Supporting Information

High-Performance Trichloroacetic Acid Sensor Based on the Intramolecular Hydrogen Bond Formation and Disruption of a Specially Designed Fluorescent *o*-Carborane Derivative in the Film State

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Contents

1. Synthesis and Characterization

The structure and synthesis routes for CB-BT-OCH_3 and Ph-BT-OCH_3 are illustrated in **Scheme S1**.

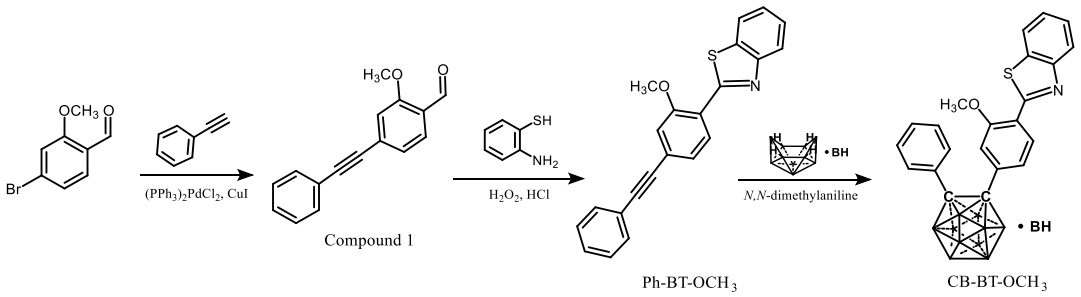
Synthesis of Ph-BT-OCH_3

Ph-BT-OCH_3 was synthesized according to a literature method.[1] A mixture of compound **1** (0.474 g, 2.0 mmol) and 2-aminothiophenol (0.25 g, 2.0 mmol) in distilled ethanol (30 mL) was stirred at room temperature, and then H_2O_2 (1.2 mL) and HCl (0.72 mL, 36%) were added. The solution was stirred at room temperature for another 2 h, and the filtered precipitation was washed several times with ethanol and water respectively. Further purification was carried out by column chromatography on silica gel using dichloromethane/*n*-hexane (*v*/*v*, 1/3) to obtain a white solid. ^{1}H NMR (CD_2Cl_2, 600 MHz, ppm): δ 8.59 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 6.3 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.51-7.40 (m, 4H), 4.15 (s, 3H). ^{13}C NMR (CD_2Cl_2, 150 MHz, ppm): δ 162.16, 156.98, 152.20, 136.24, 131.66, 128.52, 124.38, 122.78, 122.72, 122.33, 121.30, 114.66, 91.46, 88.91, 55.91. HRMS of $C_{22}H_{15}NOS$ (ESI, positive mode): Calcd. for [$(M+H)^+$]: 342.0947, found: 342.0940.

Synthesis of CB-BT-OCH_3

CB-BT-OCH_3 was synthesized according to a known literature method.[2] A mixture of decaborane ($B_{10}H_{14}$, 0.36 g, 3.0 mmol) and *N*,*N*-dimethylaniline (0.46 g, 3.3 mmol) in distilled toluene (30 mL) was stirred at room temperature for 30 min under N_2 atmosphere, and then the temperature was raised to 100 °C for 2 h. At 40 °C, Ph-BT-OCH_3 (0.34 g, 1.0 mmol) was added to the reaction mixture and the latter was refluxed for another 5 h. After cooling down to room temperature and quenched with methanol, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using dichloromethane/*n*-hexane (*v*/*v*, 1/3) as the eluent. Product CB-BT-OCH_3 was obtained as a white powder. ^{1}H NMR (CD_2Cl_2, 600 MHz, ppm): δ 8.36 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 7.9 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.25 (t, J = 7.5 Hz, 2H), 7.11 (s, 1H), 3.95 (s, 3H). ^{11}B NMR (CD_2Cl_2, 192 MHz, ppm): δ -2.29, -2.99, -8.81, -9.90, -10.73, -11.68. ^{13}C NMR (CD_2Cl_2, 150 MHz, ppm): δ 161.19, 156.38, 152.04, 136.23, 133.55, 130.75, 130.56, 130.43, 128.91, 128.54, 126.13, 125.04, 123.84, 123.42,

122.89, 121.34, 114.26, 85.64, 84.49, 55.90. HRMS of $C_{22}H_{25}B_{10}NOS$ (ESI, Positive mode): Calcd. for [$(M+H)^+$]: 460.2744, found: 460.2749.



Scheme S1. Synthetic route for the fluorophores.

2. Fluorescence Property and Crystal Structure of Ph-BT-OCH_3

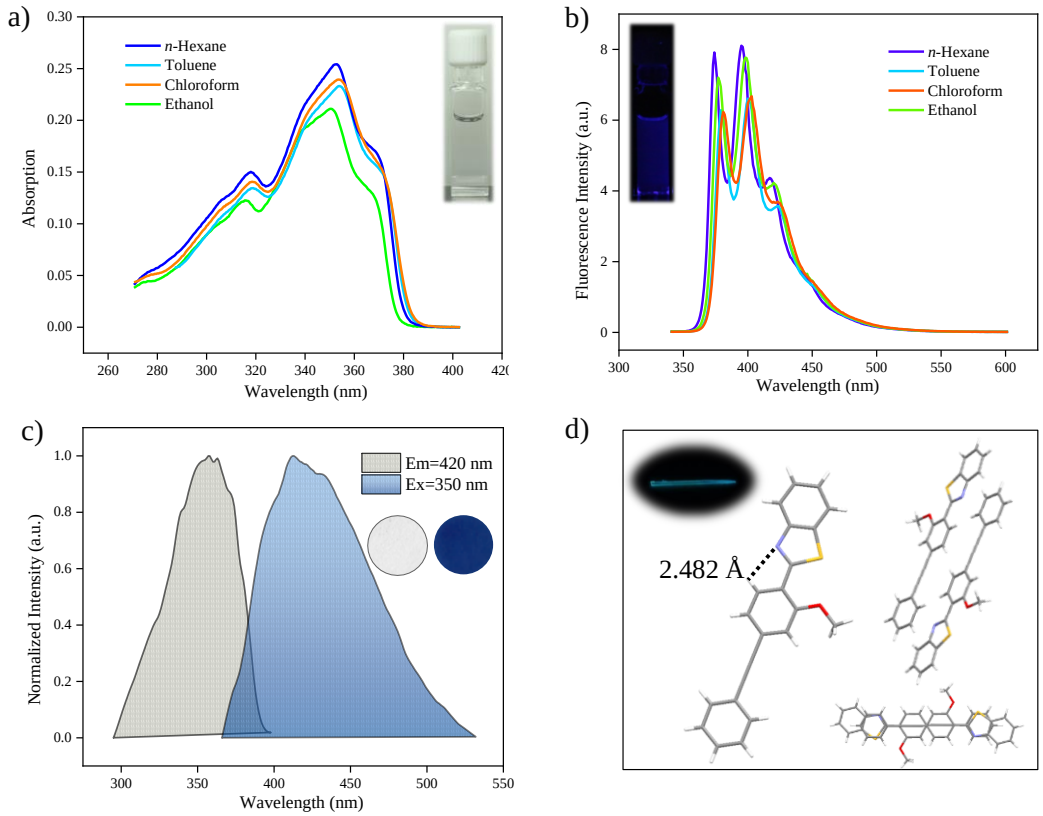


Fig. S1 UV-vis absorption spectra (a) and fluorescence emission spectra (b) of Ph-BT-OCH_3 recorded in *n*-hexane, toluene, chloroform and ethanol, respectively (c = 5.0 × 10^{-6} mol·L^{-1}, 298 K, λ_{ex} = 350 nm); (c) Fluorescence excitation and emission spectra of Ph-BT-OCH_3-based film; (d) Single-crystal structure of Ph-BT-OCH_3, inset shows the fluorescent photography of the crystal.

3. Fluorescence Spectra and Lifetime Changes

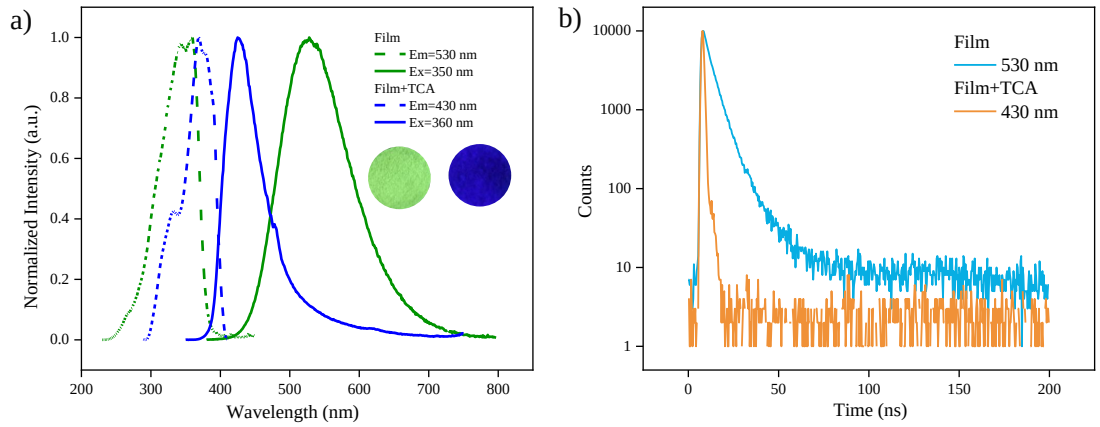


Fig. S2 Fluorescence spectra (a) and fluorescence lifetime changes (b) of CB-BT-OCH_3-based film in the absence and presence of gaseous TCA.

4. Partial H-H COSY Spectra of CB-BT-OCH_3

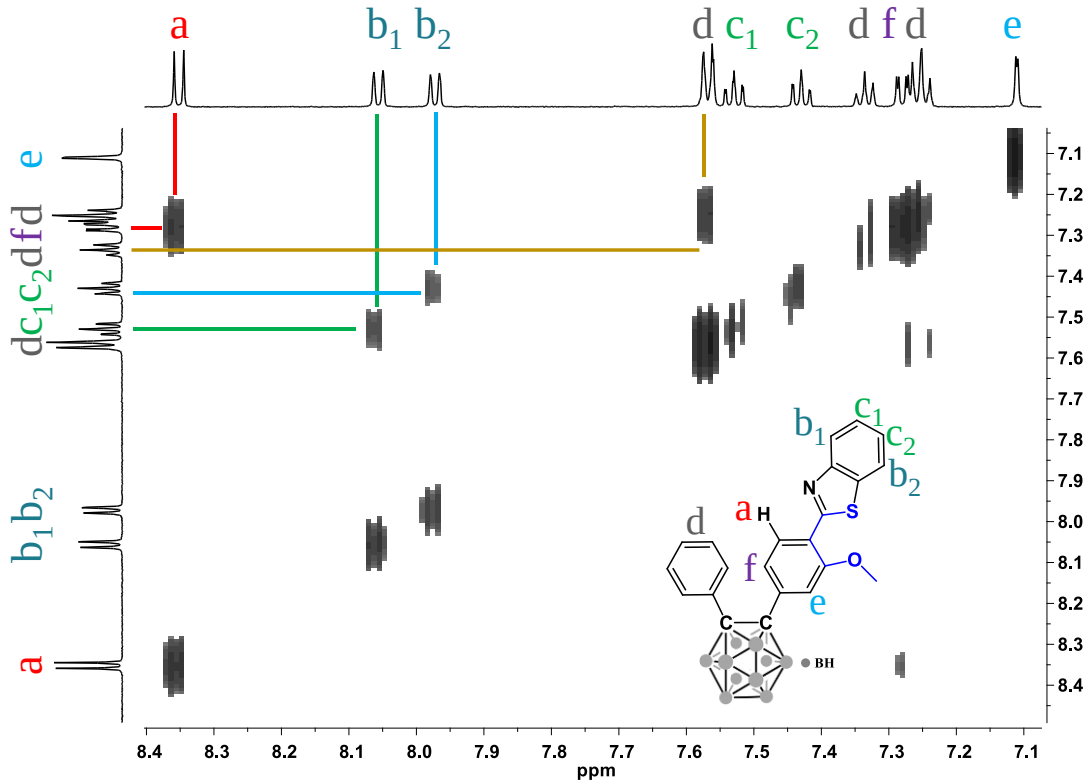


Fig. S3 Partial H-H COSY spectra of CB-BT-OCH_3 at the concentration of 1.0 mM (600 MHz, CD_2Cl_2).

5. ^{1}H NMR Titration of CB-BT-OCH$_3$ by TCA

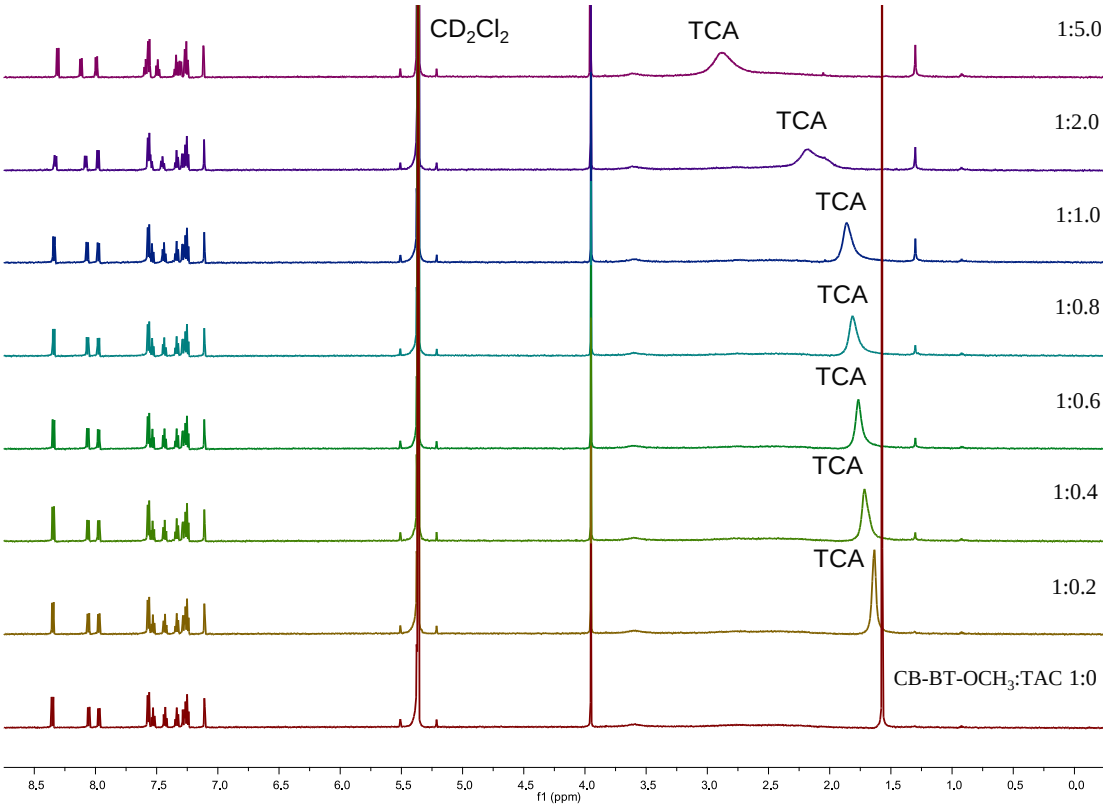


Fig. S4 ^{1}H NMR spectra of CB-BT-OCH$_3$ (1.0 mM) with increasing titration amounts of TCA (0-5.0 equiv., 600 MHz, CD_2Cl_2).

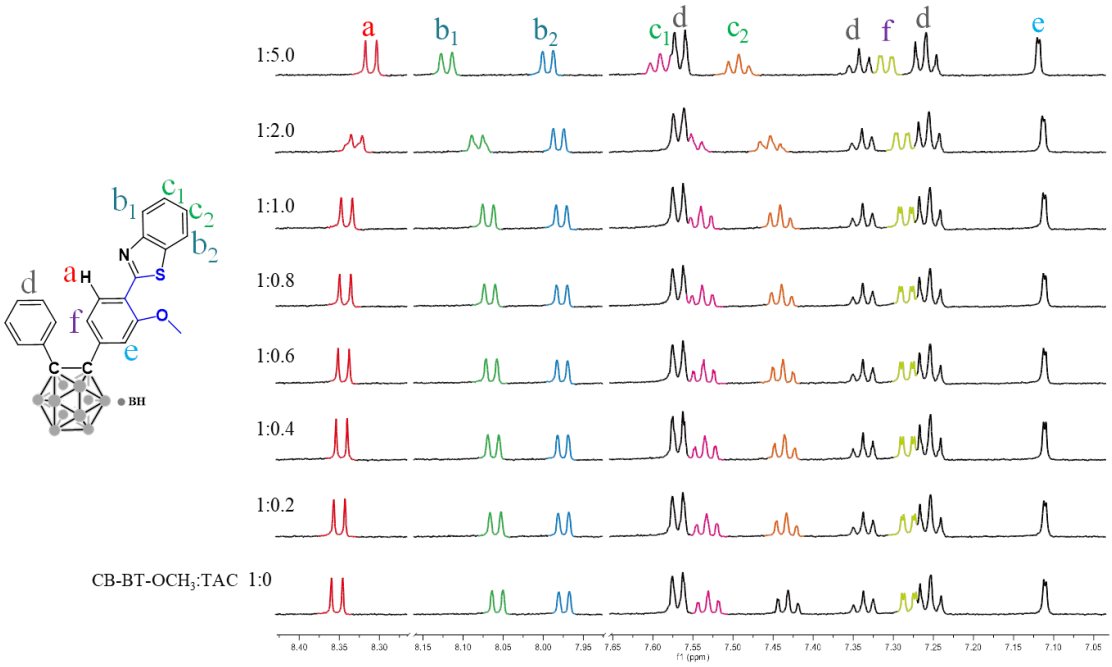


Fig. S5 Partial ^{1}H NMR spectra of CB-BT-OCH_3 (1.0 mM) with increasing titration amounts of TCA (0-5.0 equiv., 600 MHz, CD_2Cl_2).

6. Fluorescence Titration of CB-BT-OCH_3 by TCA

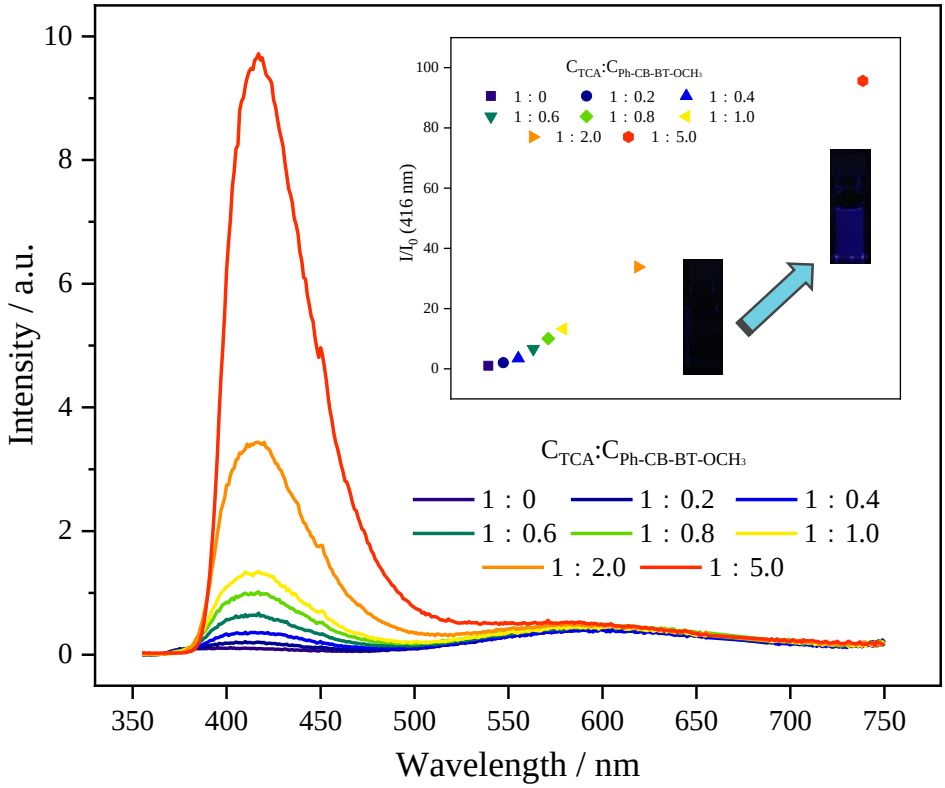


Fig. S6 Fluorescence emission spectra of CB-BT-OCH_3 (1.0 mM) with increasing titration amounts of TCA (0-5.0 equiv.).

7. Crystallographic Data of CB-BT-OCH_3 and Ph-BT-OCH_3

Table S1. Crystallographic data of CB-BT-OCH_3.

Identification code	20200613zh_kjhz2835_2_0m_a
Empirical formula	$C_{22}H_{25}B_{10}NOS$
Formula weight	459.59
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.2548(3) Å α= 90°
	b = 18.8293(7) Å β= 102.2480(10)°
	c = 16.0124(5) Å γ = 90°
Volume	2432.19(15) $Å^3$
Z	4
Density (calculated)	1.255 Mg/m^3
Absorption coefficient	0.151 mm^{-1}
F(000)	952
Crystal size	0.120 x 0.110 x 0.080 mm^3
Theta range for data collection	2.525 to 27.481°.
Index ranges	$-10 \le h \le 10$, $-24 \le k \le 23$, $-20 \le l \le 20$
Reflections collected	21667
Independent reflections	5536 [R(int) = 0.0362]
Completeness to theta = 25.242°	99.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5536 / 0 / 317
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.1451
R indices (all data)	R1 = 0.0635, wR2 = 0.1614
Extinction coefficient	n/a
Largest diff. peak and hole	0.379 and -0.331 e. $Å^{-3}$

Table S2. Crystallographic data of Ph-BT-OCH_3.

Identification code	20200821LI_ZNZ9929_0m_a
Empirical formula	$C_{22}H_{15}NOS$
Formula weight	341.41
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.0974(5) Å α= 90°
	b = 15.0431(10) Å β= 105.686(2)°
	c = 11.5466(6) Å γ = 90°.
Volume	1688.57(17) $Å^3$
Z	4
Density (calculated)	1.343 Mg/m^3
Absorption coefficient	0.201 mm^{-1}
F(000)	712
Crystal size	0.120 x 0.110 x 0.080 mm^3
Theta range for data collection	2.381 to 27.500°.
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 17$, $-14 \le l \le 13$
Reflections collected	15400
Independent reflections	3863 [R(int) = 0.0338]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3863 / 0 / 227
Goodness-of-fit on F^2	0.895
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1149
R indices (all data)	R1 = 0.0561, wR2 = 0.1276
Extinction coefficient	n/a
Largest diff. peak and hole	0.488 and -0.302 e. $Å^{-3}$

8. Comparison of Analytical Performances of TCA Sensors

Table S3 Comparison of the performances of the conceptual fluorescent film sensor as developed with some of the methods reported recently in literatures

References	Sensing Techniques	Sample	LODs	Response Time	Reusability	Conceptual Sensor	Safety Limit*
This work	Fluorescence	Vapor	0.2 ppm (experimental value)	< 0.2 s (detectable intensity change)	Reusable	Yes	**Vapor:** 1 ppm **Solution:** 0.1 μg/mL (0.6 μM)
3	Gas chromatography mass spectrometry	Solution	0.005 μg/mL (calculated value)	10 min	Not available	Not available	
4	Covalent Organic Frameworks (COFs)	Vapor Solution	Not mentioned	Not mentioned	Not available	No	
5	Electrochemical method	Solution	1.1 μg/mL (practical value)	5 s	Not mentioned	No	
6	Metal Organic Framework (MOFs)	Solution	1.89 nM (calculated value)	Not mentioned	Not available	No	
7	Electrochemical method	Solution	30 nM (calculated value)	Not mentioned	Not mentioned	No	

* The safety limit concentration for TCA described in national standard of the threshold limit values (TLVs) and biological exposure indices (BEIs) booklet issues by American conference of governmental industrial hygienists (ACGIH), Cincinnati, 2011 (https://www.cdc.gov/niosh/pel88/76-03.html).

9. NMR and HRMS Spectra of the Synthesized Compounds

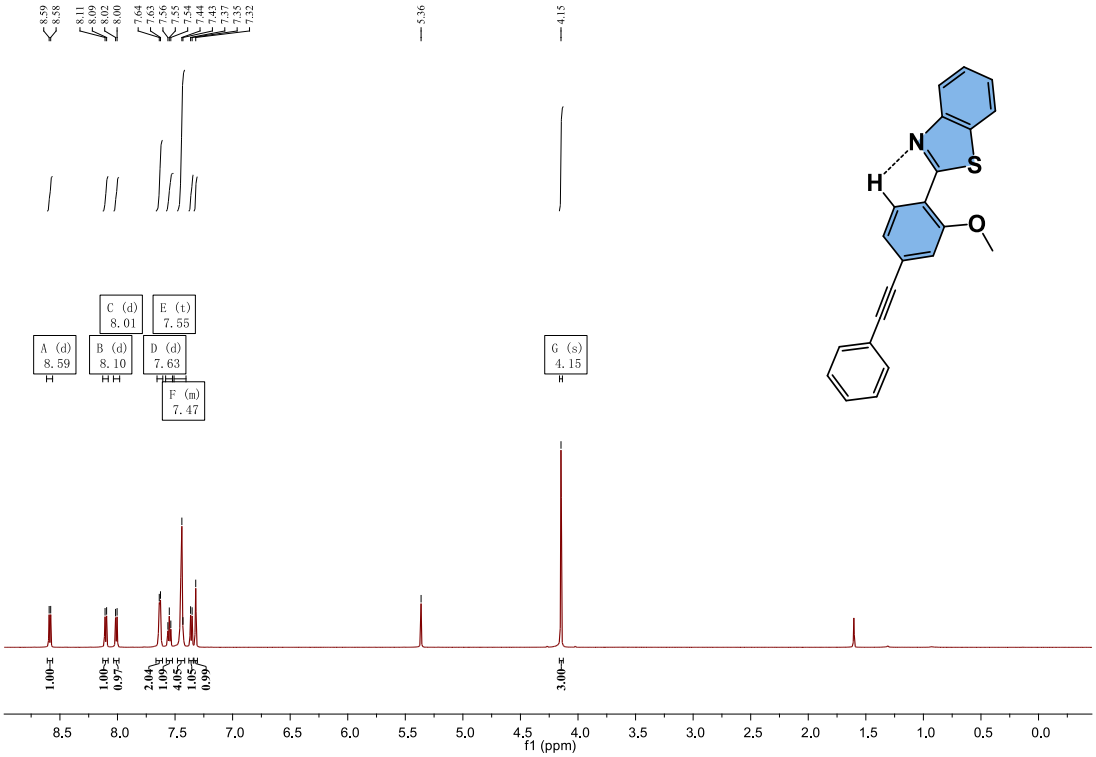


Fig. S7 ^{1}H NMR spectrum of Ph-BT-OCH_3 in CD_2Cl_2.

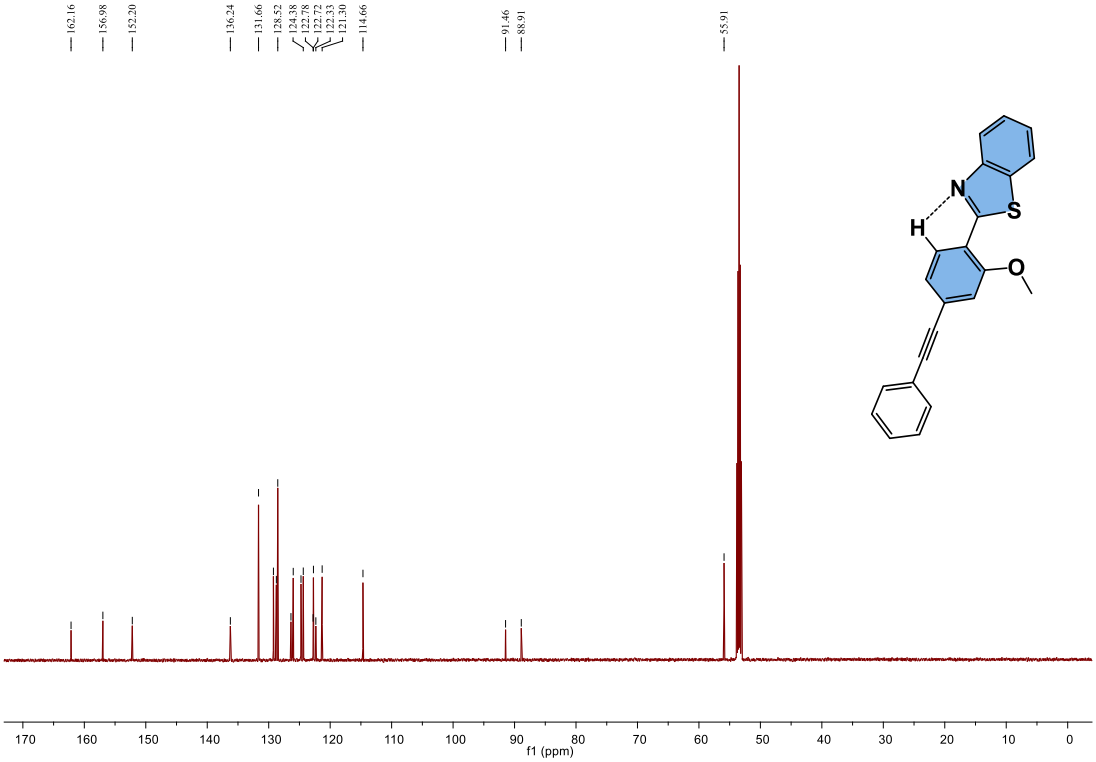


Fig. S8 ^{13}C NMR spectrum of Ph-BT-OCH_3 in CD_2Cl_2.

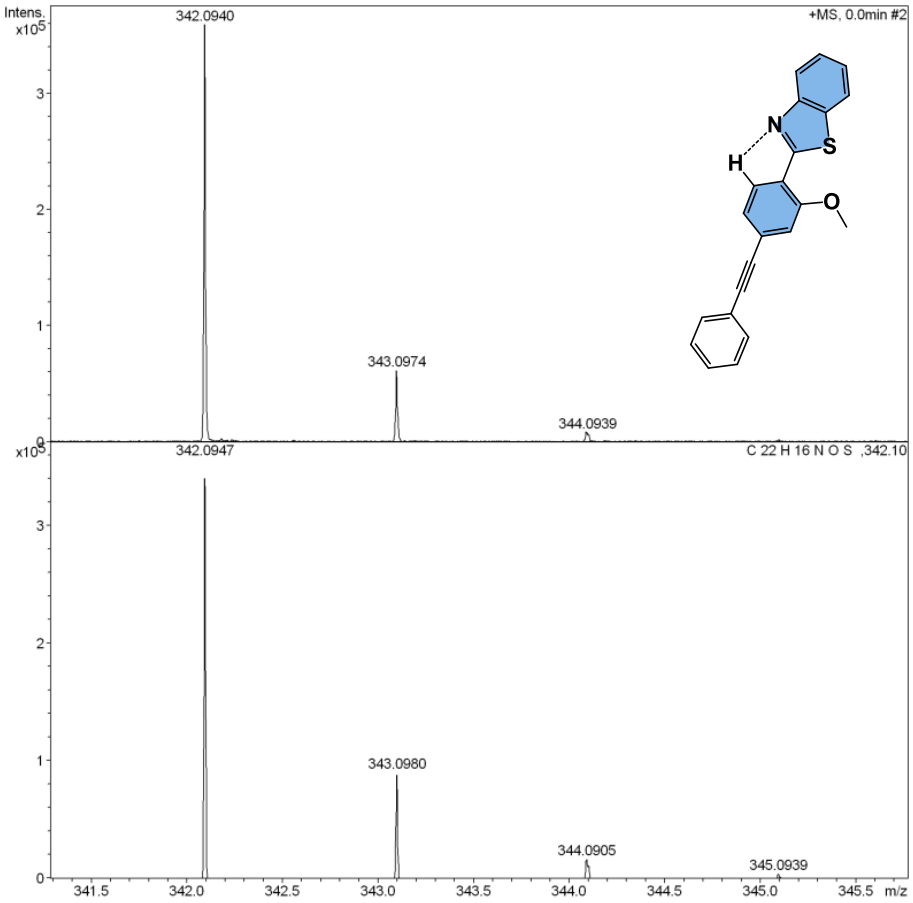


Fig. S9 HRMS spectrum of Ph-BT-OCH_3.

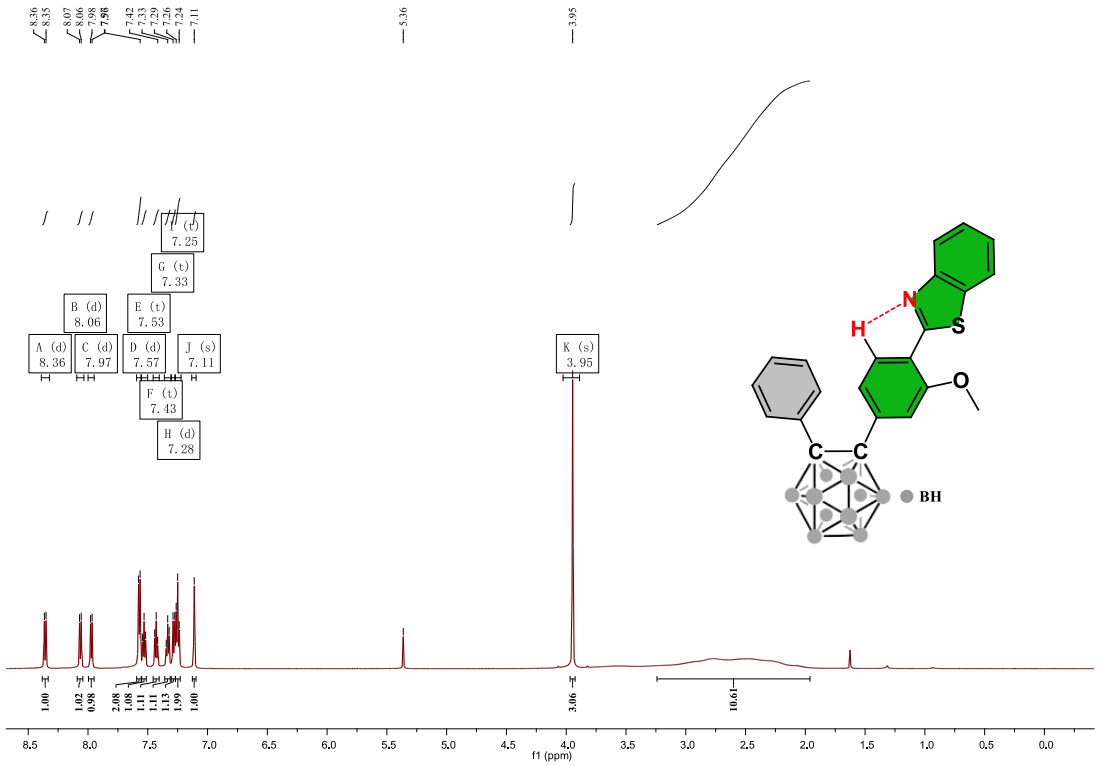


Fig. S10 ^{1}H NMR spectrum of CB-BT-OCH_3 in CD_2Cl_2.

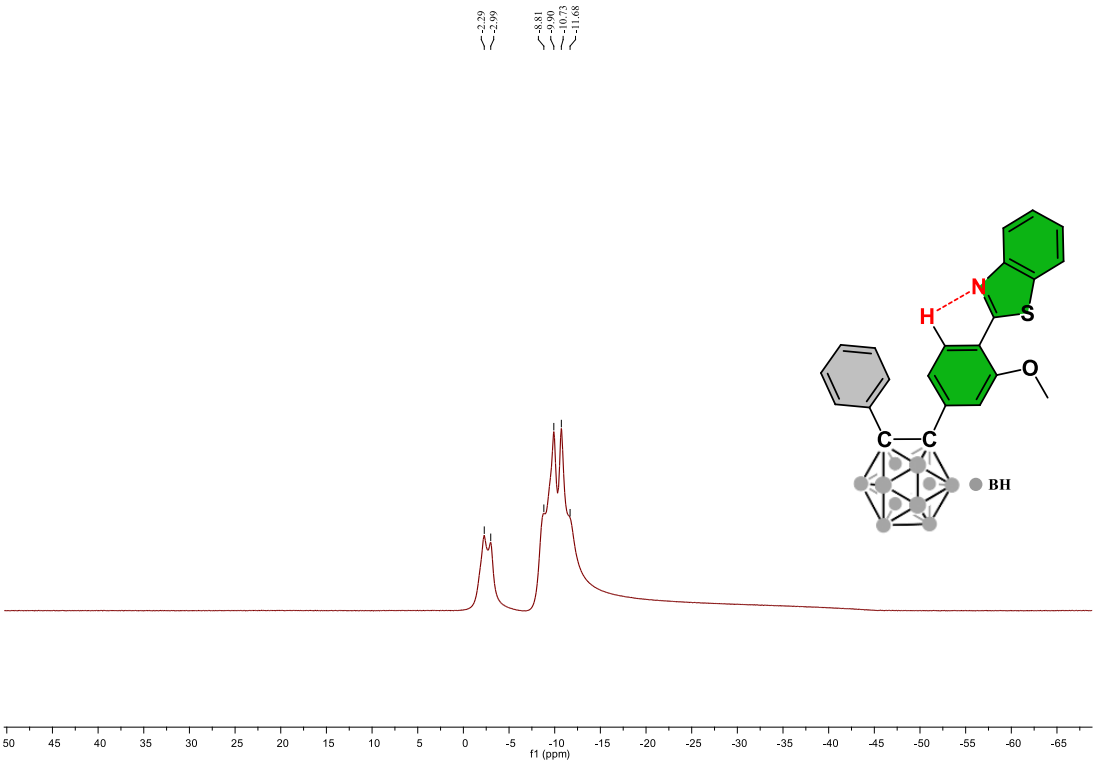


Fig. S11 ^{11}B NMR spectrum of CB-BT-OCH_3 in CD_2Cl_2.

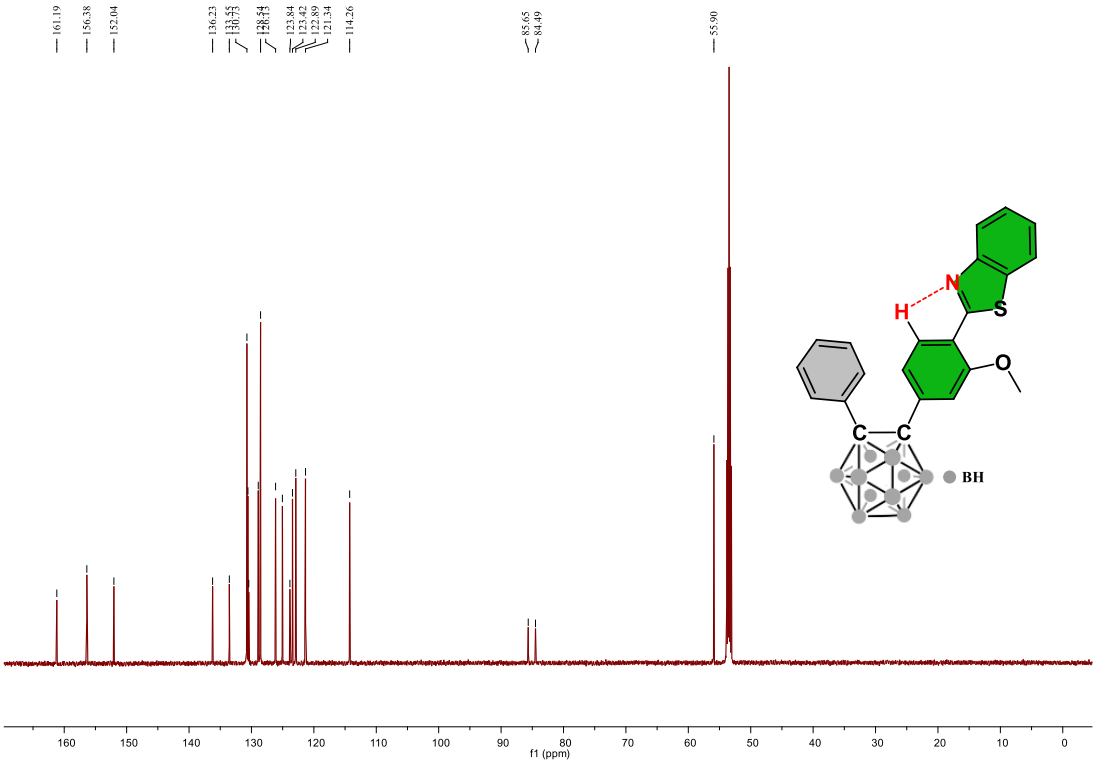


Fig. S12 ^{13}C NMR spectrum of CB-BT-OCH_3 in CD_2Cl_2.

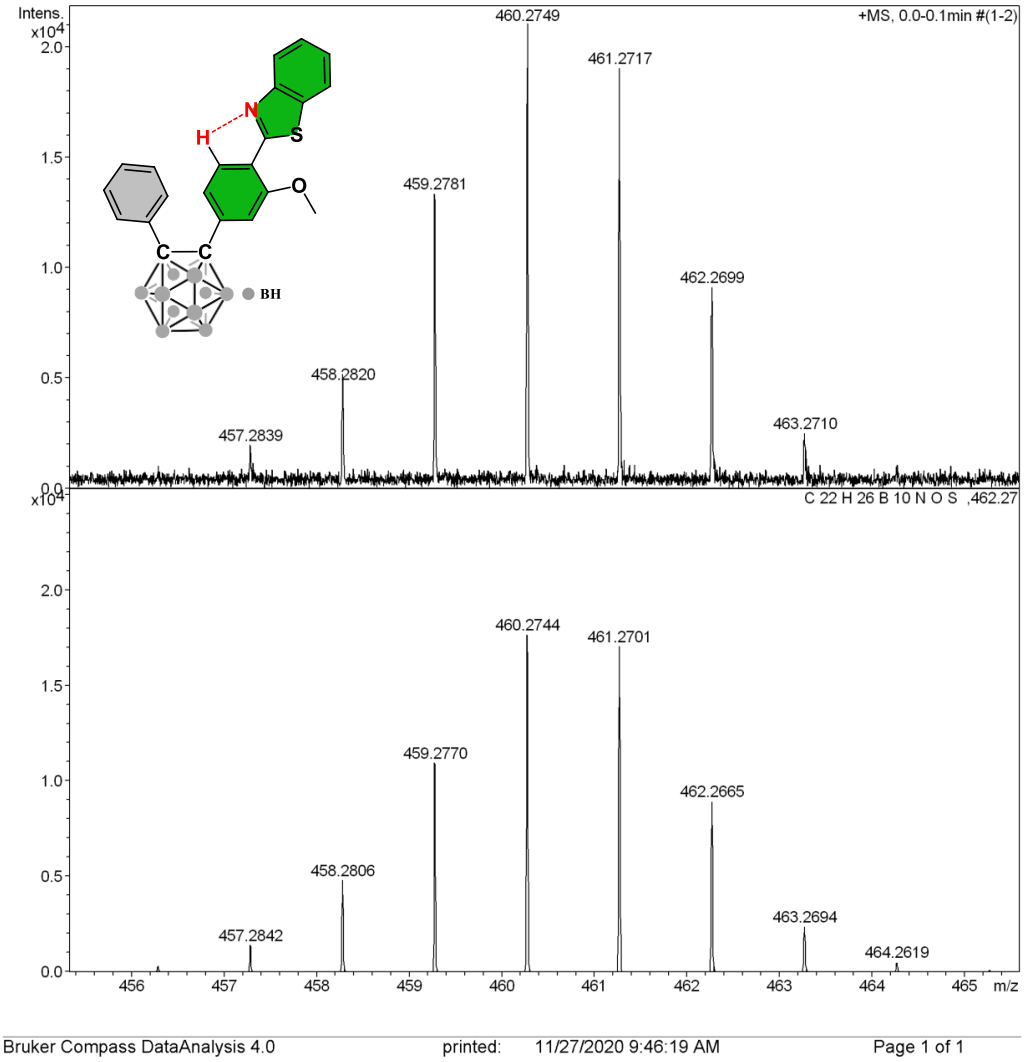


Fig. S13 HRMS spectrum of CB-BT-OCH_3.

References

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