

Supporting Information

Progress Toward Colorimetric and Fluorescent Detection of Carbonyl Sulfide

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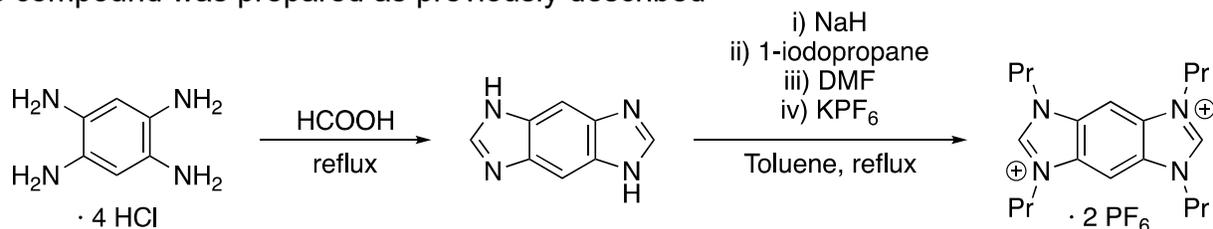
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Materials and Methods

Reagents were purchased from Sigma-Aldrich, TCI, Fisher Scientific, or Combi-Blocks and used as received. Non-fritted gas washing bottles were purchased from ChemGlass (CG-1112). UV-Vis spectra were acquired on a Cary 100 spectrophotometer equipped with a Quantum Northwest TLC-42 dual cuvette temperature controller set at 25.00 ± 0.05 °C. Fluorescence spectra were obtained on a Quanta Master 40 spectrofluorometer (Photon Technology International) equipped with a Quantum Northwest TLC-50 temperature controller set at 25.00 ± 0.05 °C. Air-free manipulations were performed under an inert atmosphere using an Innovative Atmospheres N₂-filled glove box. IR spectroscopy was performed with a Bruker Alpha Compact FT-IR spectrometer equipped with an ATR accessory.

Synthesis of TBBi

This compound was prepared as previously described¹



Synthesis and Purification of Carbonyl Sulfide (COS)

This procedure was adapted and modified from a previous report.²

KSCN (25 g, 0.26 mol) was dissolved in deionized H₂O (150 mL) and added to a closed addition funnel. Concentrated H₂SO₄ (50 mL) and a stir bar were added to a three-necked round bottom flask. KOH (100 g, 1.78 mol) was dissolved in deionized H₂O (100 mL) and added to the first gas washing bottle. Aniline (25 mL, 0.27 mol) was dissolved in anhydrous ethanol (75 mL) and added to the second gas washing bottle. Ice chips were added directly to the third gas washing bottle. Concentrated H₂SO₄ (50 mL) was added directly to the fourth gas washing bottle. A sulfide-quenching solution containing Zn(OAc)₂ (24 g, 0.13 mol), sodium citrate dihydrate (2.25 g, 7.65 mmol), NaOH (1.66 g, 41.5 mmol), and bleach (300 mL) was added to a 1 L graduated cylinder. The solution was filled to 1 L with deionized H₂O. The gas washing bottles were sealed with vacuum grease and the system was assembled as shown below (**Figure S1**).



Figure S1. Assembled glassware for synthesis and purification of COS.

The assembled system was charged with a stream of nitrogen and sparged for approximately 1 hour. The potassium thiocyanate and concentrated H₂SO₄ solutions were both sparged for 30 min. To begin the synthesis of COS, nitrogen sparging was stopped and aqueous potassium thiocyanate was added dropwise to concentrated H₂SO₄.

Note: *This reaction is very exothermic.*

The purified COS was collected in a 500 mL round bottom, Schlenk storage flask with a Teflon Kontes screw valve with a 14/20 sidearm joint. After approximately two-thirds of the potassium thiocyanate solution was added, the storage flask was sealed, and the excess COS gas was bubbled directly into the sulfide-quenching solution.

The purity of the synthesized COS (g) could be assessed by ¹³C NMR (**Figure S2**). The gas was bubbled directly into an NMR tube containing 0.5 mL CD₃CN briefly.

¹³C{¹H} (126 MHz, CD₃CN), δ (ppm): 154.34.

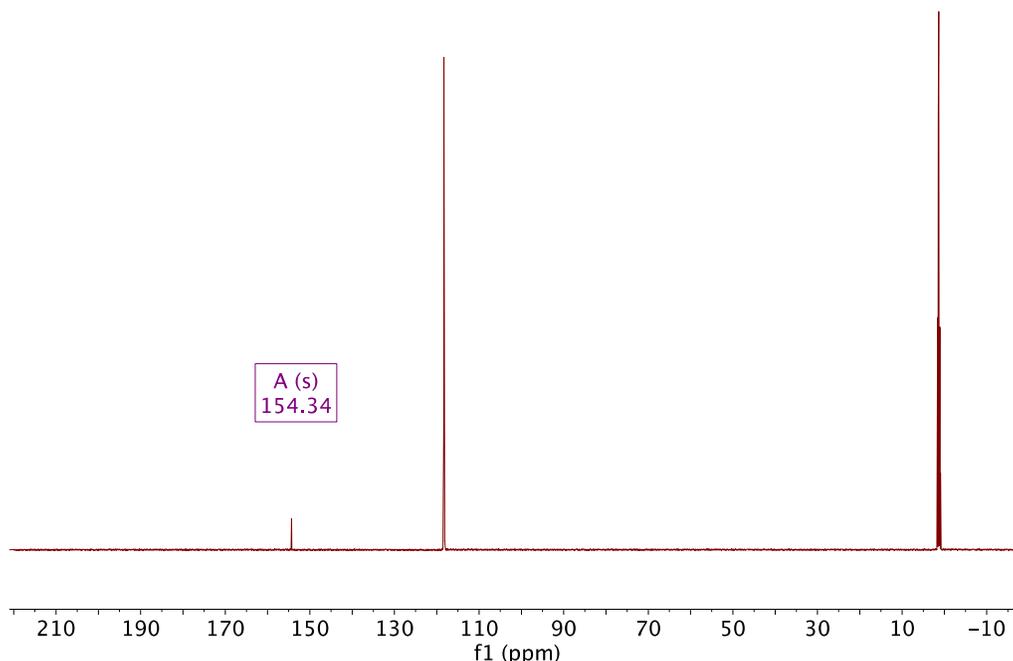


Figure S2. ¹³C{¹H} NMR spectrum of COS (g) in CD₃CN.

General Procedure for UV-Vis Measurements

A septum-sealed cuvette was charged with 3.00 mL of MeCN containing 1% (v/v) deionized H₂O and 20 μL of 2.5 mM **TBBI** in anhydrous MeCN for a final concentration of 15 μM **TBBI**. An initial UV-Vis absorbance spectrum was recorded (250-450 nm). A 6.75 mM solution of TBAF in anhydrous MeCN was prepared *via* dilution of 1.0 M TBAF in THF and 40 μL was added to the cuvette solution for a final concentration of 90 μM TBAF (6.0 equiv.) Another UV-Vis absorbance spectrum was recorded (250-450 nm). A 5.0 mL gastight Hamilton syringe was charged with COS (g) and added in 0.5 mL increments to the cuvette solution. A UV-Vis absorbance spectrum was recorded (250-450 nm) between additions.

General Procedure for Fluorescence Intensity Measurements

A septum-sealed cuvette was charged with 3.00 mL of MeCN containing 1% (v/v) deionized H₂O and 20 μ L of 2.5 mM **TBBI** in anhydrous MeCN for a final concentration of 15 μ M **TBBI**. An initial fluorescence spectrum was recorded ($\lambda_{\text{ex}} = 321$ nm, $\lambda_{\text{em}} = 330$ -600 nm). A 6.75 mM solution of TBAF in anhydrous MeCN was prepared *via* dilution of 1.0 M TBAF in THF and 40 μ L was added to the cuvette solution for a final concentration of 90 μ M TBAF (6.0 equiv.) Another fluorescence spectrum was recorded ($\lambda_{\text{ex}} = 321$ nm, $\lambda_{\text{em}} = 330$ -600 nm). A 5.0 mL gastight Hamilton syringe was charged with COS (g) and added in 0.5 mL increments to the cuvette solution. A fluorescence measurement was recorded ($\lambda_{\text{ex}} = 321$ nm, $\lambda_{\text{em}} = 330$ -600 nm) between additions.

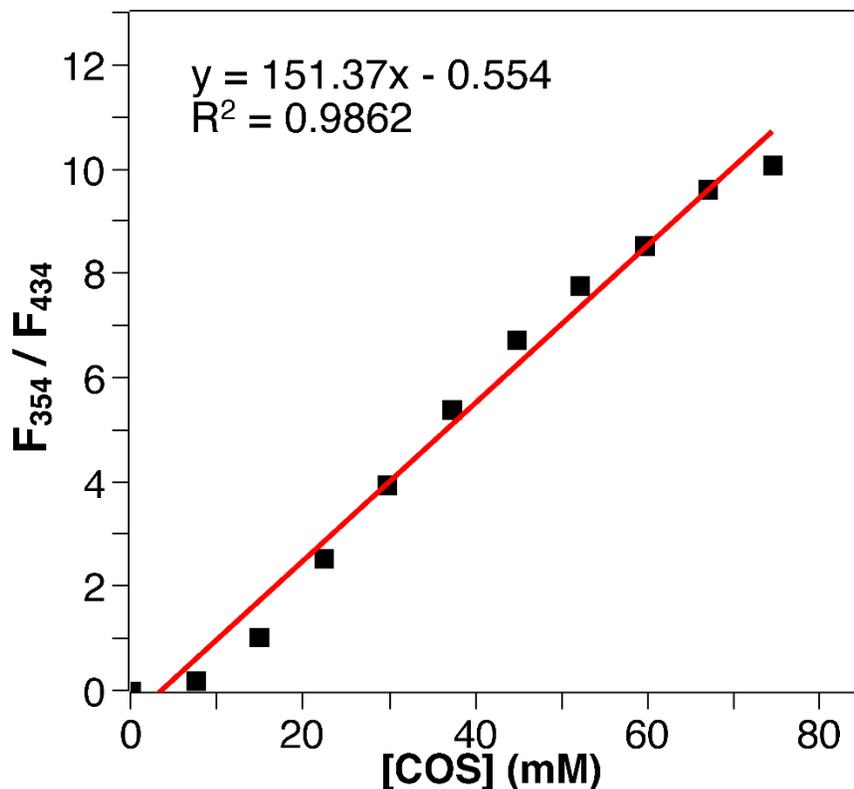


Figure S3. Plot of COS concentrations (mM) against the ratio of fluorescence intensities at 354 and 434 nm.

Synthesis of crude **TBBI**•**COS** Adduct (**TBBI**•(**COS**)₂)

In an N₂-filled glovebox, a 20 mL scintillation vial equipped with a stir bar was charged with **TBBI** (30.8 mg, 0.0467 mmol) and 1.35 mL THF-d₈ (34.4 mM). To this slurry was added ~2.0 equiv. of KHMDS (20.8 mg, 0.104 mmol) was added while stirring, and the reaction immediately began to turn orange. After 30 minutes, the dark orange homogeneous solution was transferred to a septum sealed NMR tube. Both ¹H and ¹³C{¹H} NMR spectra were acquired. Under positive N₂ pressure, ~10 equiv. COS (g) (10 mL, 0.45 mmol) was added with a gas tight syringe causing the solution to immediately turn dark brown. After 30 min, the reaction solution had become a light orange/yellow color. Both ¹H and ¹³C{¹H} NMR spectra were acquired. The solvent was removed under reduced pressure to afford the crude product and an IR spectrum was obtained under a N₂ atmosphere (Figure S4, Figure S5, Figure S6).

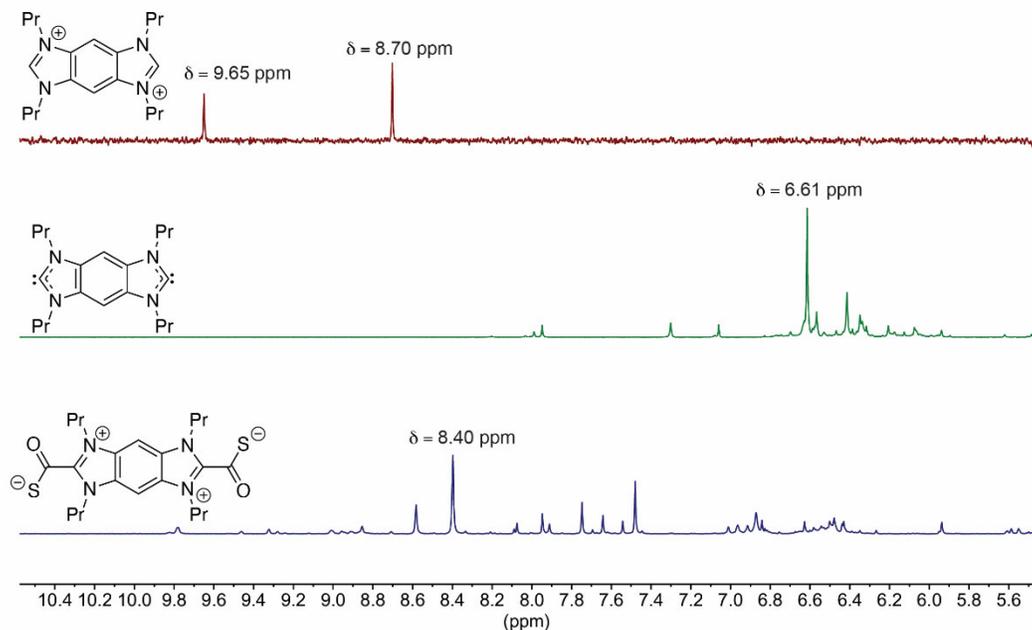


Figure S4. ^1H NMR spectra in THF-d_8 of (a) **TBI** (b) **TBI** after the addition of KHMDS (c) **TBI** after the addition of KHMDS and the addition of COS (g).

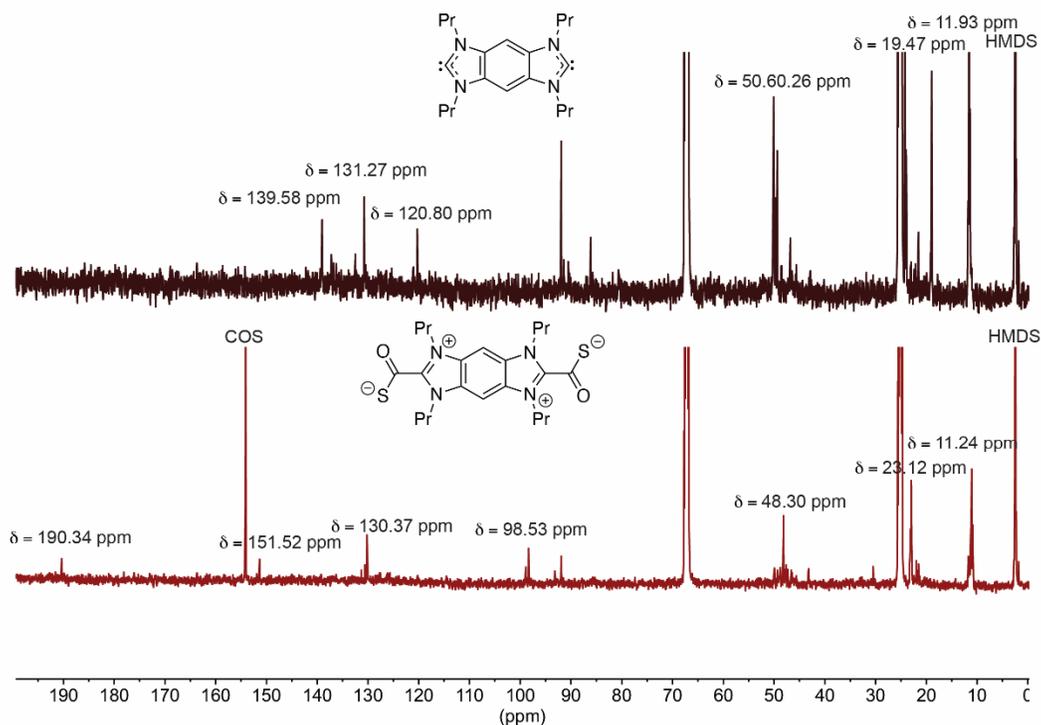


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in THF-d_8 of (a) **TBI** after the addition of KHMDS (b) **TBI** after the addition of KHMDS and the addition of COS (g).

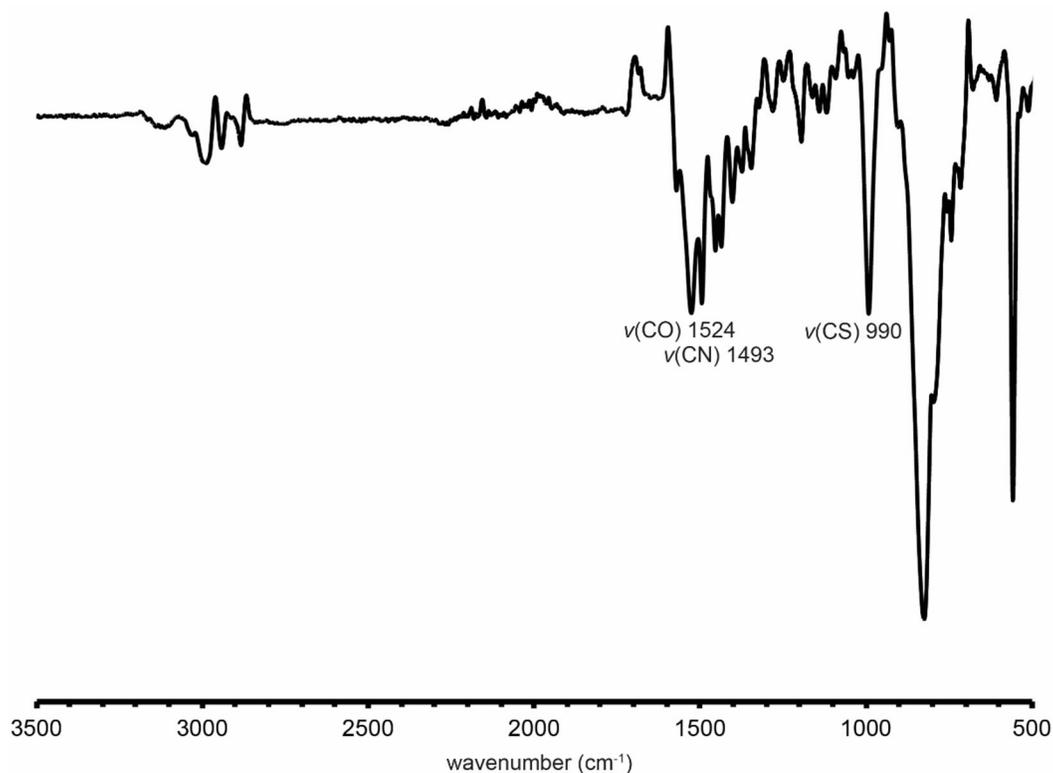


Figure S6. IR spectrum (ATR) of **TBBI** after the addition of KHMDS and the addition of COS (g).

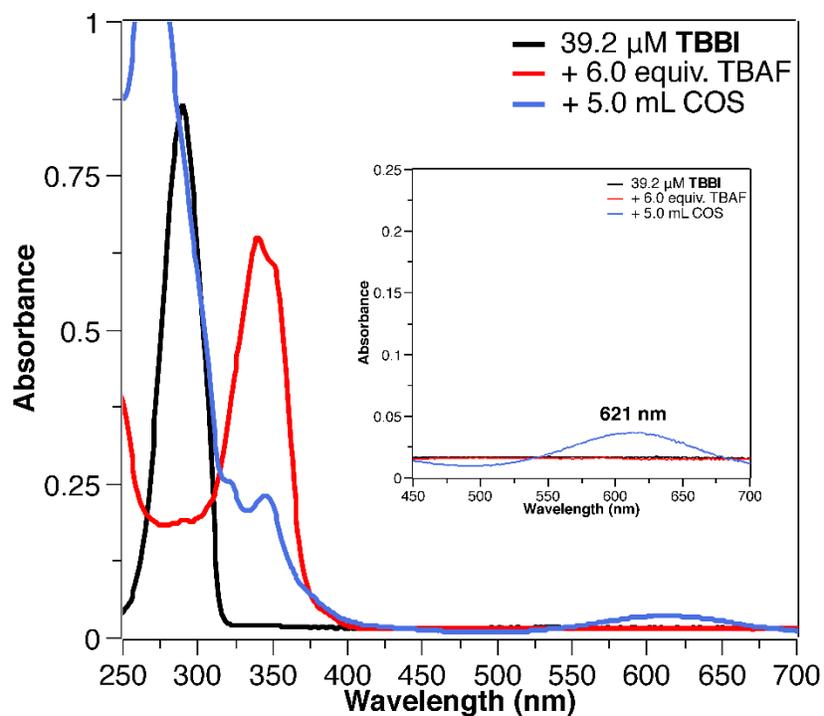


Figure S7. UV-Vis spectra (250-700 nm) of **TBBI** (39.2 μM), TBAF (6.0 equiv.), and COS (5.0 mL) reveals the presence of a low energy absorption (621 nm).

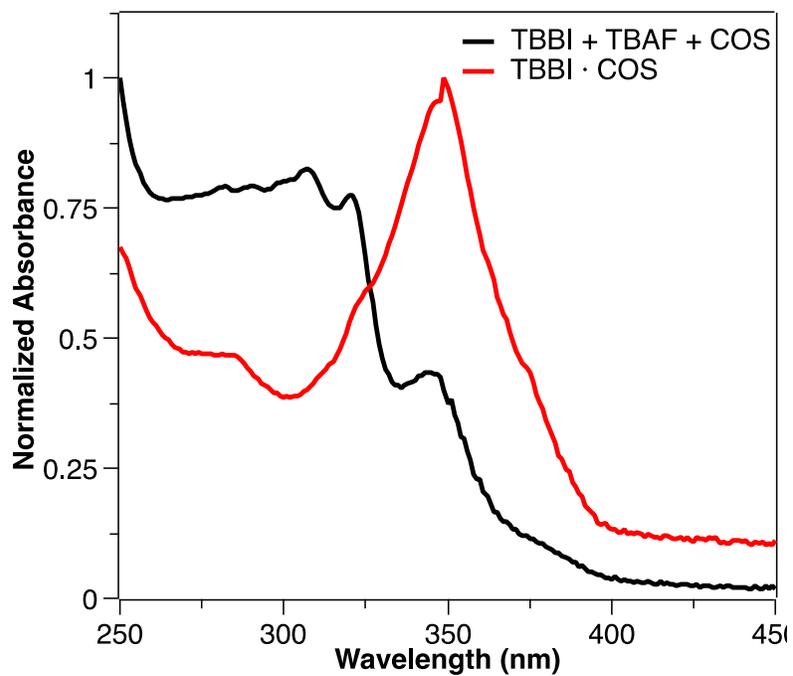


Figure S8. Normalized UV-Vis spectra of **TBBI** (15 μ M), TBAF (6.0 equiv.), and COS (5.0 mL) (black trace) against **TBBI·(COS)₂**.

References

1. Guo, Z.; Song, N.R.; Moon, J.H.; Kim, M.; Jun, E.J.; Choi, J.; Lee, J.Y.; Bielawski, C.W.; Sessler, J.L.; Yoon, J. "A Benzobisimidazolium-Based Fluorescent and Colorimetric Chemosensor for CO₂" *J. Am. Chem. Soc.* **2012**, *134*, 17846-17849
2. Pursglove, L.A.; Wainwright, H.W. "Colorimetric Determination of Carbonyl Sulfide in Synthesis Gas" *Anal. Chem.* **1954**, *26*, 1835-1839.