Supporting Information:

NBu_4SH Provides a Convenient Source of HS^- Soluble in Organic Solution for H_2S and Anion-Binding Research

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Experimental Details

Materials and Methods. All manipulations were performed under an inert atmosphere using standard Schlenk techniques or an Innovative Atmospheres N₂-filled glove box unless otherwise noted. All chemicals were used as received. Tetrabutylammonium chloride was purchased from Sigma-Aldrich. NaSH (anhydrous) was purchased from Strem chemicals and handled under nitrogen. *Note:* Hydrogen sulfide and its salts are highly toxic and should be handled carefully to avoid exposure. Spectroscopic grade acetonitrile was degassed by sparging with argon followed by passage through a Pure Process Technologies solvent purification system to remove water and stored over 4\AA molecular sieves in an inert atmosphere glove box. Acetonitrile- d_3 was purchased from Cambridge Isotope laboratories and distilled from calcium hydride, deoxygenated by three freeze-pump-thaw cycles, and stored in an inert atmosphere glove box.

Spectroscopic Methods. UV-Vis measurements were acquired on an Agilent Cary 100 UV-Vis spectrophotometer equipped with a QNW dual cuvette temperature controller at 25.00 \pm 0.05 °C. All spectroscopic samples were prepared under an inert atmosphere in septum-sealed cuvettes obtained from Starna Scientific. NMR spectra were acquired on a Brüker Avance-III-HD 600 spectrometer with a Prodigy multinuclear broadband cryoProbe at 25.0 °C. Chemical shifts are reported in parts per million (δ) and are referenced to residual solvent resonances. IR spectra were acquired on a Thermo Scientific Nicolet 6700 spectrometer equipped with a diamond crystal Smart ATR Attachment. Cyclic voltammetry was performed at 25 °C on a CH Instruments 620D electrochemical workstation. A 3-electrode set-up was employed comprising a glassy carbon working electrode, platinum wire auxiliary electrode, and a silver quasi-reference electrode. Triply recrystallized NBu₄PF₆ was used as the supporting electrolyte. All electrochemical data were referenced externally to the ferrocene/ferrocenium couple at 0.00 V.

X-ray crystallography details. Diffraction intensities for NBu₄SH were collected at 173(2) K on a Bruker Apex2 CCD diffractometer using CuK_{α} source, λ = 1.54178 Å. The space group was determined based on systematic absences. Absorption corrections were applied by SADABS.¹ The structure was solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. The H atoms for the NBu₄⁺ cation were refined in calculated positions using the rigid group model. The H atom in the HS⁻ anion was not explicitly located. The solvent molecule (toluene) was disordered around an inversion center and was not involved in specific intermolecular interactions, therefore was treated by SQUEEZE.² Corrections of the X-ray data by SQUEEZE results in a change of 232 electron/cell, which matches well with the expected value of 200 electron/cell for four toluene molecules in the full unit cells. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.³

- 1. G. M. Sheldrick, Bruker AXS, Madison, WI, 1998.
- 2. P. van der Sluis and A. L. Spek, Acta Cryst. A. 1990, 46, 194-201.
- 3. G. M. Sheldrick, BRUKER ACS Inc., Madison, WI, 2000.

NMR Spectroscopic Data



Figure S1. ¹H (600 MHz, CD₃CN) NMR spectrum of NBu₄SH.



²⁰ 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 **Figure S2.** ${}^{13}C{}^{1}H{}(151 \text{ MHz, }CD_{3}CN{}) \text{ NMR spectrum of }NBu_{4}SH.$



Figure S3. ¹H NMR spectra demonstrating that H_2S is not sufficiently nucleophilic to react with BnCl. Only upon deprotonation to form HS⁻ does nucleophilic attack on BnCl occur. a) A saturated solution of H_2S gas in CD₃CN. b) Addition of BnCl does not result in any reaction. c) Addition of NEt₃ (TEA) to deprotonated H_2S generates HS⁻, which is quickly trapped by BnCl to form Bn₂S.



Figure S4. ¹H NMR spectrum of the reaction of NBu₄SH with BnCl to form Bn₂S and BnSH. Unlike in Figure S3, no added base is required for this reaction to occur. Bottom: NBu₄SH in CD₃CN. Top: Addition of 3 equiv. of BnCl.

IR Spectroscopic Data



Figure S5. FTIR (ATR, neat) spectrum of NBu₄SH.



Figure S6. FTIR (ATR, neat) spectrum of NaSH.

X-Ray crystallographic data

	NBu ₄ SH
Empirical formula	$C_{19.50}H_{41}NS$
	$[C_{16}H_{36}N]^{+}[SH]^{-}(C_{7}H_{8})_{0.5}$
Formula weight	321.59
Wavelength (Å)	1.54178
Crystal size (mm)	0.14 x 0.13 x 0.04
Temperature (K)	173 K
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions (Å)	a = 22.043(10)
	b = 14.9292(7)
	c = 14.8080(6)
	$\beta = 118.618(3)^{\circ}$
Volume (Å 3)	4277.7(3)
Z	8
Calculated density (Mg/m^3)	0.999
$\mu (\text{mm}^{-1})$	1.295
F(000)	1448
$2\theta_{\rm max}$	135.36°
Reflections collected	14231
Independent reflections	3729
R _{int}	0.0489
$[I > 2\sigma(I)]$	
R1	0.0741
wR2	0.2044
GOF	1.053
	3729 reflections
	163 parameters
R1	0.934
wR2	0.2180
GOF	1.053
	All reflections
Residual electron density $(e/Å^3)$ Max	Max = 0.565
• ` ` '	Min = -0.330

Table S1. Crystal data and structure refinement for NBu₄SH.