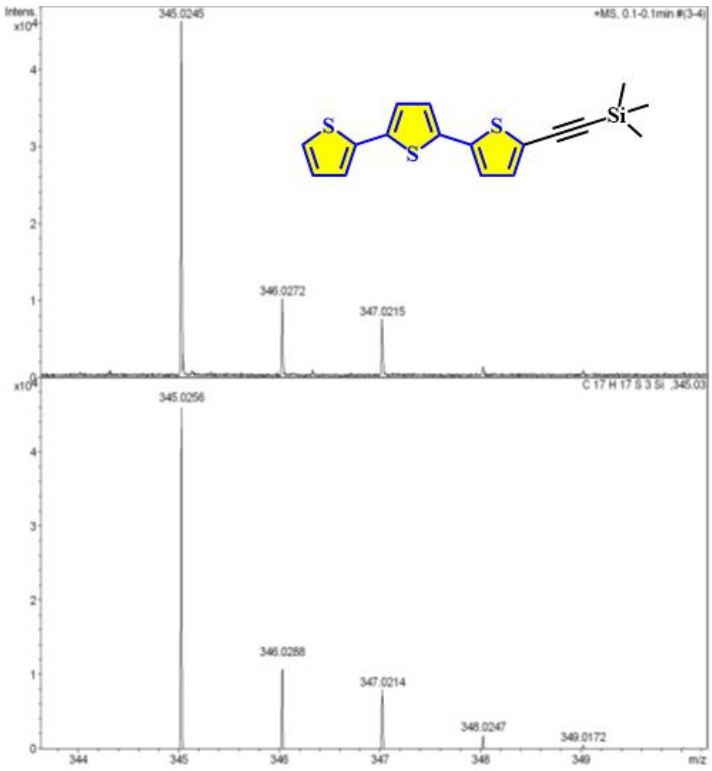


Figure S22. HRMS spectrum of compound **3T-acetylene-TMS**.

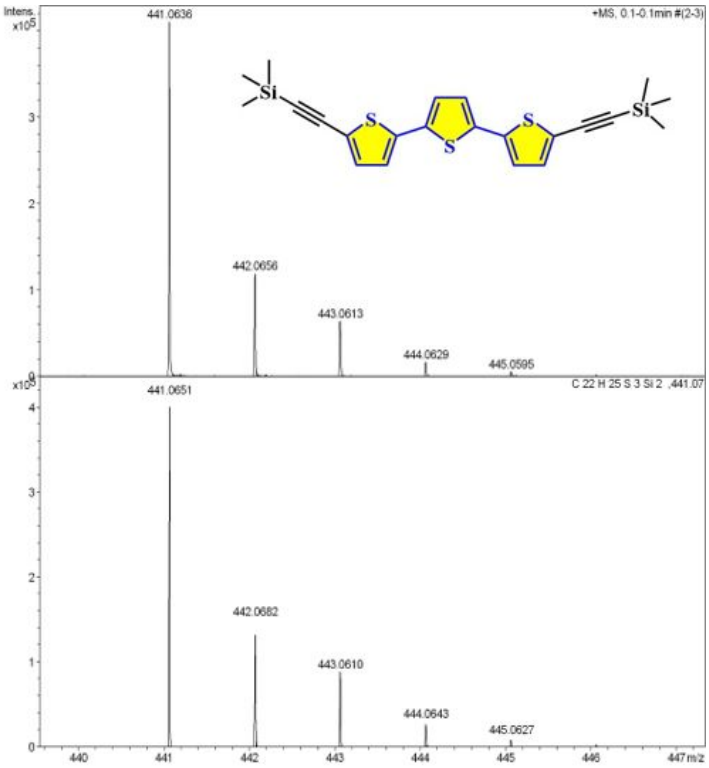


Figure S23. HRMS spectrum of compound **bis(TMS-acetylene)-3T**.

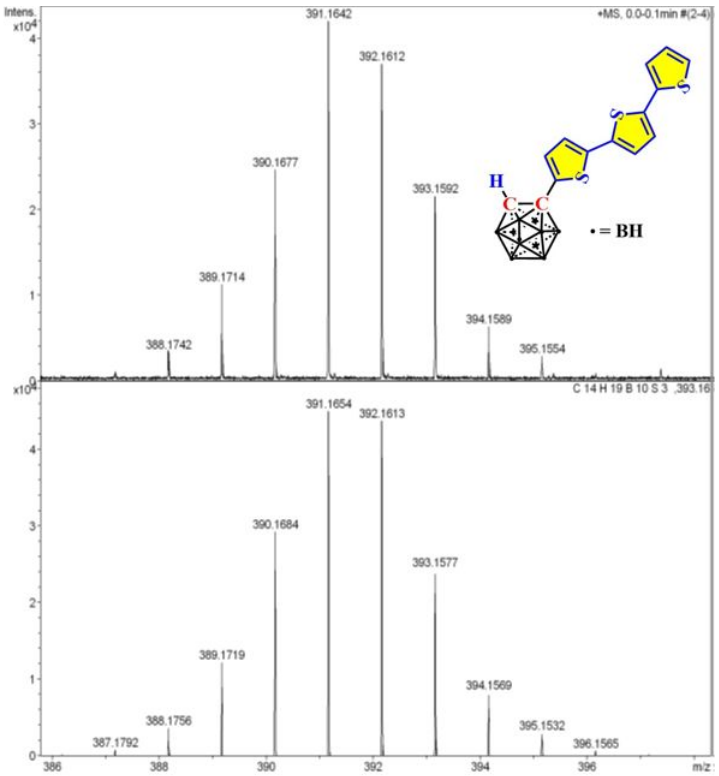


Figure S24. HRMS spectrum of compound **1-1**.

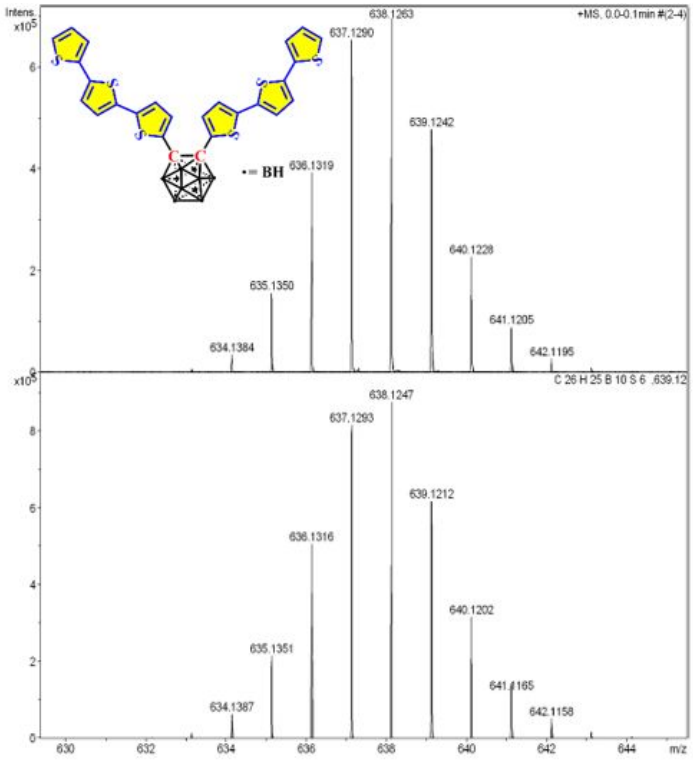


Figure S25. HRMS spectrum of compound **1-2**.

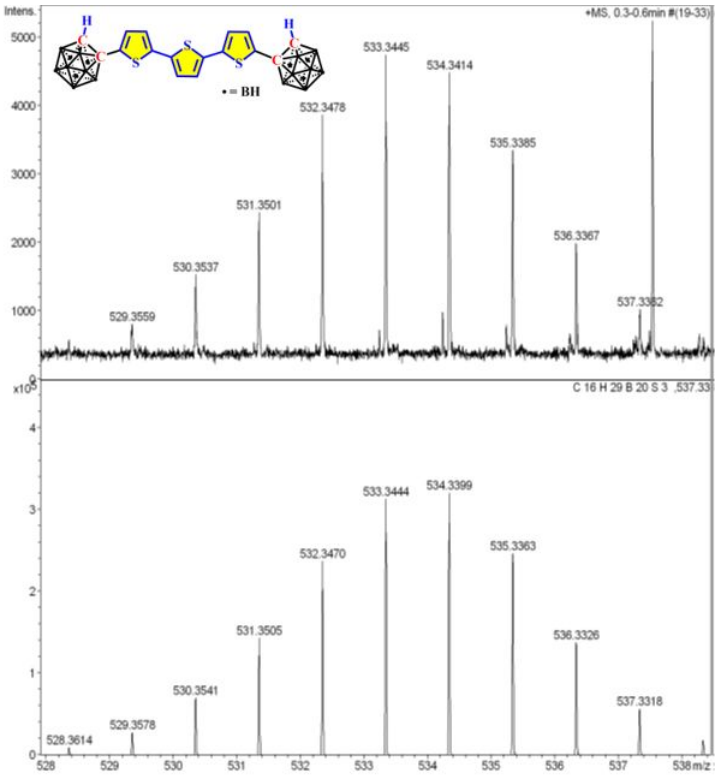


Figure S26. HR-MS spectrum of compound **2-1**.

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