

A pyrene-based fluorescent and colorimetric chemodosimeter for detection of ClO⁻ ions

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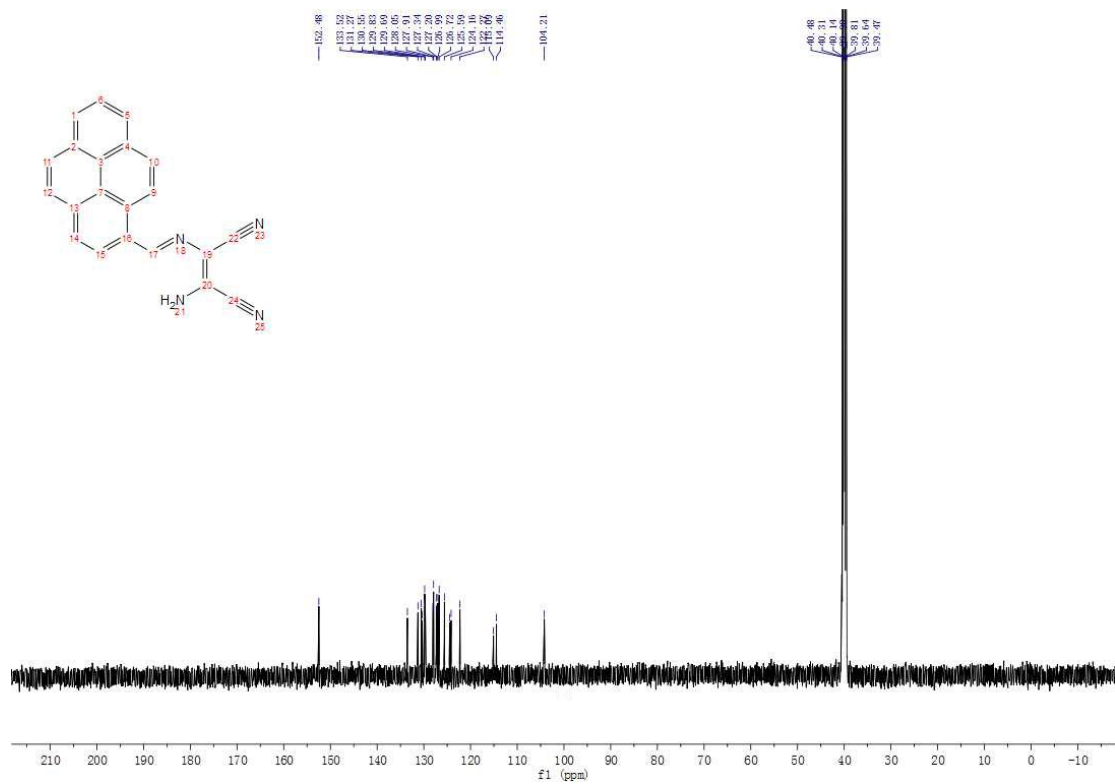
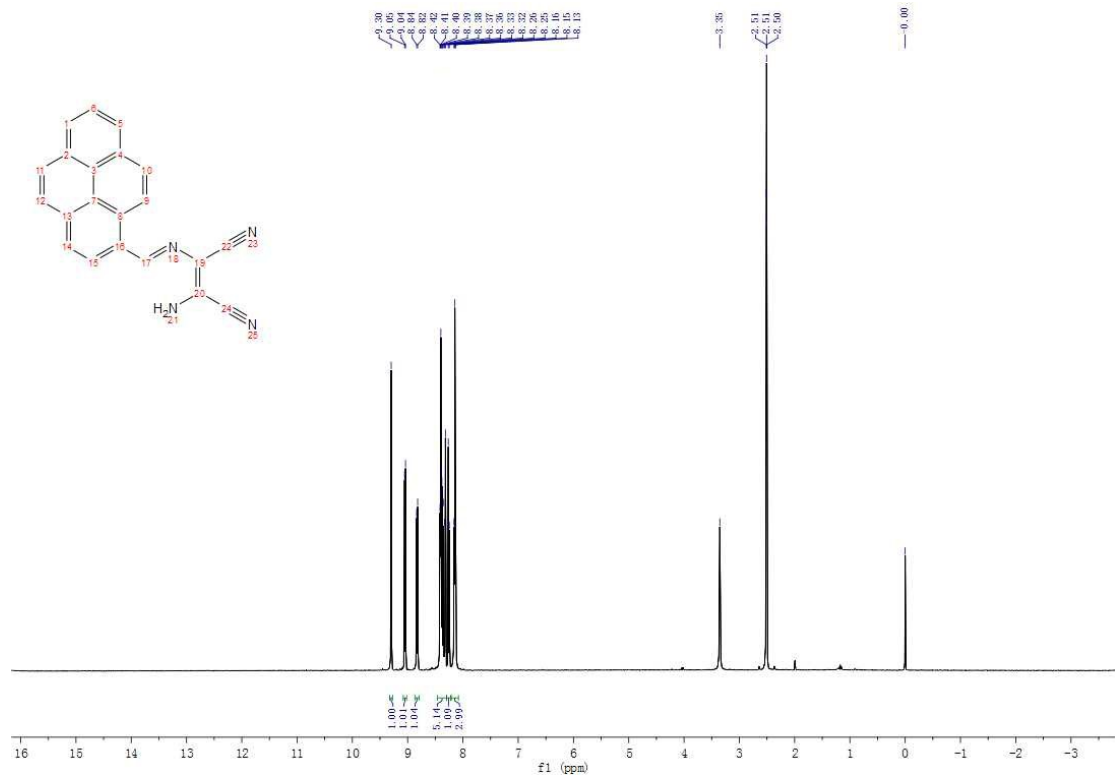
1. Materials and methods

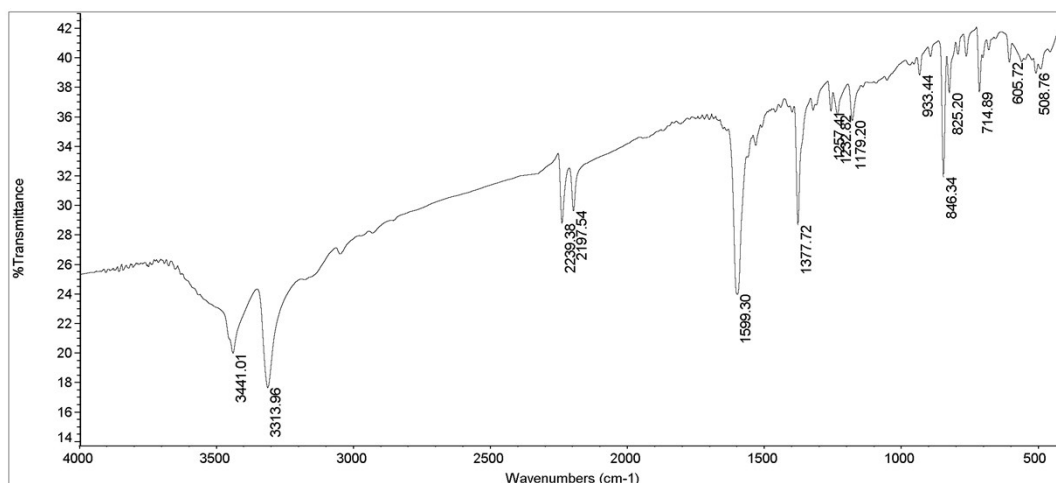
Most of the metal salts were purchased from Tianjin Damao Chemical reagent Factory and used as received. 1-pyrenecarboxaldehyde was procured from TCI (Shanghai) Development Co. Ltd. 2,3-diaminomaleonitrile was procured from Adamas Reagent Ltd. Ethanol (AR grade) was purchased from Beijing Chemical Reagent Plant and purified before use. Water used for the experiment was double distilled.

Stock solution (1×10^{-2} M) of the aqueous sodium and potassium salts of Cl^- , Br^- , I^- , ClO^- , ClO_3^- , BrO_3^- , IO_3^- , NO_2^- , NO_3^- , S^{2-} , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CO_3^{2-} , AcO^- , $\text{C}_2\text{O}_4^{2-}$ and H_2O_2 were prepared. Stock solution (1×10^{-2} M) of the aqueous nitrate and chloride salts of Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , Zn^{2+} were prepared. High concentration of the stock solutions PYCN (1.0×10^{-4} M) were prepared in EtOH- H_2O . The stock solutions could be diluted to desired concentrations with water when needed, and the pH values were adjusted with the aid of a pH meter.

The sensing activity was investigated by adding various anions and ROS into PYCN solution (EtOH- H_2O , 8:2, v/v). The mixed solutions were shaken for 10 min before spectroscopic test in order to make the anions react with the sensors sufficiently. To investigate the kinetic behavior of the detection system, the fluorescence signal was recorded after the addition of ClO^- to the probe solution at $\lambda_{\text{ex/em}}=355/420$ nm as a function of reaction time.

2. NMR and IR copies of PYCN





FIND PEAKS:

Region: 4000.00 400.00
 Absolute threshold: 39.995
 Sensitivity: 50

Position:	Intensity:
508.76	38.925
605.72	39.651
714.89	37.629
825.20	37.575
846.34	31.858
933.44	38.799
1179.20	35.698

3. Photophysical responses of PYCN to ClO^- .

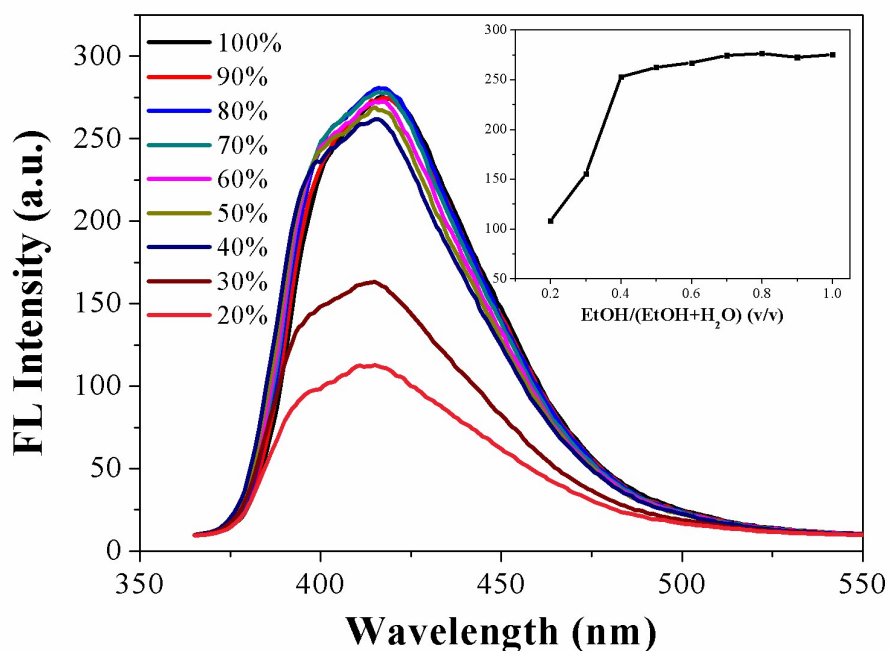


Fig. S1. The effect of the EtOH content on the fluorescence intensity of PYCN (10 μM) in the presence of ClO^- (10 Eq).

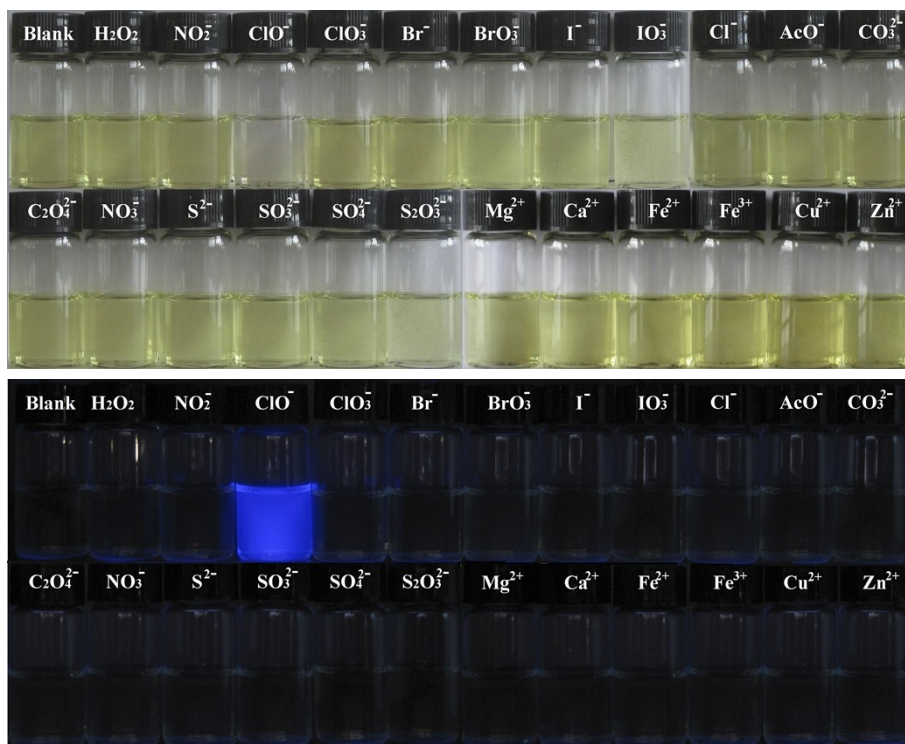


Fig. S2. Photograph of PYCN (10 μM) showing the color (top) and the fluorescent (bottom) changes in the presence of various ions (10 Eq).

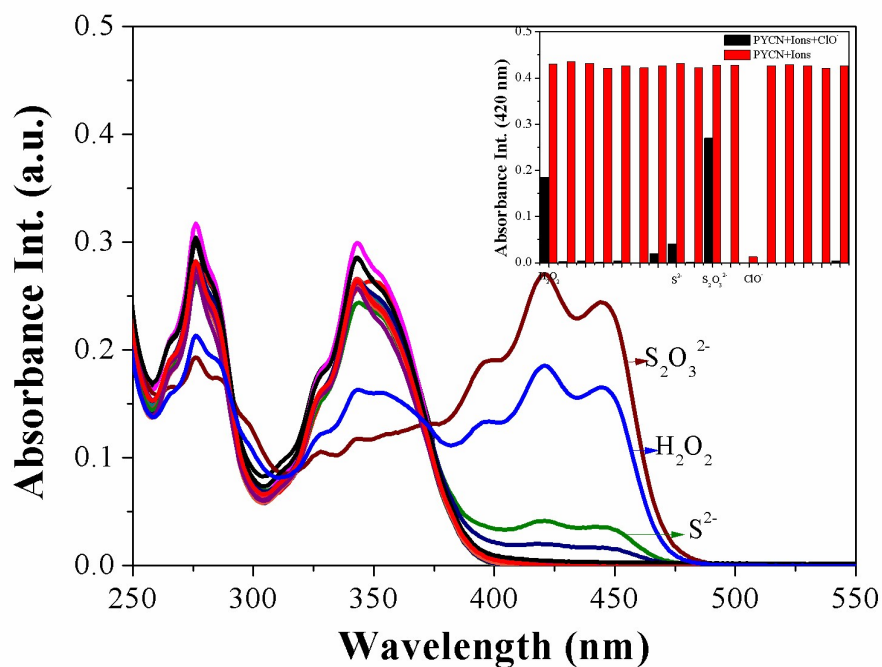


Fig. S3. Changes in the absorbance spectra of PYCN (10 μM) in presence of various anions and ClO⁻ (10 Eq). The inset shows the relative absorption value at 420 nm in presence of different anions and ClO⁻.

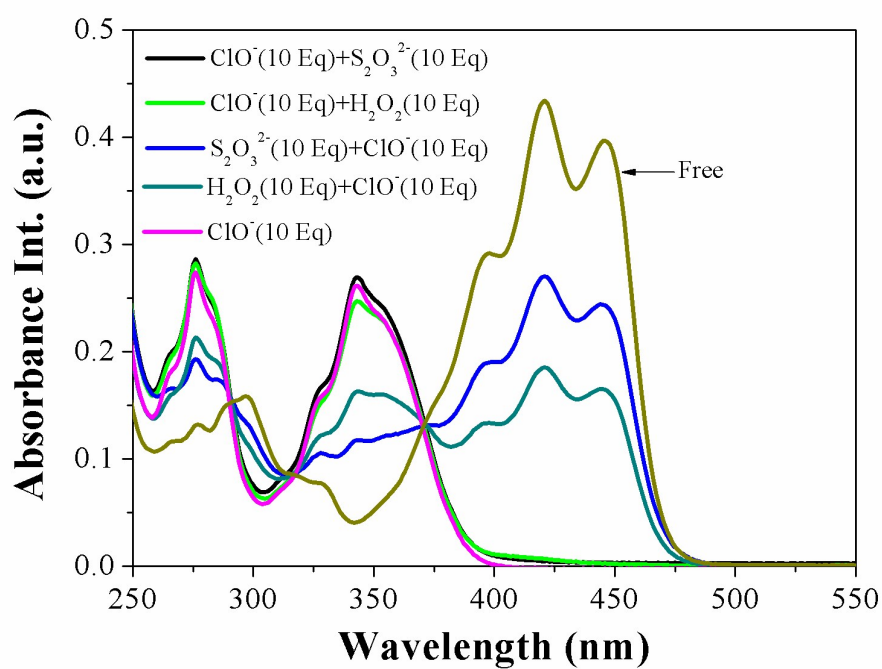


Fig. S4. Absorbance responses of PYCN (10 μM) by alternated adding ClO⁻ and H₂O₂ (S₂O₃²⁻) in EtOH-H₂O (4:1, v/v).

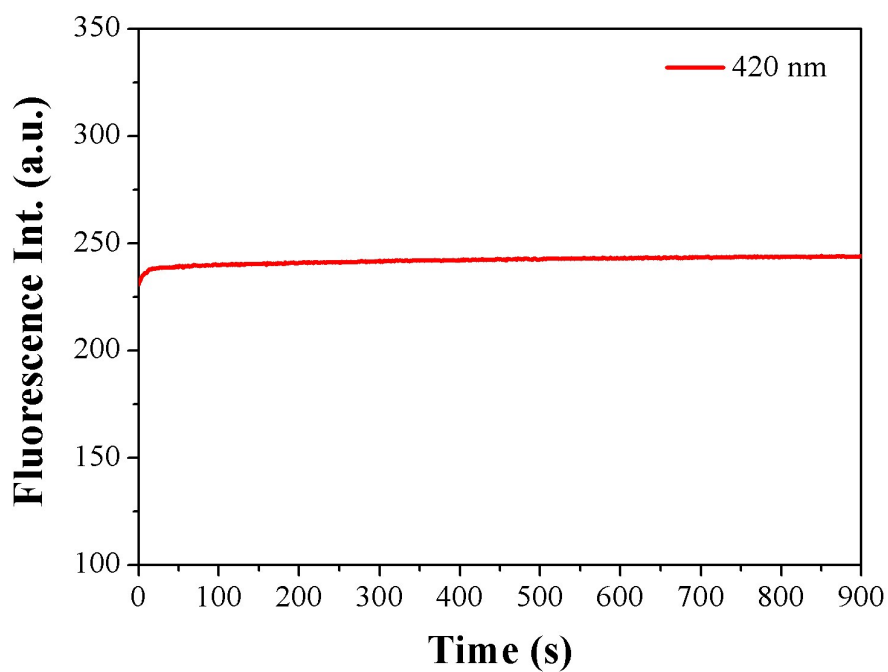


Fig. S5. Effects of reaction time on the fluorescence intensity of PYCN (10 μM) with 10 equiv of ClO⁻ ions at pH 7.0.

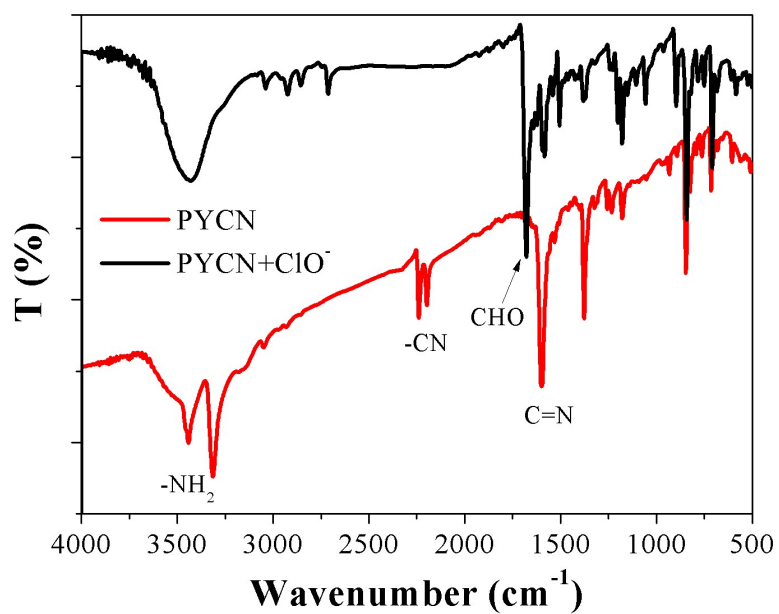


Fig. S6. FT-IR spectra of PYCN in the absence (a) and presence of ClO^- (10 equiv.)

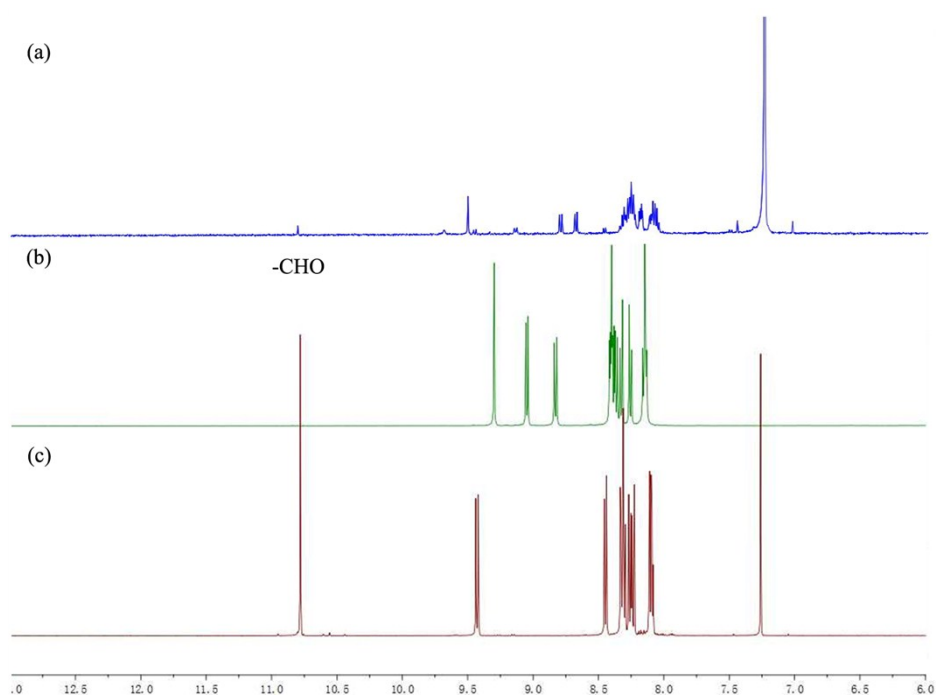


Fig. S7. NMR spectra of PYCN in presence of ClO^- (a), PYCN (b) and 1-pyrenecarboxaldehyde (c)