Electronic Supplementary Information (ESI)

Electron-enriched thione enables strong Pb-S interaction for stabilizing high quality $CsPbI_3$ perovskite films with low-temperature processing

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1. Optical spectra of $CsPbI_3$ films with and without 4-PT

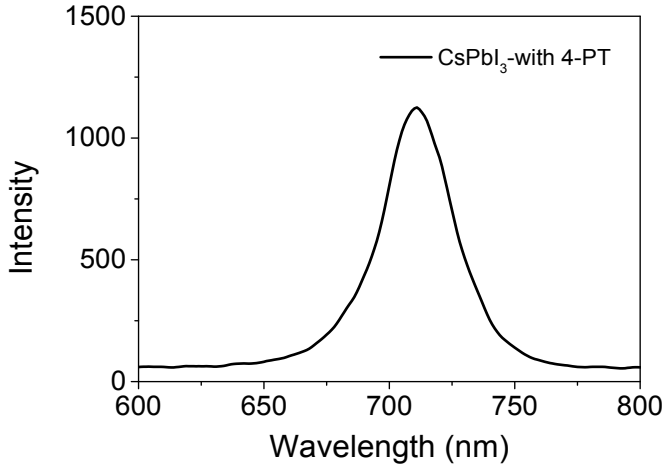


Fig. S1 PL spectrum of black-phase $CsPbI_3$ perovskite film stabilized by 4-PT. The excitation wavelength was set as 470 nm.

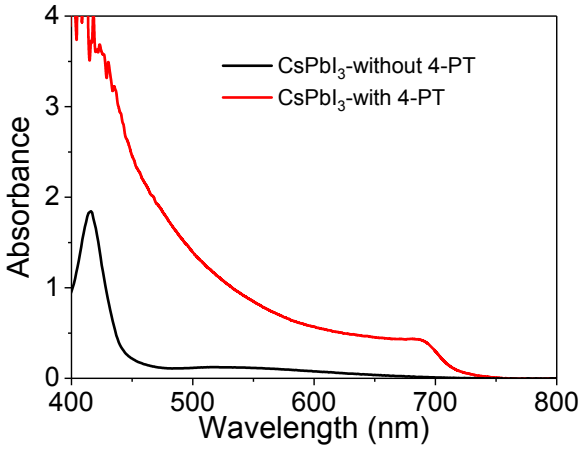


Fig. S2 Absorption spectra of $CsPbI_3$ films without or with 4-PT.

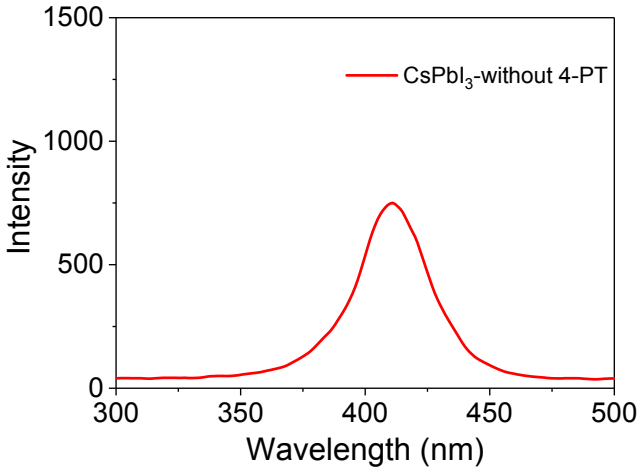


Fig. S3 PL spectrum of yellow-phase $CsPbI_3$ film without 4-PT. The excitation wavelength was set as 300 nm.

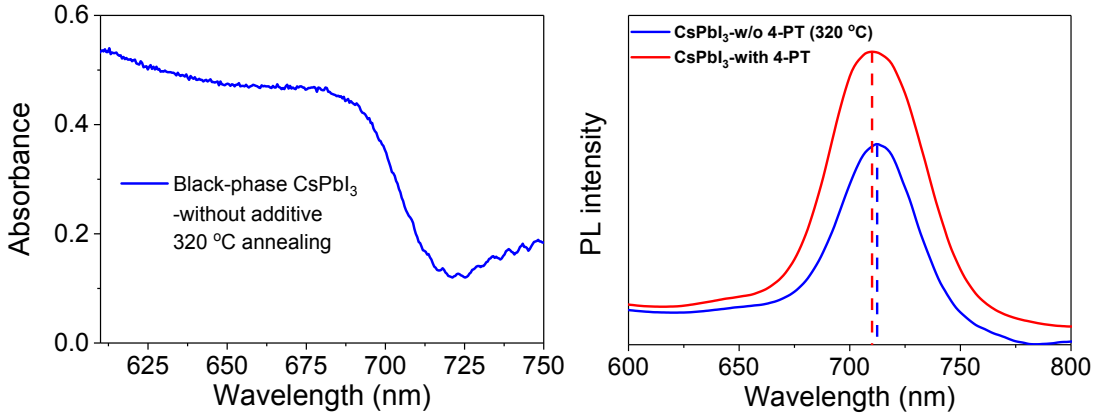


Fig. S4 Left: Absorption spectrum of the additive-free black-phase $CsPbI_3$ film annealed at 320 °C for 10 minutes. The spectrum was acquired by a homemade optical fiber based in-situ spectroscopy. **Right:** PL spectra of black-phase $CsPbI_3$ films with or without 4-PT (excited at 480 nm). The black-phase $CsPbI_3$ film without 4-PT was obtained by annealing at 320 °C for 10 minutes.

2. SEM images and EDS mapping of $CsPbI_3$ films

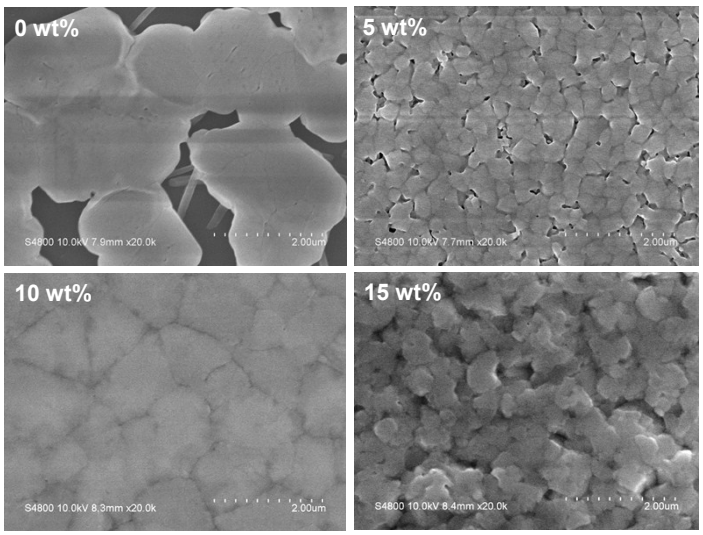


Fig. S5 SEM images of $CsPbI_3$ films fabricated with various concentration of 4-PT.

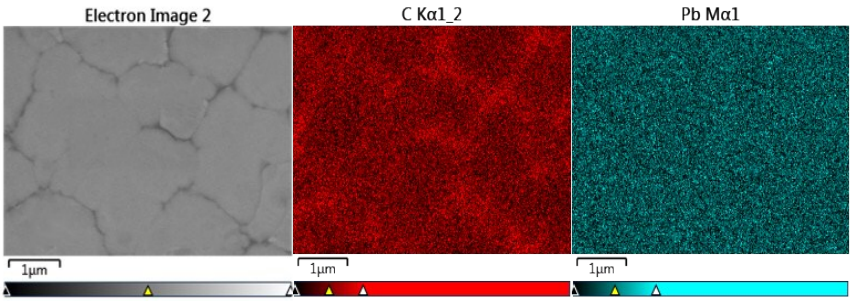


Fig. S6 EDS mapping C and Pb elements of black-phase $CsPbI_3$ with 10 wt% 4-PT.

3. Retarded crystallization process of the $CsPbI_3$ film

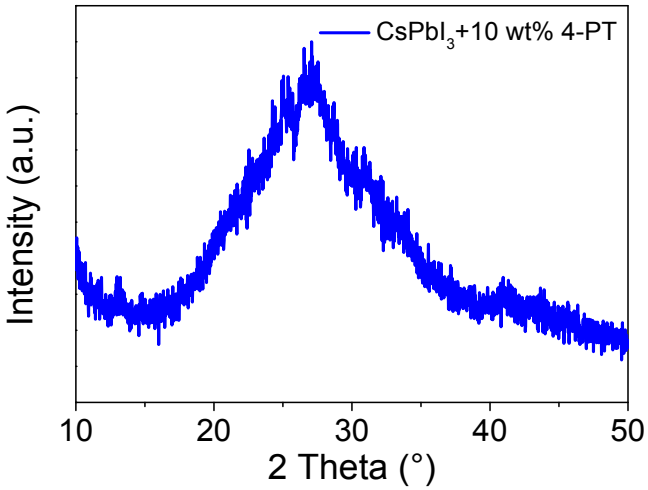


Fig. S7 XRD pattern of $CsPbI_3$ film with 10 wt% 4-PT annealed at 50 °C for 5 minutes.

4. Thermal stability test of the $CsPbI_3$ perovskite film

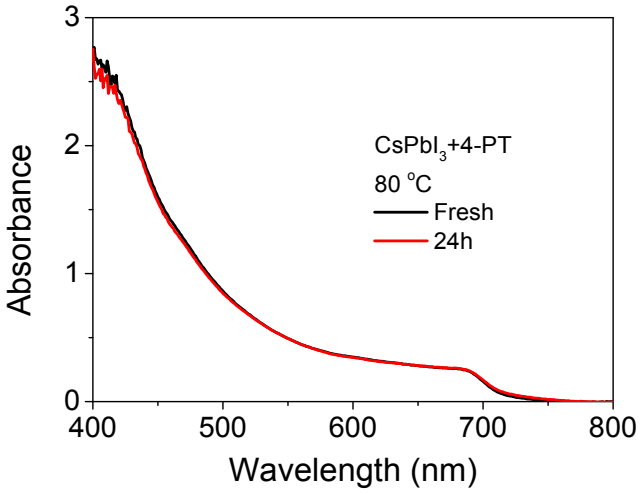


Fig. S8 Absorption spectra of the $CsPbI_3$ perovskite film measured immediately after fabrication (Fresh) and aged in nitrogen glove box at 80 °C (24 h).

5. Air stability comparison

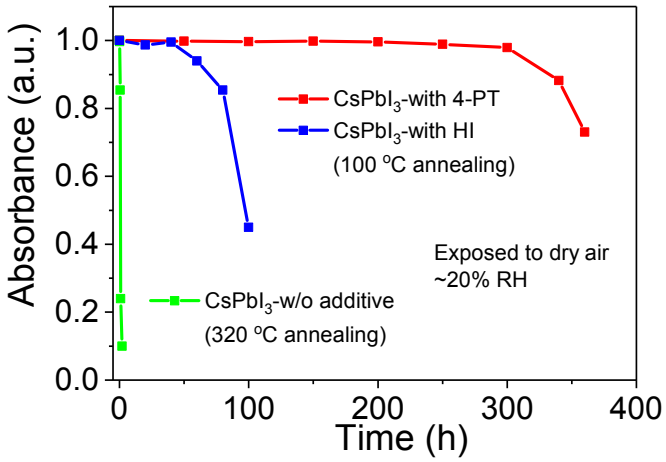


Fig. S9 Evolution of the absorbance at 690 nm for the additive-free black-phase $CsPbI_3$ film and the 4-PT or HI based black-phase $CsPbI_3$ films exposed to air (~20% RH).

6. Characterization of $CsPbI_3$ films with different additives

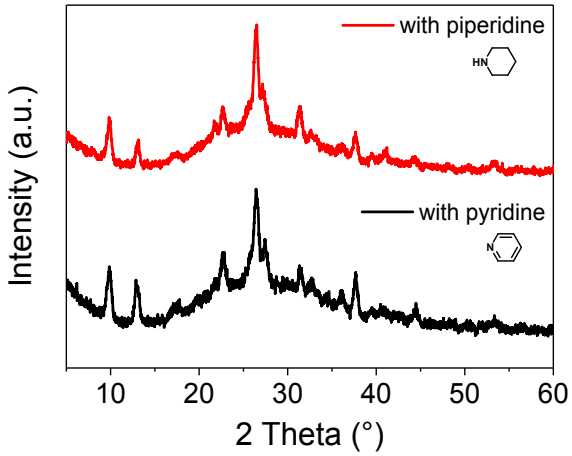


Fig. S10 XRD patterns of the $CsPbI_3$ perovskite precursor films with the addition of pyridine and piperidine.

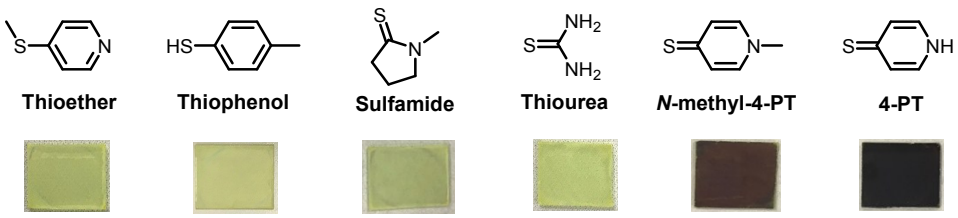


Fig. S11 Chemical structures of various additives and corresponding photos of $CsPbI_3$ films after thermal annealing.

7. Characterization of the molecular interaction between 4-PT and

$CsPbI_3$

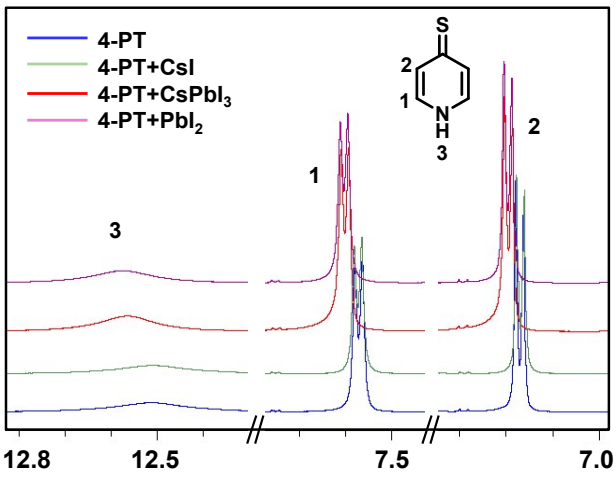


Fig. S12 ^{1}H NMR spectra of pure 4-PT, 4-PT mixed with PbI_2, CsI and $CsPbI_3$ in DMSO-d_6 solution. Specifically, the samples were prepared by dissolving 5 mg pure 4-PT alone, or a mixture of 5 mg 4-PT with perovskite precursor materials (2 mg PbI_2 or 2 mg CsI or 4 mg $CsPbI_3$) in DMSO-d_6.

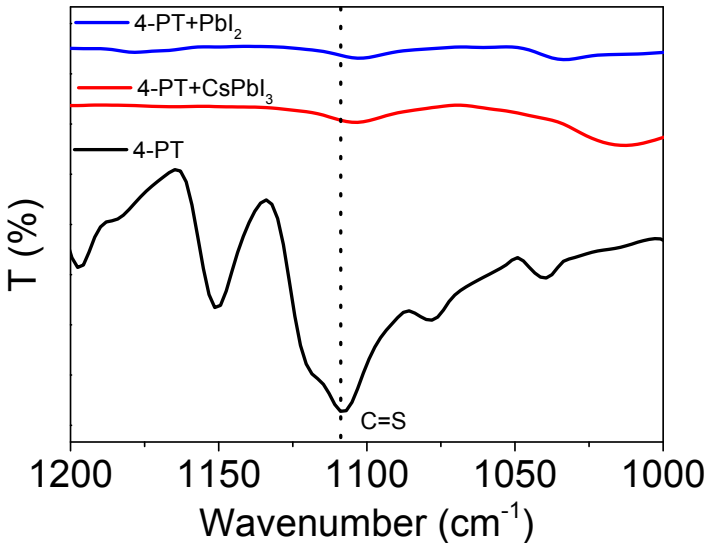


Fig. S13 Magnified Fourier transform infrared (FTIR) spectra of pure 4-PT, $CsPbI_3$ and PbI_2 precursor films mixed with 4-PT.

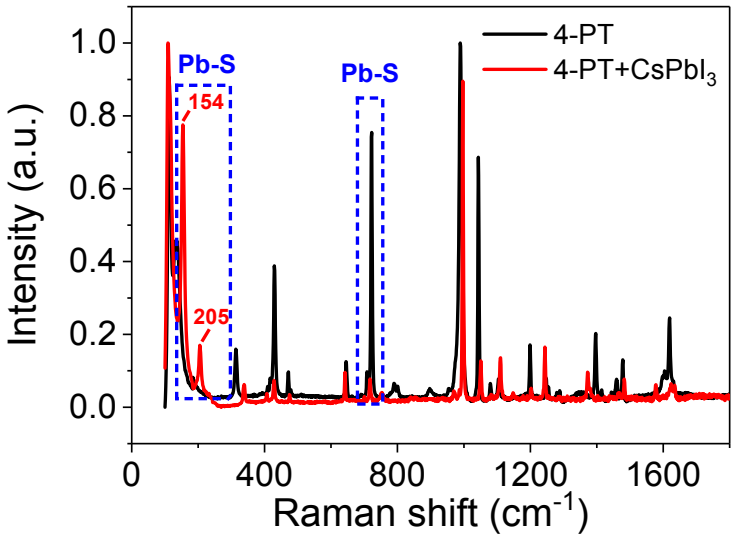


Fig. S14 Raman spectra of 4-PT and 4-PT with $CsPbI_3$ complex. Specifically, the complex was prepared by dissolving 4-PT powder in $CsPbI_3$ precursor solution at 0.8 M concentration, then the solution was dripped into large amounts of chlorobenzene to obtain the precipitate. The collected powders were dried in a vacuum oven for 12 h before Raman measurement.

8. Device characterization

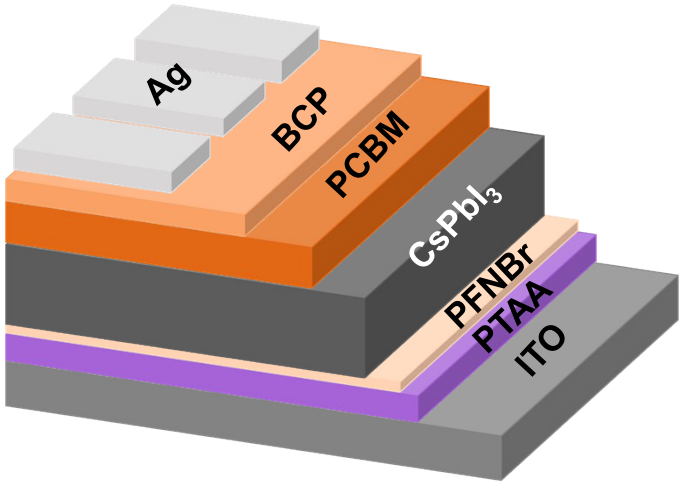


Fig. S15 Structure of $CsPbI_3$ perovskite solar cells.

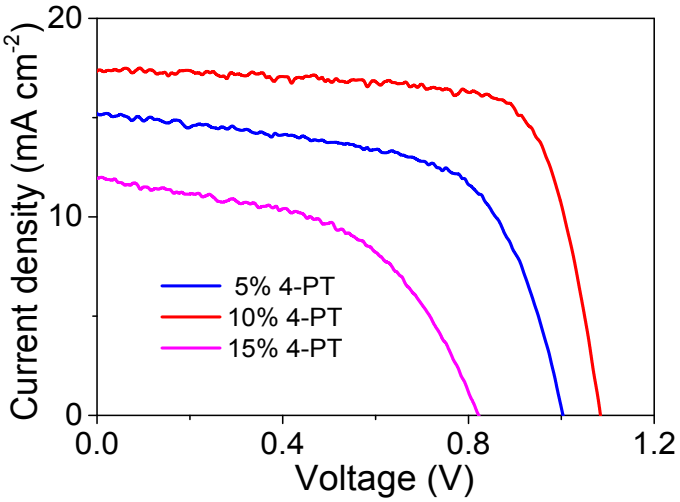


Fig. S16 *J-V* curves of $CsPbI_3$ perovskite devices with various concentrations of 4-PT.

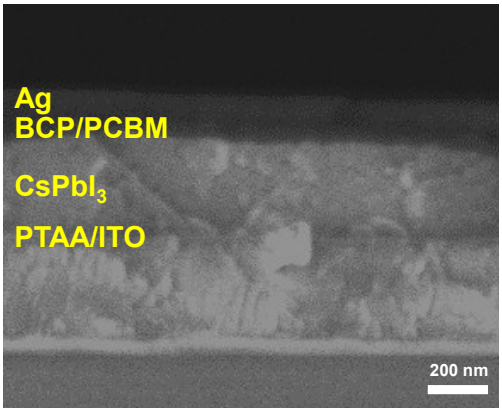


Fig. S17 Cross-sectional SEM image of $CsPbI_3$ device stabilized by 10 wt% 4-PT.

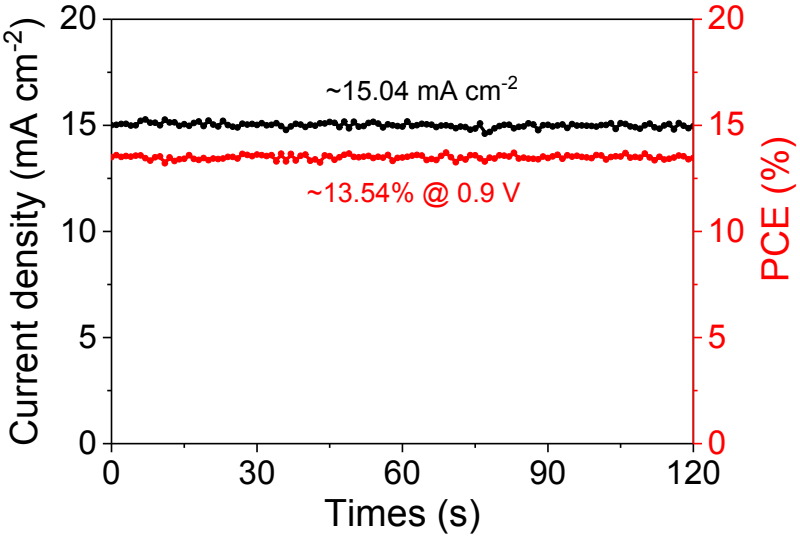
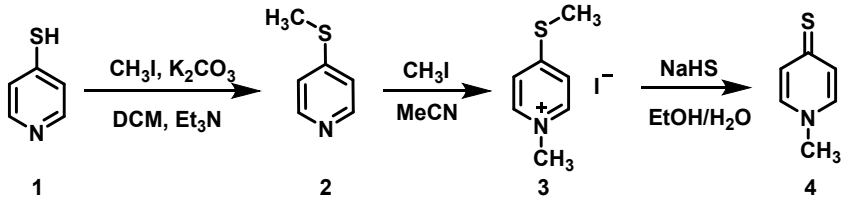


Fig. S18 Steady-state photocurrent and stabilized power output of the most efficient device.

9. Synthesis of *N*-methyl-4-pyridinethione



Scheme S1 Synthetic Route of *N*-methyl-4-pyridinethione.

N-methyl-4-pyridinethione is prepared according to previously reported method[1, 2]. The synthetic route is shown in **Scheme S1**, which involves commercially available low-cost raw materials in three-step reactions. Specifically, the starting material **1** (3.66 mmol, 0.41 g), K_2CO_3 (7.32 mmol, 1.01 g), CH_2Cl_2 (15 mL) were added to a round-bottom flask and stirred at 0 ℃ for 5 minutes. To this mixture, CH_3I (5.49 mmol, 0.35 ml) was added, followed by Et_3N (0.5 ml). After stirring at room temperature for 5-6 h, the reaction mixtures were extracted with CH_2Cl_2 (3 × 10 ml). The organic phases were combined together, dried over anhydrous Na_2SO_4 and purified by silica gel chromatography (pure CH_2Cl_2) to give yellow liquid **2** in about 45% yield (1.63 mmol, 0.20 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.38 (dd, J_1 = 6.0 Hz, J_2 = 3.2 Hz, 2 H), 7.09 (dd, J_1 = 6.4 Hz, J_2 = 2.8 Hz, 2 H), 2.48 (s, 3 H).

Then, in a round-bottom flask, the intermediate **2** (1.51 mmol, 0.19 g) and CH_3I (2.27 mmol, 0.32 g) were dissolved in CH_3CN (8.5 mL). The mixture was stirred at room temperature overnight and then dropped into ether solution. After that, the precipitate was filtered off and vacuum dried to obtain white powder **3** (1.14 mmol, 0.30 g). Yield: 75%. Finally, **3** (1.10 mmol, 0.29 g), NaHS (2.31 mmol, 0.13 g) was added to a solution of EtOH/H_2O (5.5 mL, 1/1: v/v), the mixture was stirred at room temperature for 5-6 h. The resulting mixture was extracted with CH_2Cl_2 (3 × 10 ml) and the organic phases were combined, dried with Na_2SO_4 and purification by silica gel chromatography (CH_2Cl_2: CH_3OH = 50: 1) to afford yellow powder **4**. The resulting powder was further vacuum dried and resulted in about 47% yield (0.52 mmol, 0.06 g). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.42 (d, J = 7.2 Hz, 2 H), 7.09 (d, J = 6.8 Hz, 2 H), 3.73 (s, 3 H).

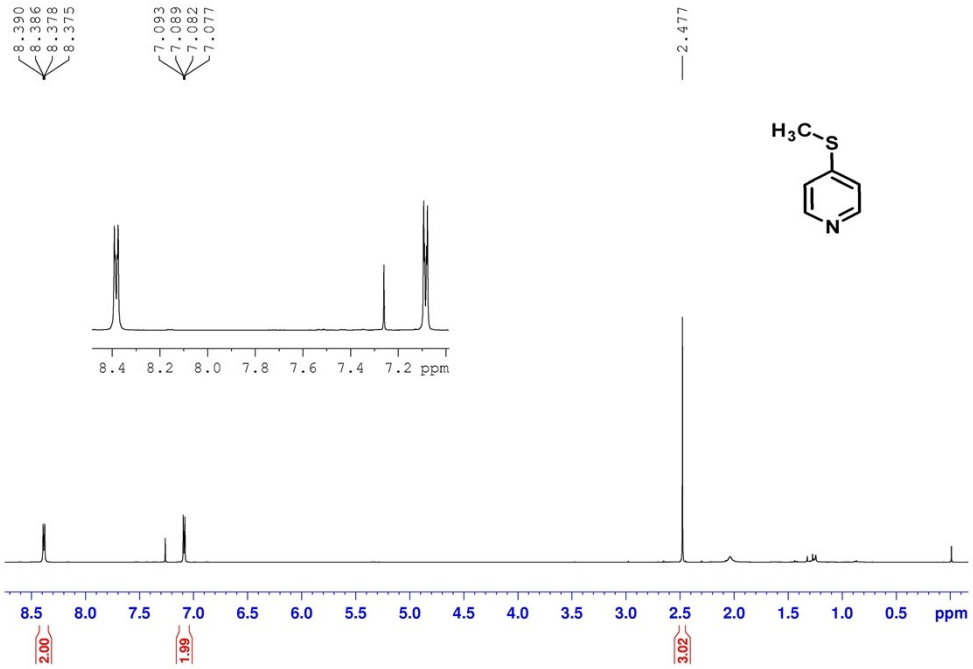


Fig. S19 ^{1}H NMR of *S*-methyl-4-mercaptopyridine recorded in $CDCl_3$.

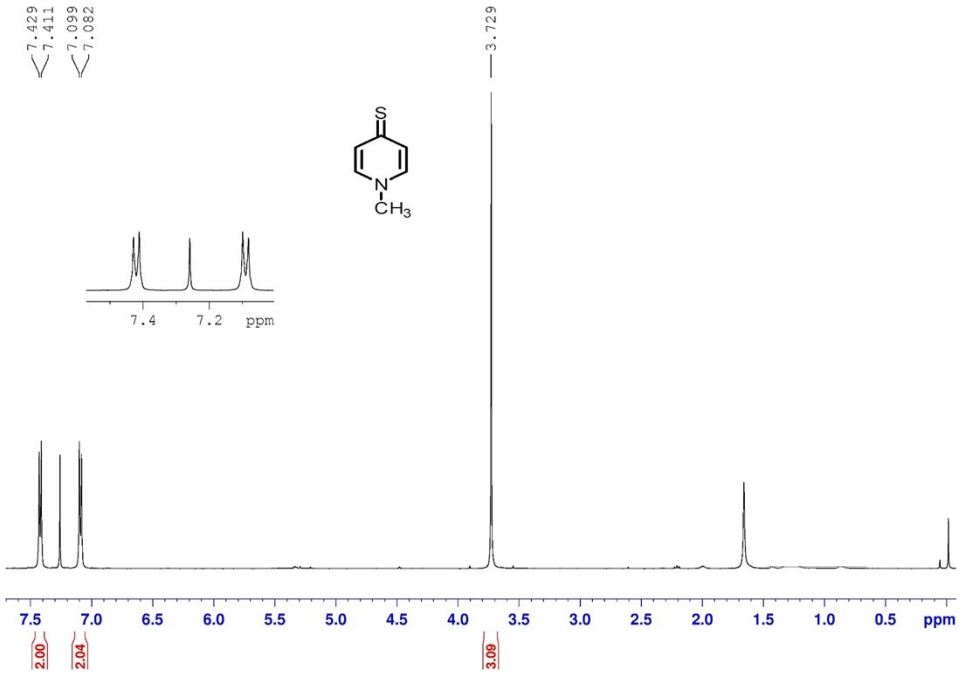


Fig. S20 ^{1}H NMR of *N*-methyl-4-pyridinethione recorded in $CDCl_3$.

10. Notes on the different ESP values of S atoms in additives

Compared to thione based additives, thioether and thiophenol lack the resonant assistance of N lone pair electrons, therefore the electron density of S atoms mainly originates from their lone pair electrons. For sulfamide and thiourea, they both have C=S double bond and adjacent N atoms. The lone pair electrons of N atom can conjugate with C=S double bond thus increases the electron density of S atoms. Compared to sulfamide, thiourea has two adjacent N atoms, therefore making the electron density of S atom higher than that in sulamide. We can draw this conclusion easily by writing the resonance formula as shown in **Fig. S21**.

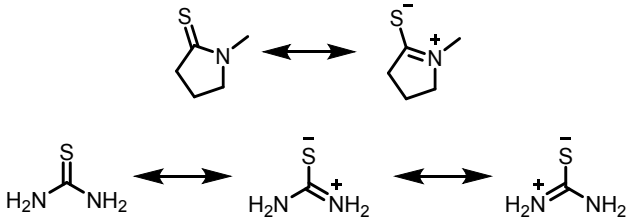


Fig. S21 The resonance formulas of sulfamide and thiourea structure.

In the pyridinethione based molecule of 4-PT (*N*-methyl-4-PT), the N atom adopts sp^2 hybridization to form covalent bonds with two C and one H ($-CH_3$) in the same plane, and its lone pair electrons will occupy the un-hybridized p orbital. In this case, the resonation of the C=S double bond to form a carbocation and a sulfur anion (as depicted in **Fig. S22**) will be beneficial to stabilize the six-membered ring structure, as the total number of their p orbital electrons becomes 6, which satisfies the Huckel's rule to obtain an aromatic structure. This might be the origin of the lowest ESP for S atoms in the pyridinethione based compounds.

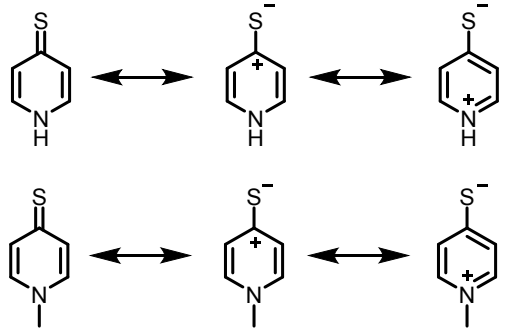


Fig. S22 The resonance formulas of pyridinethione.

References:

1. A. L. M. Porto, F. Cassiola, S. L. P. Dias, I. Joekes, Y. Gushikem, J. A. R. Rodrigues, P. J. S. Moran, G. P. Manfio and A. J. Marsaioli, *J. Mol. Catal. B-Enzym.*, 2002, **19-20**, 327-334.

2. J. Levillain, D. Paquer, A. Sene and M. Vazeux, *Synthesis*, 1998, **1998**, 99-104.