Electronic Supplementary Information

Supramolecular binding and release of sulfide and hydrosulfide anions in water

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1. Materials and general procedures

Bambusurils **wBU**, **MeBU** and **BnBU** were synthesized following the published procedures.[1-4] Sodium hydrosulfide hydrate (NaHS), Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$), *N,N*-Diethyl-*p*-phenylenediamine (DEPPDA, ≥97%), Iron (III) chloride ($FeCl_3$, ≥97%), 1,4-Dimethoxybenzene ($(C_6H_4(OCH_3)_2$, 99%) were purchased from Aldrich and were used as received. Water was of MilliQ quality and the pH was adjusted by addition of NaOH. For NMR measurements, all the deuterated solvents were purchased from Aldrich on the highest quality.

The ^1H NMR measurements were performed on a Bruker Avance III 300 spectrometer with working frequency 300.15 MHz, using the deuterated solvents mentioned above. All experiments were recorded at 303.15 K. NMR chemical Shifts (δ) are reported in ppm using the residual solvent signal as a reference for the measured spectra D_2O (^1H = 4.79), CD_3OD (^1H = 3.31) and DMSO-d_6 (^1H = 2.50).

The UV/Vis spectral measurements were performed at room temperature using 1-cm quartz cuvettes. The absorption spectra were recorded with a CARY 60 spectrophotometer from Agilent Technologies.

2. Experimental procedures

2.1. ^1H NMR titrations

Binding constants were obtained by NMR titrations by addition of the corresponding sulfide salt (direct titration) or competitor (competitive titration) to a constant concentration solution of **BU**. The fitting of the binding was done according to previously published procedures using Origin8.[5,6]

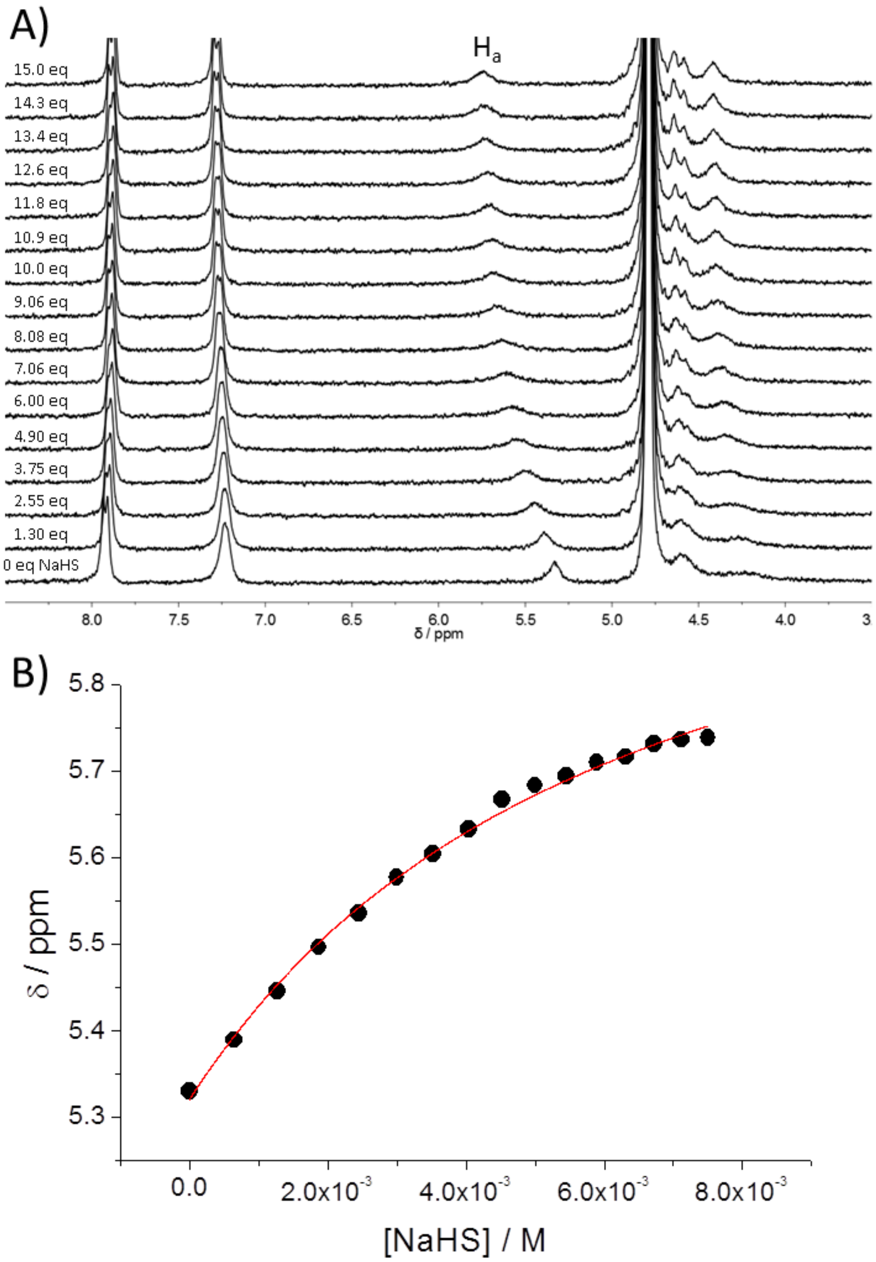

Fig. S1 A) ^{1}H NMR titration (300 MHz, D_2O, 12 mM Na_3PO_4) of **wBU** (c(BU) = 0.5×10^{-3} M) with NaHS at pD 11.3. B) Plot of the chemical shifts of the methane protons H_a in the presence of increasing NaHS concentration.

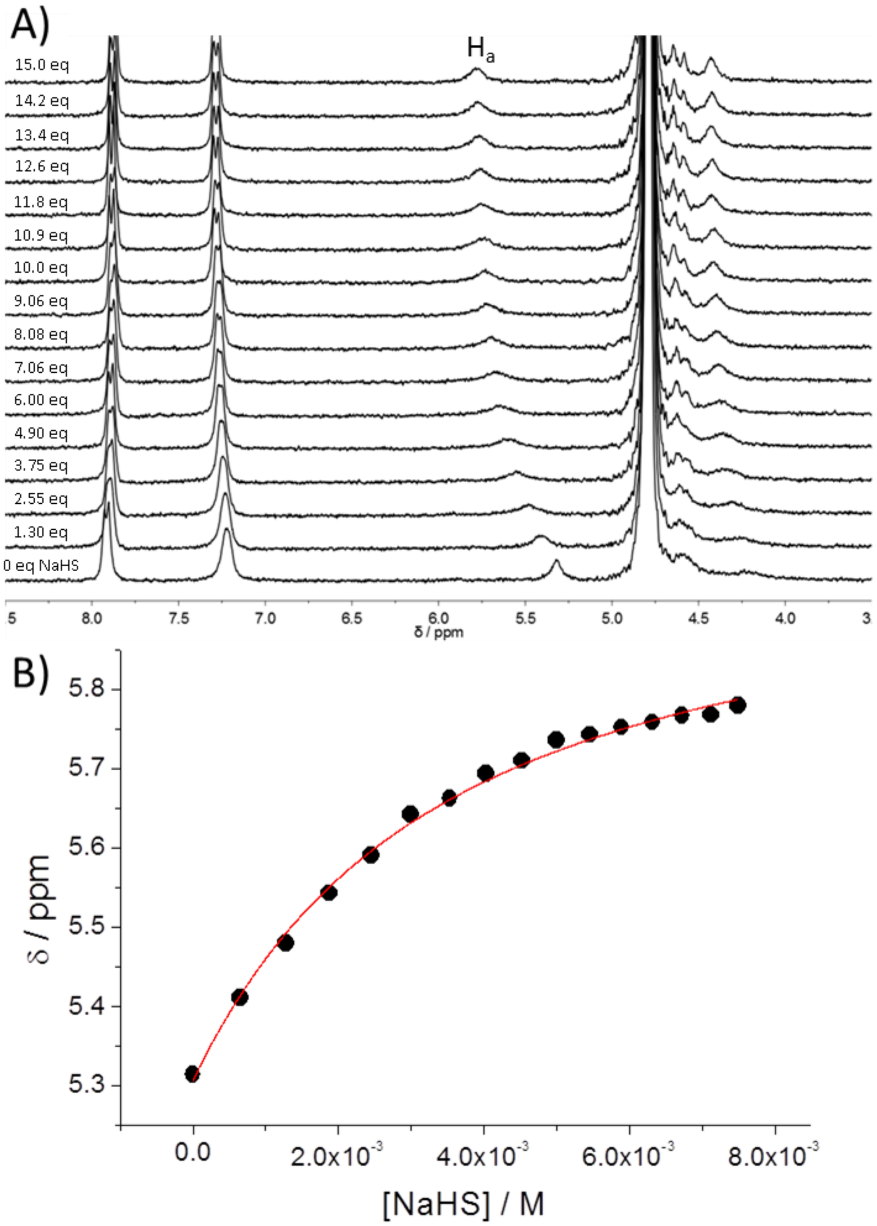

Fig. S2 A) ^{1}H NMR titration (300 MHz, D$_2$O, 17 mM Na$_3$PO$_4$) of **wBU** (c(BU) = 0.5 × 10^{-3} M) with NaHS at pD 11.7. B) Plot of the chemical shifts of the methane protons H$_a$ in the presence of increasing NaHS concentration.

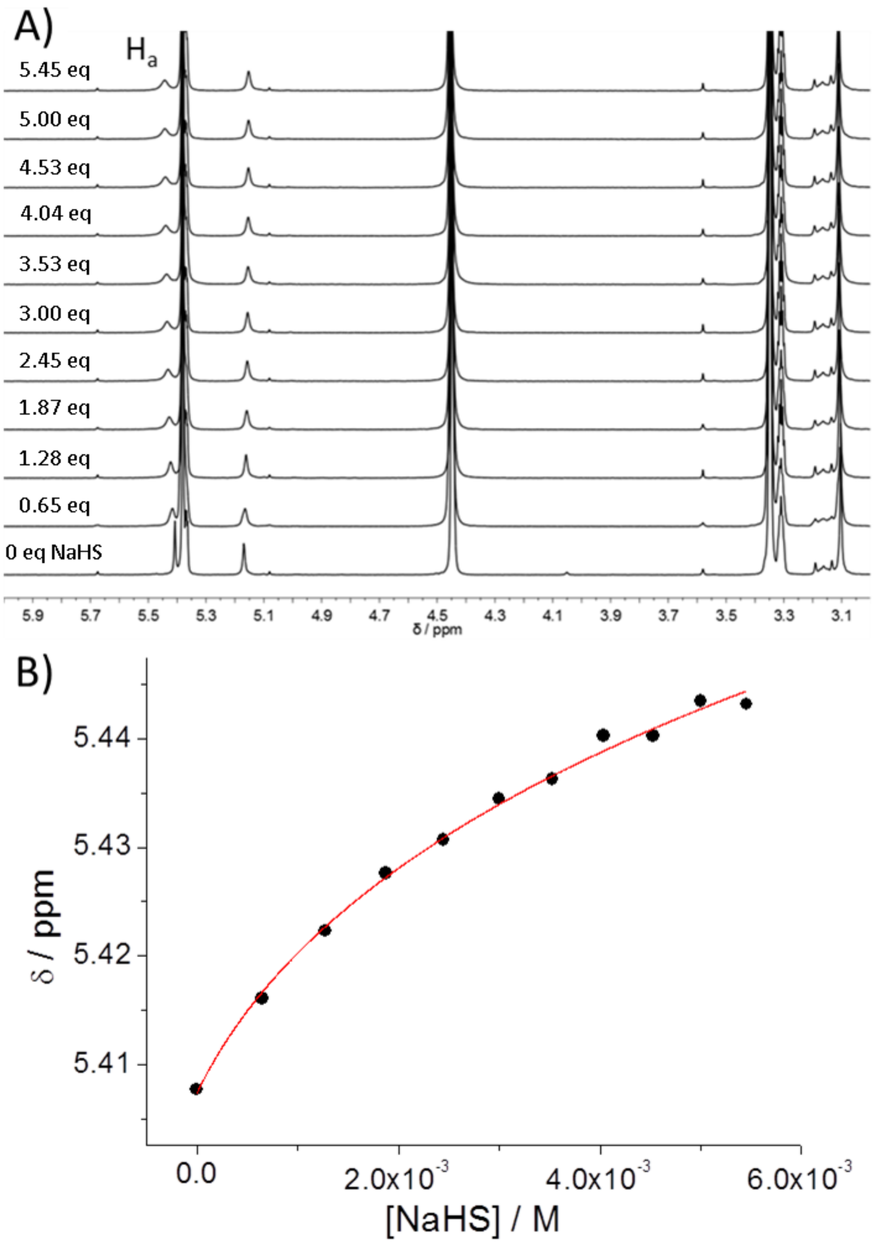

Fig. S3 A) ^{1}H NMR competitive titration (300 MHz, CD_3OD/DCM-d_2) of **MeBU** (c(BU) = 1 × 10^{-3} M) and TBACl (c(TBACl) = 1.2 × 10^{-3} M) with NaHS. B) Plot of the chemical shifts of the methane protons H_a in the presence of increasing NaHS concentration.

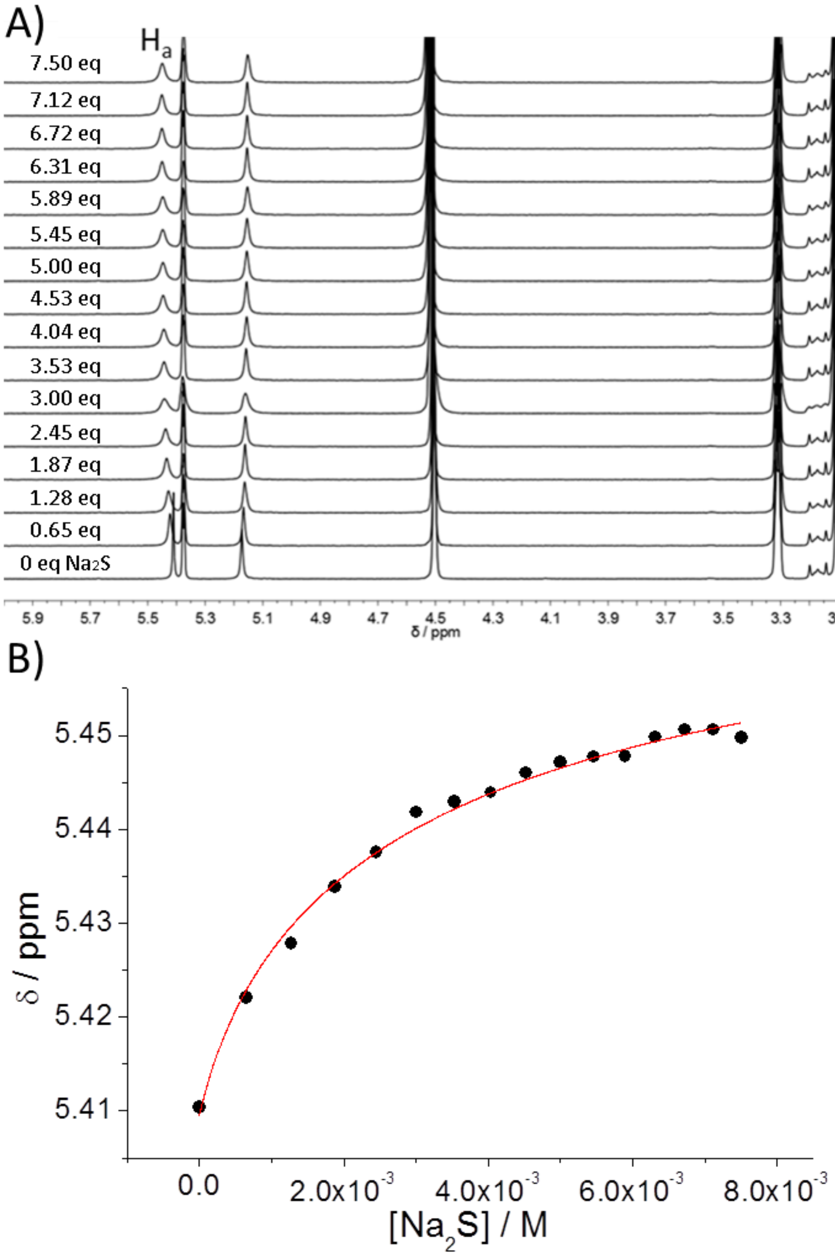

Fig. S4 A) ^{1}H NMR competitive titration (300 MHz, CD$_3$OD/DCM-d$_2$) of **MeBU** (c(BU) = 1 × 10^{-3} M) and TBACl (c(TBACl) = 1.2 × 10^{-3} M) with Na$_2$S**.** B) Plot of the chemical shifts of the methane protons H$_a$ in the presence of increasing NaHS concentration.

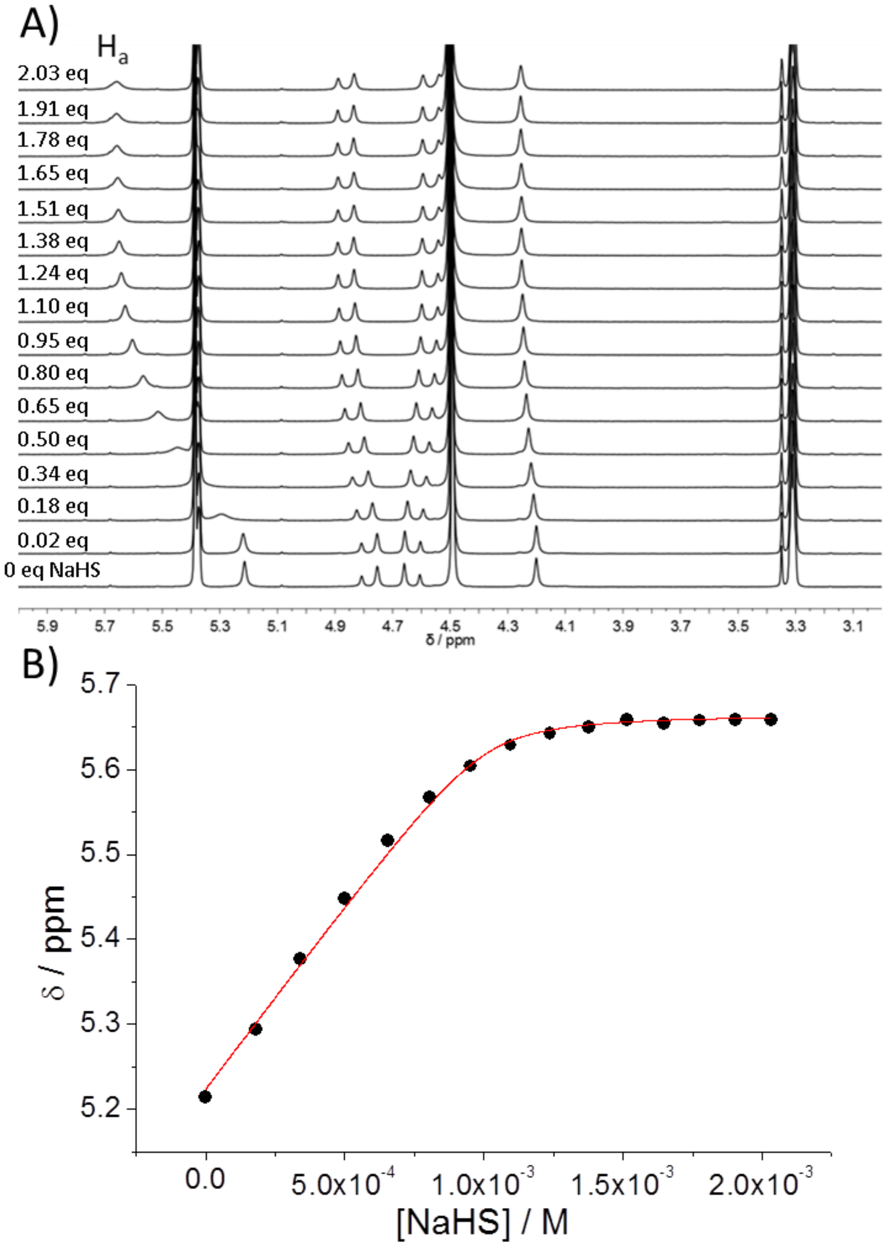

Fig. S5 A) ^{1}H NMR titration (300 MHz, CD_3OD/DCM-d_2) of **BnBU** (c(BU) = 1 × 10^{-3} M) with NaHS. B) Plot of the chemical shifts of the methane protons H_a in the presence of increasing NaHS concentration.

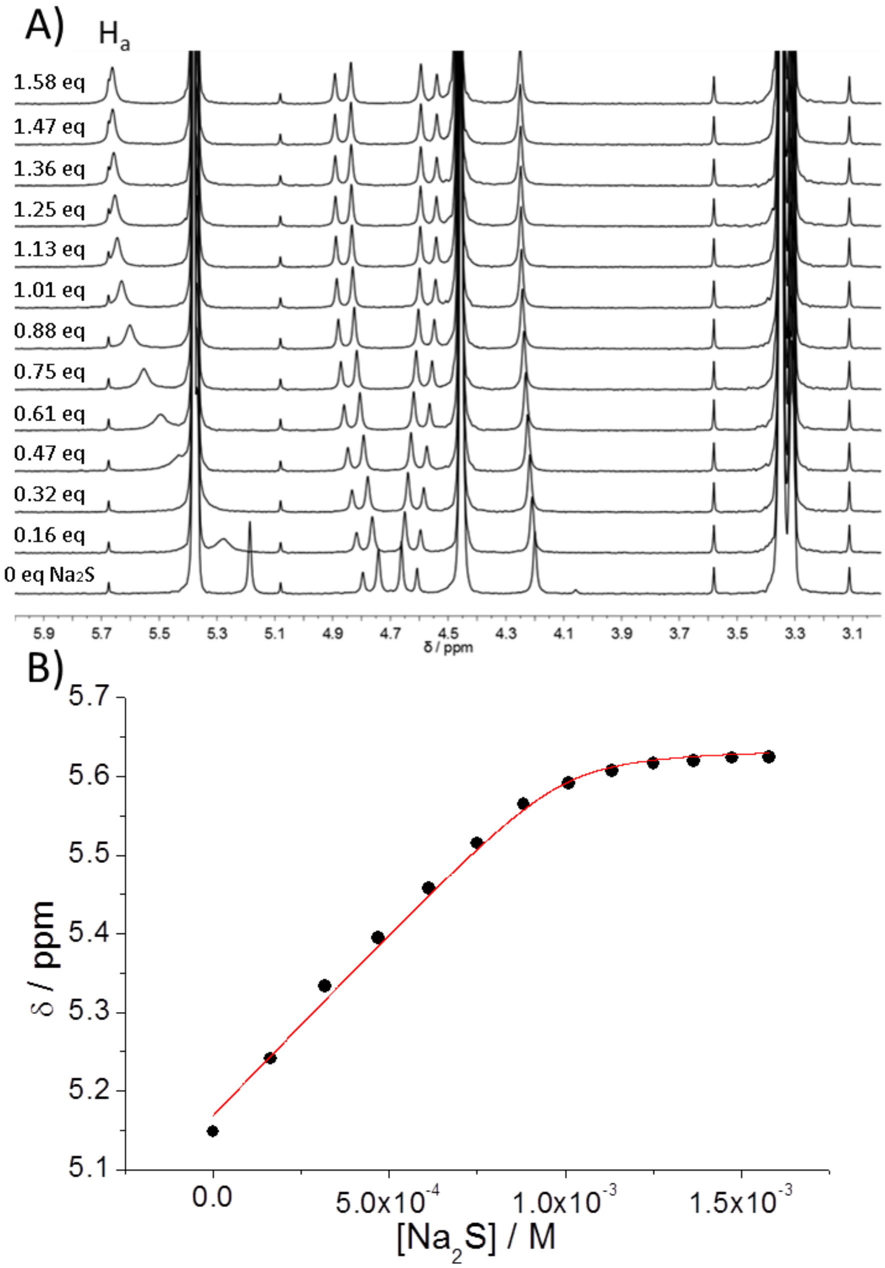

Fig. S6 A) ^{1}H NMR titration (300 MHz, CD_3OD/DCM-d_2) of **BnBU** (c(BU) = 1 × 10^{-3} M) with Na_2S. B) Plot of the chemical shifts of the methane protons H_a in the presence of increasing NaHS concentration.

2.2. DFT calculations

Geometry optimization of **MeBU**·S^{2-} was performed using Spartan '14 software.[7] The structures were built in silico and their geometries were optimized using the BLYP[8, 9] level of theory with the 6-31G basis set.

2.3. Isolation of complexes

MeBU was dissolved in DCM:MeOH (1:1) mixture containing 0.5 equivalents of Na_2S. The solvent was then evaporated and the **MeBU**·Na_2S complex was isolated as a white solid along with the excess of macrocycle. The complex was characterized by NMR in DMSO-d_6 in the presence of 1,4-Dimethoxybenzene as internal standard.

BnBU was dissolved in DCM:EtOH (1:1) mixture containing 0.5 equivalents of Na_2S. The solvent was then evaporated and the **BnBU**·Na_2S complex in the presence of anion free bambusuril was isolated as a white solid. The complex was characterized by NMR in DMSO-d_6 (Figure S8).

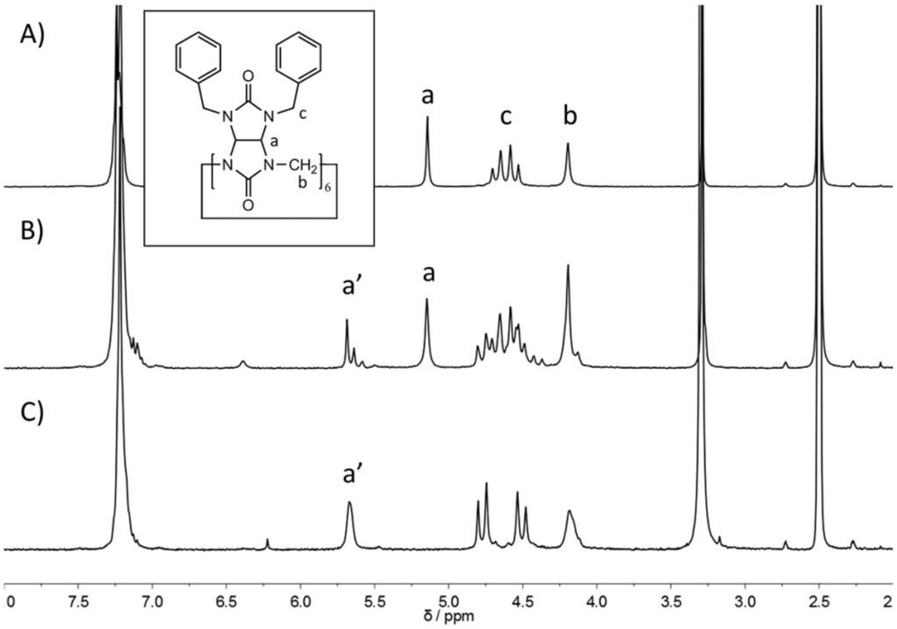

Fig. S8 ^1H NMR measurement (300 MHz, DMSO-d_6) of A) **BnBU**, B) **BnBU**·S^{2-} (2:1) and C) **BnBU**·S^{2-} (1:1). The presence of complex was confirmed by the signal a' at 5.68 ppm.

2.4. Ethylene Blue method

The ethylene blue method involves the reaction of sulfide anions with DEPPDA in the presence of the oxidizing agent Fe^{3+} in hydrochloric acid to form ethylene blue. The absorption of the resulting solution is linear to the initial concentration of sulfide in solution. (Fig. S9)

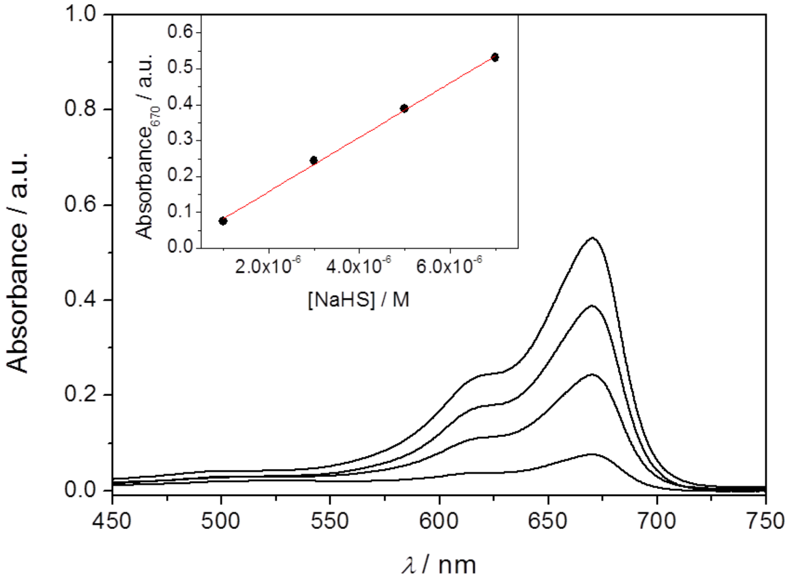

Fig. S9 UV/vis absorption spectra obtained by the Ethylene blue method with different concentrations of NaHS. Inset: Linear dependence of the absorption at 670 nm with concentration of NaHS.

For the experiments mentioned in the main text, the complex of Na_2S with **BnBU** or **MeBU** (30-50 mg) was added into water (10 mL) and started stirring. 250 µL aliquots were transfer to vials, mixed with 133 µL of 15mM DEPPDA in 1.5 M HCl and 266 µL of 4 mM $FeCl_3$ in 1.5 M HCl. The solution was then incubated for 15 minutes to allow the color to develop before measuring the absorbance at 670 nm. An extra dilution was required in order to keep the absorbance in the optical cell between 0.1 - 1 a.u. The yields of concentration shown below were calculated including all the dilutions employed on each individual experiment.

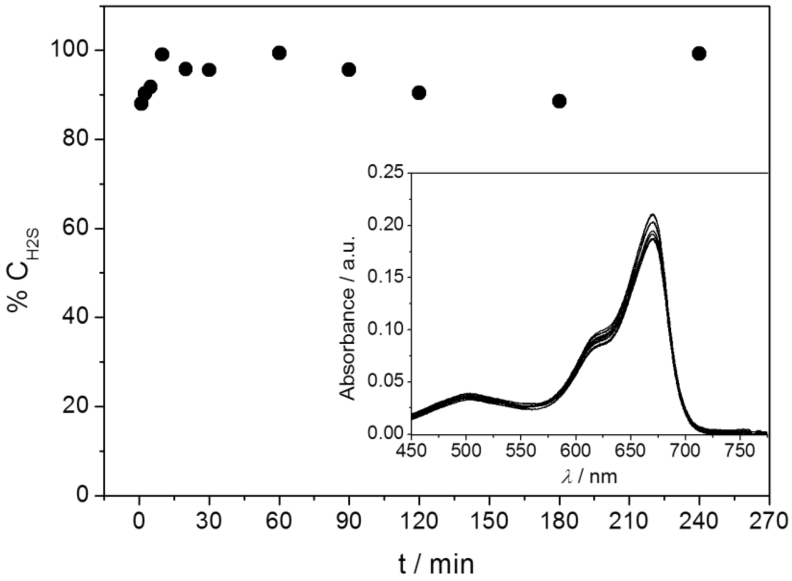

Fig. S10 Blank experiment for the concentration of H_2S in water from 2.6 mg Na_2S salt. Insets: Absorption spectra of ethylene blue solutions corresponding to the concentration of H_2S in water.

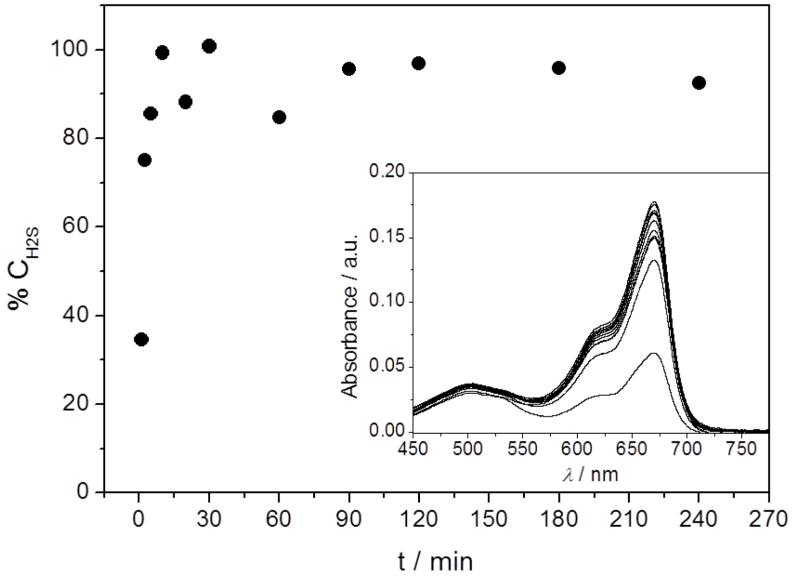

Fig. S11 Experiment **1** for the release yield of H_2S in water from its isolated complex with **MeBU** (22.5 mg, fresh sample) as a function of time. Insets: Absorption spectra of ethylene blue solutions corresponding to the amount of S^{2-} anion released within time from its complex.

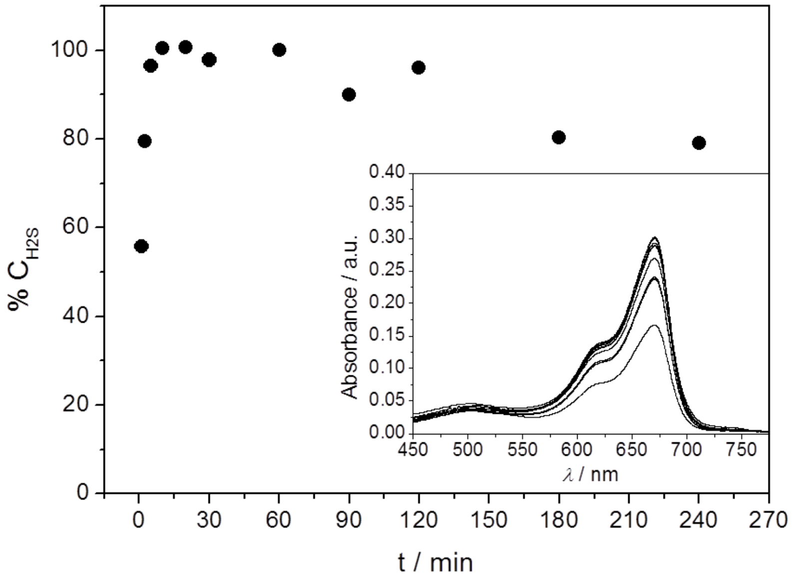

Fig. S12 Experiment **2** for the release yield of H_2S in water from its isolated complex with **MeBU** (36 mg, 4 days old sample) as a function of time. Insets: Absorption spectra of ethylene blue solutions corresponding to the amount of S^{2-} anion released within time from its complex.

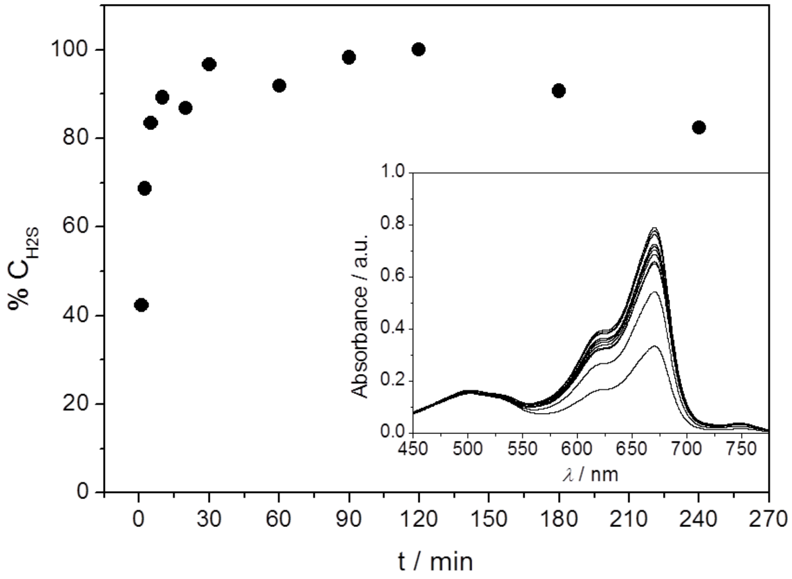

Fig. S13 Experiment **1** for the release yield of H_2S in water from its isolated complex with **BnBU** (51.5 mg, fresh sample) as a function of time. Insets: Absorption spectra of ethylene blue solutions corresponding to the amount of S^{2-} anion released within time from its complex.

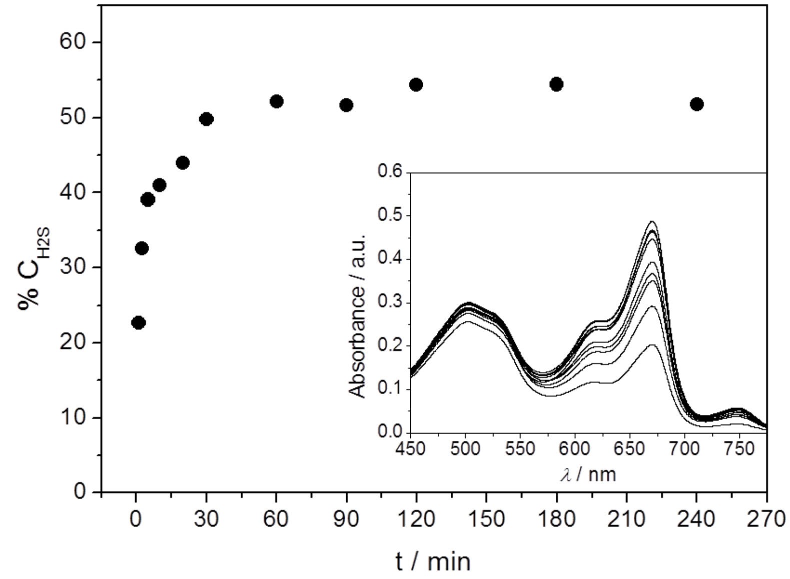

Fig. S14 Experiment **2** for the release yield of H_2S in water from its isolated complex with **BnBU** (51 mg, 4 days old sample) as a function of time. Insets: Absorption spectra of ethylene blue solutions corresponding to the amount of S^{2-} anion released within time from its complex.

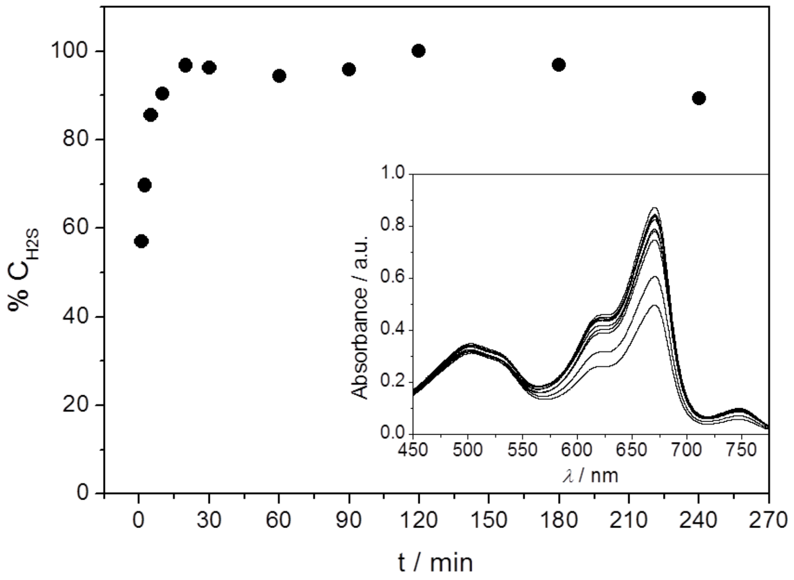

Fig. S15 Experiment **3** for the release yield of H_2S in water from its isolated complex with **BnBU** (53.5 mg) in the presence of 100 mM NaCl as a function of time. Insets: Absorption spectra of ethylene blue solutions corresponding to the amount of S^{2-} anion released within time from its complex.

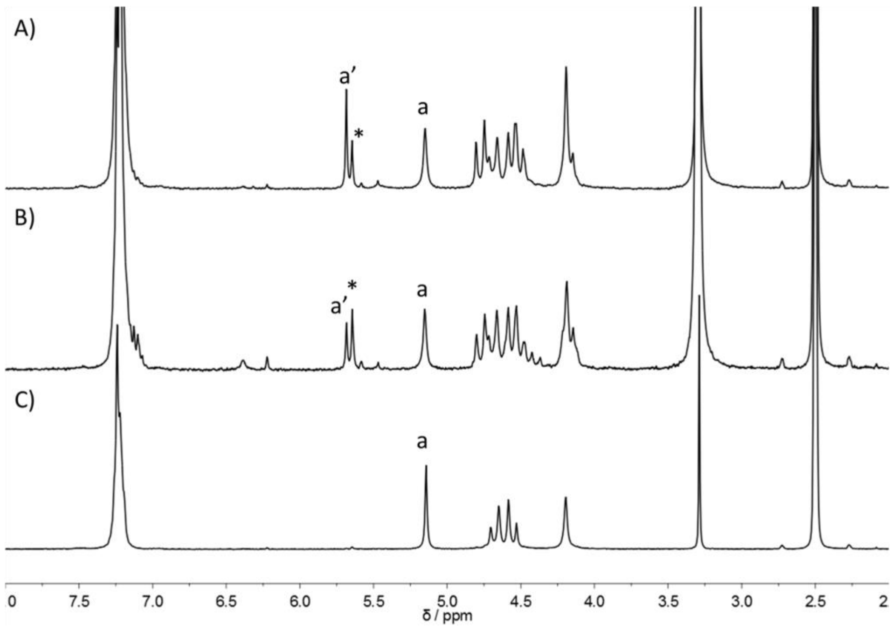

Fig. S16 ^{1}H NMR measurement (300 MHz, DMSO-d_6) of A) **BnBU**·S^{2-} (fresh sample), B) **BnBU**·S^{2-} (4 days olds sample) and C) filtrated solid from water after 4 hours stirring for Ethylene Blue experiments. The peaks are marked as **BnBU**·S^{2-} complex (a'), anion free **BnBU** (a), and **BnBU**·$S_3^{\cdot-}$ (*).

3. References

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