Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Fluorescent paper sensor fabricated by carbazole-based probes for dual visual detections of Cu^{2+} and gaseous H_2S

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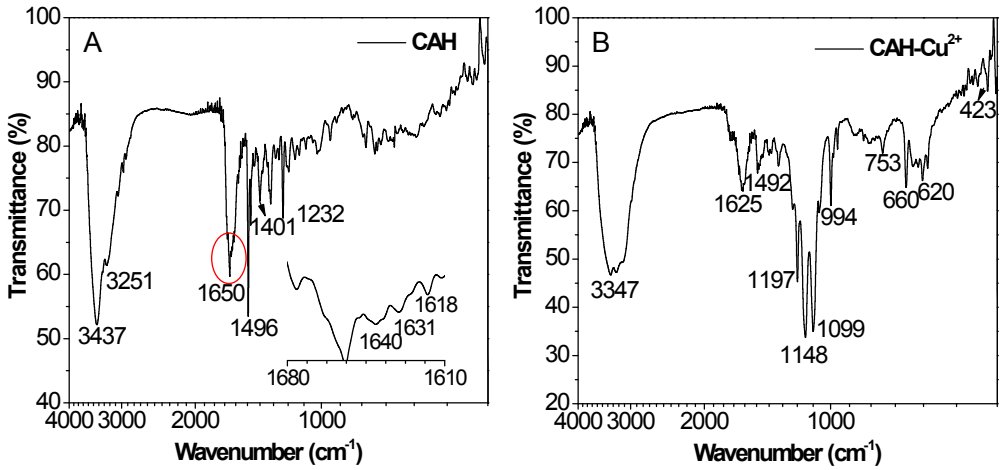

Fig. S1 FT-IR spectra of compound (A) CAH and (B) CAH-Cu^{2+}.

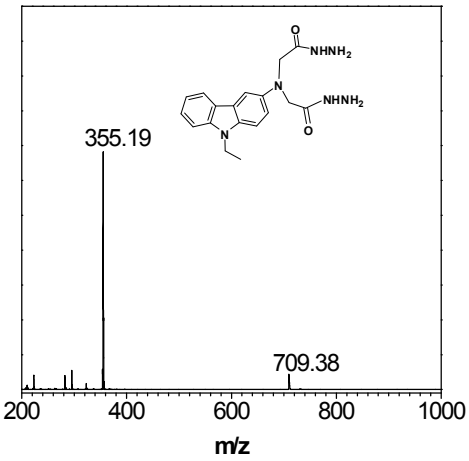

Fig. S2 ESI-MS spectrum of CAH (positive mode, calculated for CAH $[M+H]^+$ = 355.19).

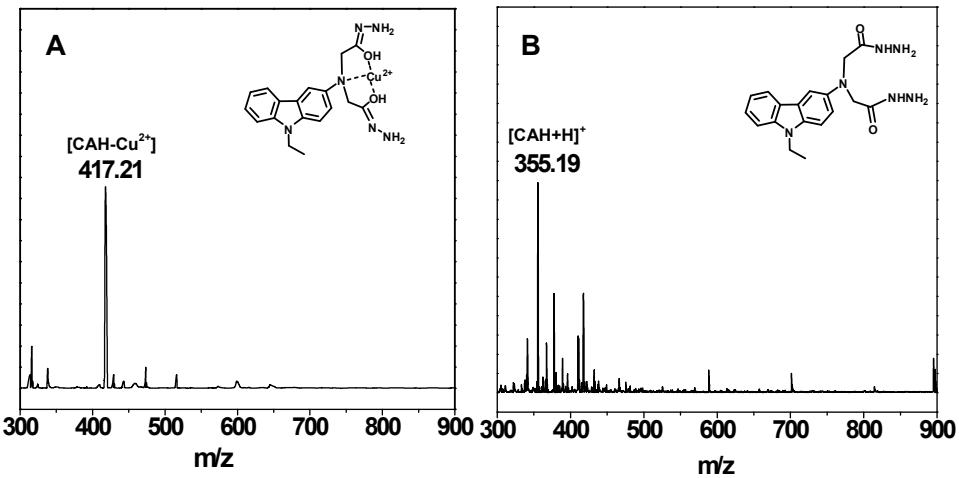

Fig. S3 ESI-MS spectra of CAH-Cu^{2+} before and after the addition of Na_2S. The positive mode, calculated for (A) CAH-Cu^{2+}, $[CAH\text{-}Cu^{2+}]$ = 417.11; (B) CAH-Cu^{2+}+Na_2S, $[CAH+H]^+$ = 355.19).

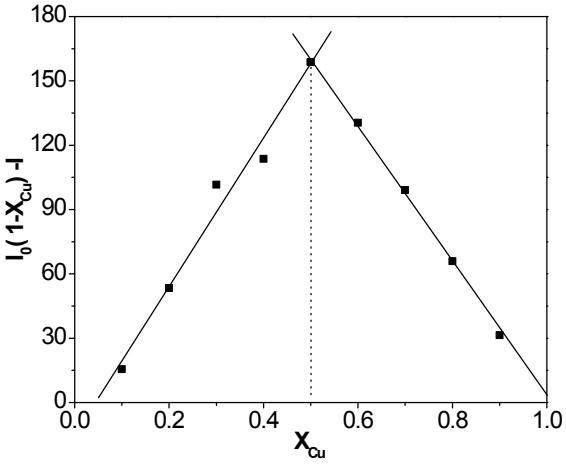

Fig. S4 Job's plot for determining the stoichiometry of CAH and Cu^{2+} in HEPES buffer solution (10 mM HEPES, 1% DMF, pH= 7.4). The total concentration of CAH and Cu^{2+} is 5 μM, X_{Cu} = $[Cu^{2+}]/([Cu^{2+}]+[CAH])$.

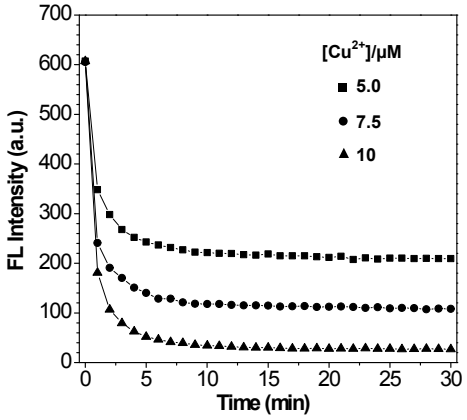

Fig. S5 Time-dependent fluorescence intensity (425 nm) change of CAH (5 μM) with Cu^{2+} (5.0, 7.5 and 10 μM) in HEPES buffer solution (10 mM HEPES, 1% DMF, pH = 7.4).

Photoluminescence quantum yield measurements: Quinine sulfate in 0.1 M H_2SO_4 (quantum yield 0.54 at 350 nm) was chosen as a standard for the fluorescence quantum yield measurement.[S1] The values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation:

$$QY_{sample} = QY_q \cdot \frac{A_{sample}}{A_q} \cdot \frac{F_q}{F_{sample}} \cdot \frac{\eta_{sample}^2}{\eta_q^2} \quad (1)$$

$$F = 1 - 10^{-D} \quad (2)$$

Where QY is the quantum yield, A is the measured integrated emission intensity, and F which is caculated by equation 2 is the fraction of light absorbed. D is the absorbance at the excitation wavelength, and η is the refractive index. The subscript "q" refers to the reference fluorophore quinine sulfate of known quantum yield. The results are presented in Fig. S4 and Table S1.

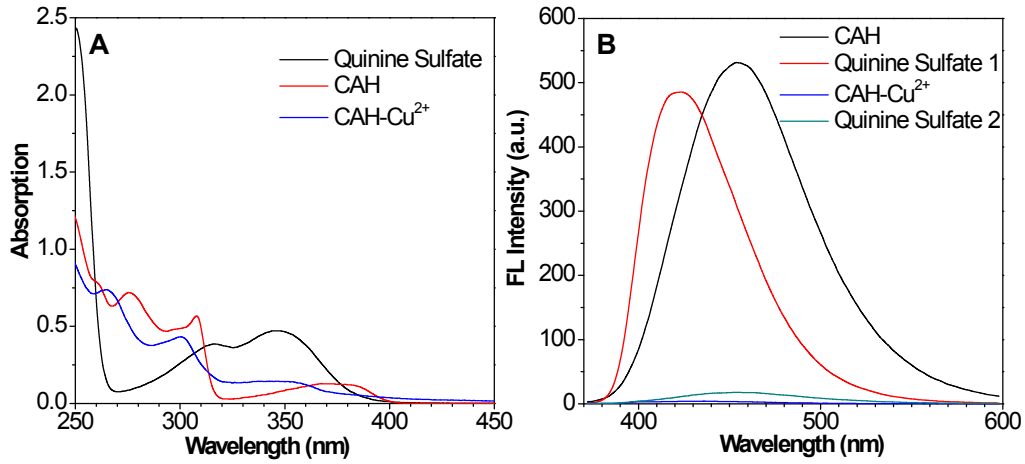

Fig. S6 (A) UV-vis absorption of quinine sulfate (10 μM) in 0.1 M H_2SO_4, CAH (30 μM) and CAH-Cu^{2+} (30 μM) in HEPES buffer solution (10 mM HEPES, 1% DMF, pH= 7.4). (B) Fluorescence spectra of quinine sulfate 1 (2.5 μM) and quinine sulfate 2 (78 nM) in 0.1 M H_2SO_4, CAH (10 μM) and CAH-Cu^{2+} (10 μM) in HEPES buffer.

Table S1. Example for the fluorescence quantum yield calculation of CAH and CAH-Cu^{2+} in HEPES buffer based on the standard.

Sample	A	F_{350nm}	η	Φ
Quinine Sulfate 1	44132	2.8×10^{-2}	1.33	0.54
CAH	33429	2.8×10^{-2}		0.40
Quinine Sulfate 2	1618	8.6×10^{-4}		0.54
CAH-Cu^{2+}	372	3.7×10^{-2}		0.003

Association constant calculation: Generally, for the formation of 1:1 complexation species formed by the chemosensor compound and the guest cations, the following Benesi–Hildebrand equation was used:[S2]

$$\frac{1}{I - I_0} = \frac{1}{K_a (I_0 - I_{min}) [Cu^{2+}]} + \frac{1}{I_0 - I_{min}} \quad (3)$$

where I and I_0 represent the fluorescence emission of CAH in the presence and absence of Cu^{2+}, respectively, I_{min} is the saturated emission of CAH in the presence of excess amount of Cu^{2+}; $[Cu^{2+}]$ is the concentration of Cu^{2+} ion added, and K_a is the binding constant.

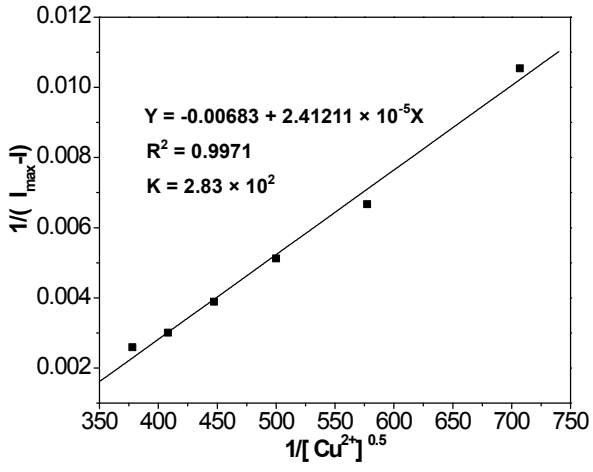

Fig. S7 The binding constant (K) of the CAH-Cu^{2+} derived from the fluorescence titration data was found to be 2.83×10^2 using Benesi-Hildebrand plot.

The Detection Limit: The limit of detection (LOD) was calculated on the basis of the fluorescence titration. The fluorescence emission spectrum of CAH was measured 10 times, and the standard devivation of blank measurement was achieved. The fluorescence intensity change at 425 nm versus a different concentration of Cu^{2+} was plotted.

So the detection limit was calculated with the following equation:[S3,S4]

$$LOD = 3\sigma/k \quad (4)$$

Where slope "k" is the calibration sensitivity of the fluorescence intensity change ($\Delta I = I_0 - I$) vs. [Cu^{2+}], and "σ" is the standard deviation of the blank signal (I_0) obtained without Cu^{2+}.

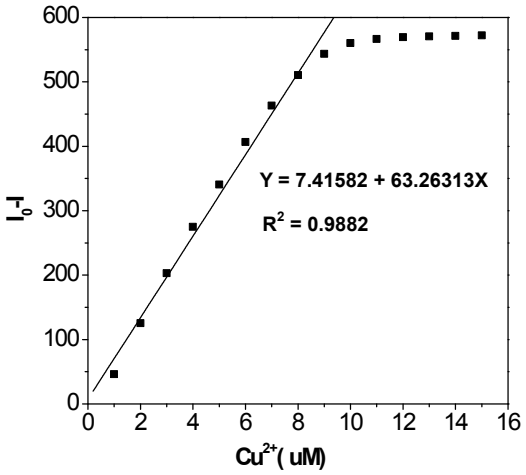

Fig. S8 Linear relationship between fluorescence intensity of CAH (5 μM) at 425 nm versus the concentration of Cu^{2+}. The detection limit of Cu^{2+} is 65 nM.

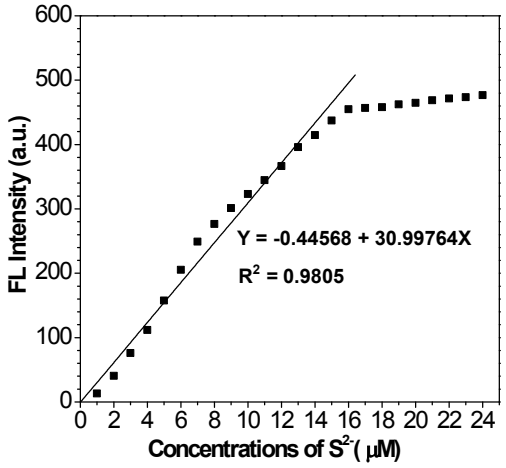

Fig. S9 Linear relationship between fluorescence intensity of CAH-Cu^{2+} (5 μM) at 425 nm versus the concentration of H_2S. The detection limit of S^{2-} is 0.29 μM.

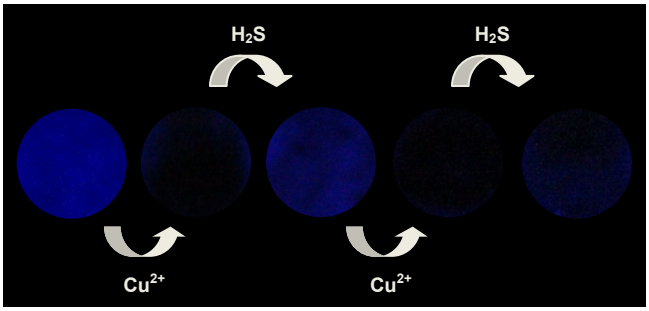

Fig. S10 The fluorescence changes of paper sensor by alternately dropping the solution of Cu^{2+} (10^{-3} M) and beeing exposed in gaseous H_2S (120 ppm) for 2 times. The corresponding photographs were taken at a 365 nm UV lamp.

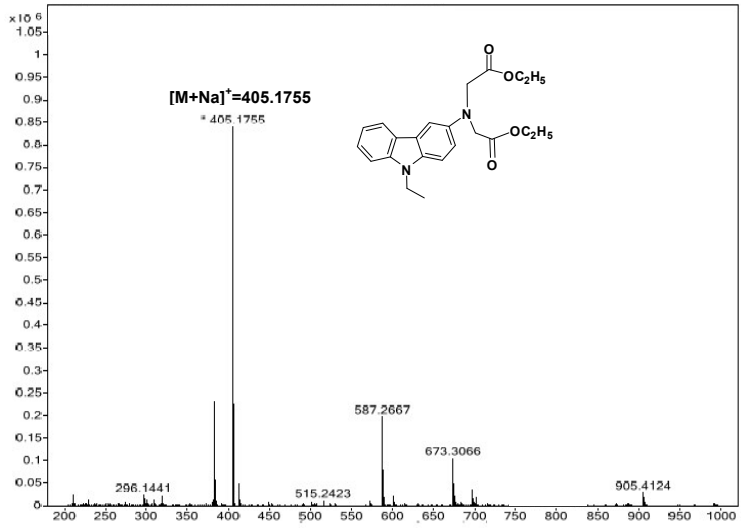

Fig. S11 ESI-MS spectrum of intermediate 2 (positive mode, calculated for intermediate 2 $[M+Na]^+$ = 405.1790).

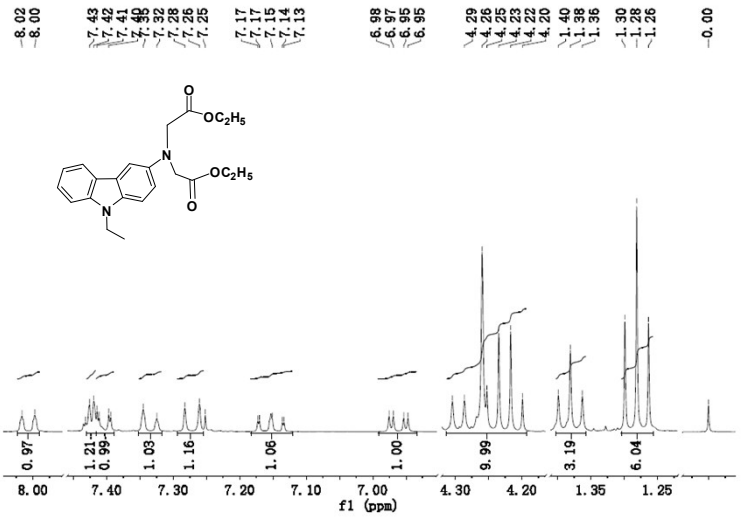

Fig. S12 ^{1}H NMR spectrum of intermediate 2 ($CDCl_3$).

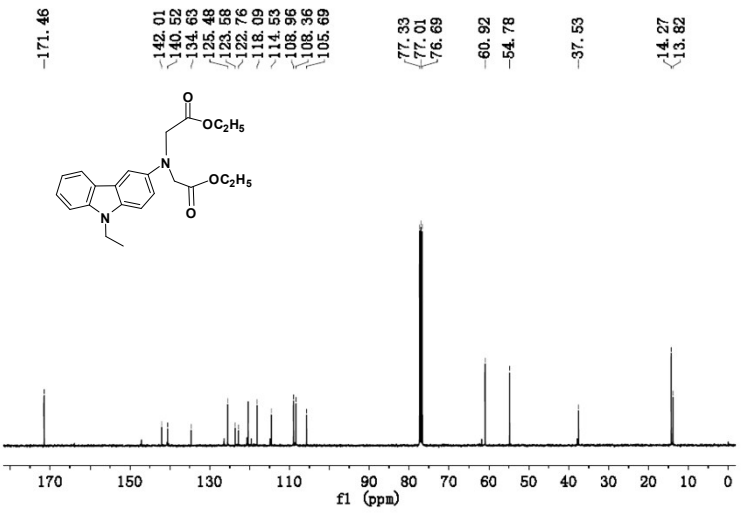

Fig. S13 ^{13}C NMR spectrum of intermediate 2 ($CDCl_3$).

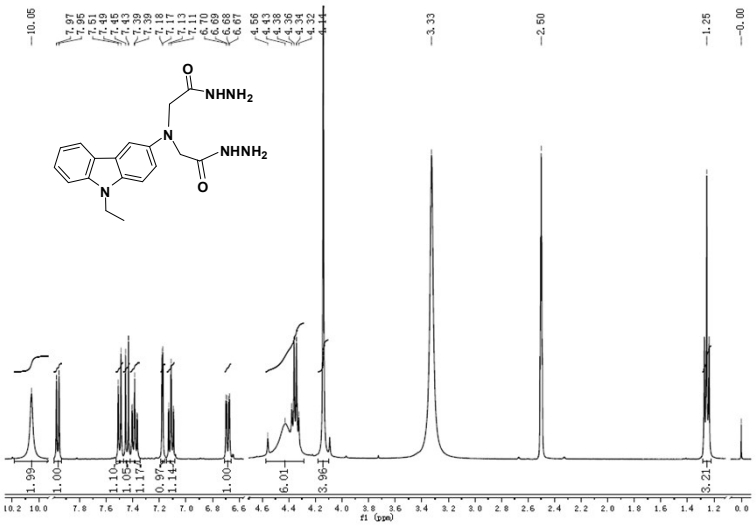

Fig. S14 [1]H NMR spectrum of compound CAH (d_6-DMSO).

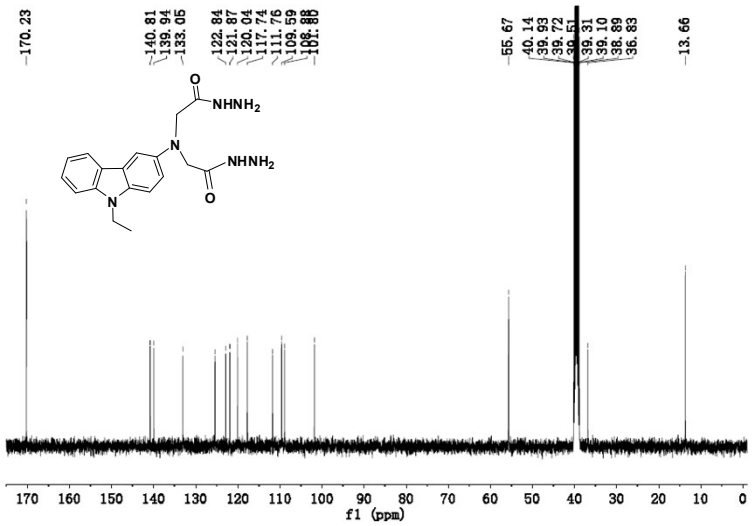

Fig. S15 [13]C NMR spectrum of compound CAH (d_6-DMSO).

References:

S1 Q. S. Mei, K. Zhang, G. J. Guan, B. H. Liu, S. H. Wang and Z. P. Zhang, *Chem. Commun.*, 2010, **46** , 7319.

S2 H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

S3 R. Koteeswari, P. Ashokkumar, E. J. P. Malar, V. T. Ramakrishnan and P. Ramamurthy, *Chem. Commun.*, 2011, **47**, 7695.

S4 K. Chirantan, D. A. Manab, R. Aiyagari and D. Gopal, *Inorg. Chem.*, 2013, **52**, 743.