# Supporting Information

# Selective and Sensitive Detection of Formaldehyde by ZIF-90-LW *via* Aza-Cope Rearrangement

Li Mengwen[a]; Shen Ao[a]; Sun Xinchao[a]; Liu Xueliang[b*]; Hao Xiaohui[a]; Liang Yueqi[a]; Zhen Hao[a]; Yang Yunxu[a]*

[a] *Department of Chemistry and Chemical Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China*

[b] *Analysis and Testing Laboratory, Xinxiang Medical University, Jinsui Road 601, Xinxiang, Henan 453003 (P.R. China)*

**Corresponding Author:** Yunxu Yang

E-mail addresses: yxyang@ustb.edu.cn (Yunxu Yang);
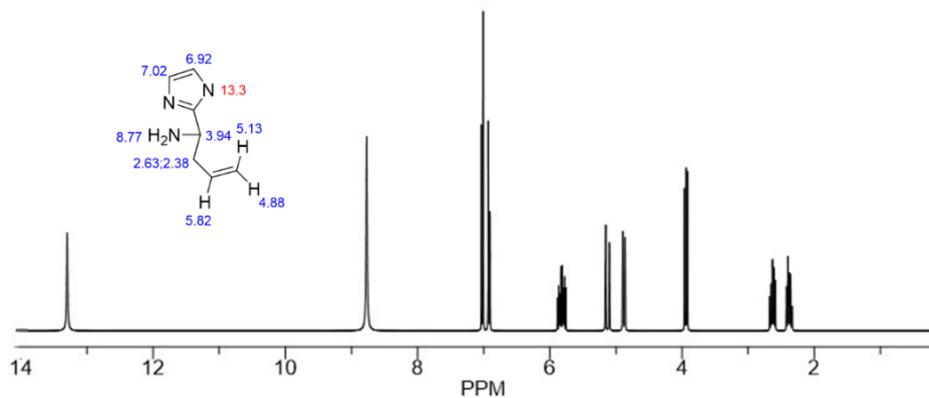
# Contents:

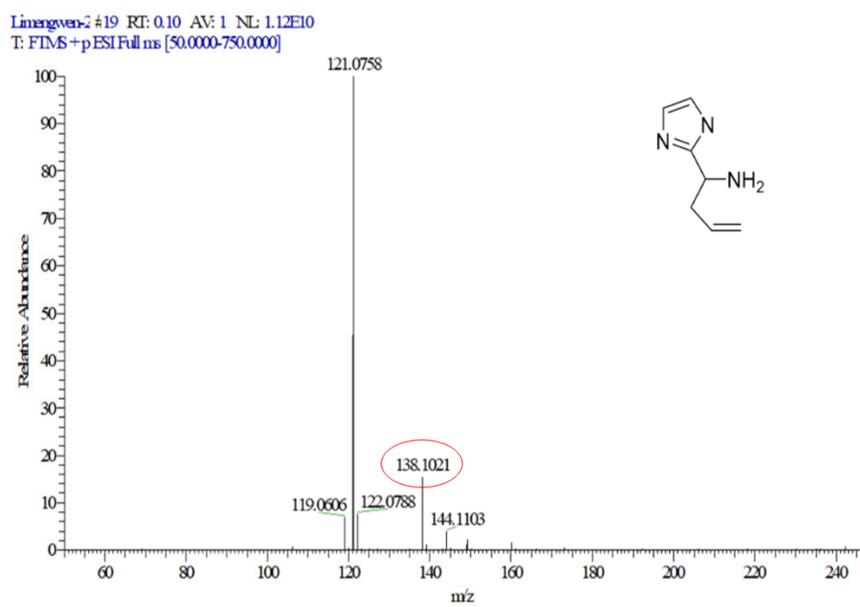**Figure S1.** ^{1}H NMR spectrum of **Ligand 1**.



**Figure S2.** HRMS spectrum of **Ligand 1**.

3

## S3. Calculation of the yield of ZIF-90-LW

Basis of 0.410g of **Ligand 1**

Wt.% of **Ligand 1** in **ZIF-90-LW** = 84.8 %

In principle, mass of synthesized **ZIF-90-LW** = 0.488 g

The activated product we obtained is 0.425 g. TGA (Figure 4) shows that the product contains 7%

DMF, so the actual mass of **ZIF-90-LW** is 0.395 g.

So the yield of **ZIF-90-LW** is: 0.395 g / 0.488 g $\times$ 100% = 81%.

## Detection limit:

The detection limit for FA was calculated by the fluorescence titration experiments. A good linear relationship between the fluorescence intensity and FA concentration (0–25 mM) could be obtained ($R^2$=0.9979). The value obtained for the FA was found to be 2.3 $\mu$M by the equation of $L_{OD}=3\delta/slope$. ($\delta$=0.0408, slope=52.768).
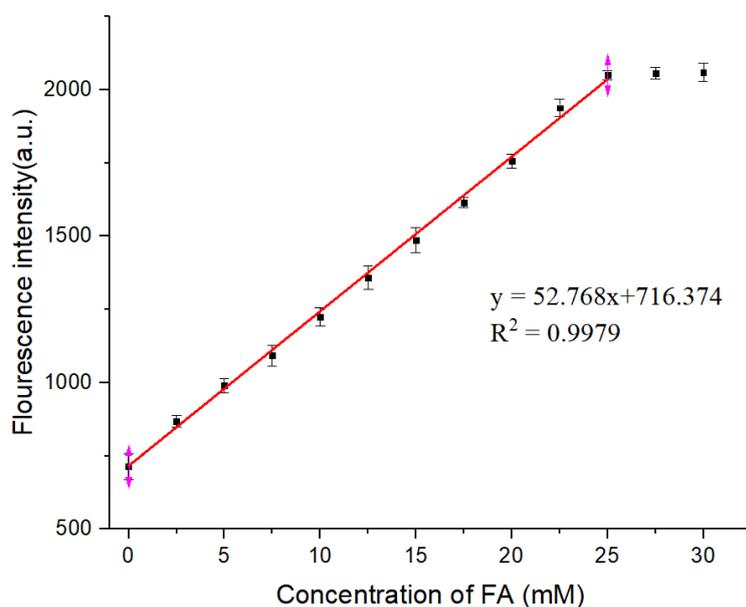


**Figure S4.** The linear relationship between the fluorescence intensity and FA concentration (0-25 mM). **ZIF-90-LW** is 25 mM (0.4 mg/mL), FA is 0-30 mM, in a mixture of DMF and Tris buffer solution (7 : 3, v/v), pH = 7.0. $\lambda_{ex}$= 380 nm, $\lambda_{em}$= 438 nm.

## Kinetic studies:

The reaction of **ZIF-90-LW** (25 mM, 0.4 mg/mL) with FA was monitored using the fluorescence intensity. The reaction was carried out at 25 ºC. The *pseudo*-first-order rate constant for the reaction was determined by fitting the fluorescence intensities of the samples to the *pseudo*-first-order equation:

Ln [(F$_{max}$ - F$_t$) / F$_{max}$] = - $k'$t

Where F$_{max}$ and F$_t$ are the fluorescence intensities at 440 nm at time t and the maximum value obtained after the reaction was complete. $k'$ is the *pseudo*-first-order rate constant. The *pseudo*-first-order plots for the reaction of **ZIF-90-LW** (25 mM, 0.4 mg/mL) with 25mM FA is shown in Figure S5, the *pseudo*-first-order rate constant $k' = 1/t_1 = 7.93$ min$^{-1}$.
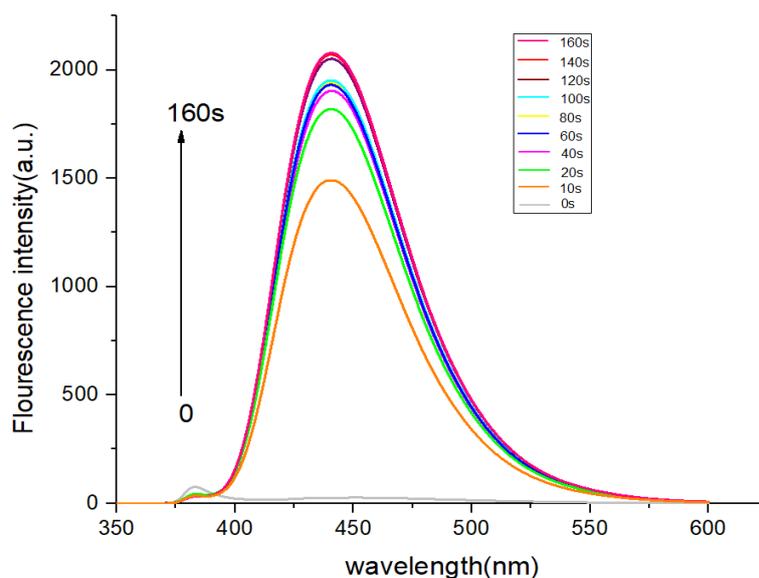


**Figure S5.** Time course of the signaling of probe by FA. **ZIF-90-LW** is 25 mM (0.4 mg/mL), FA is 25mM, in a mixture of DMF and Tris buffer solution (7 : 3, v/v), pH = 7.0. $\lambda_{ex}$= 380 nm, $\lambda_{em}$= 438 nm.
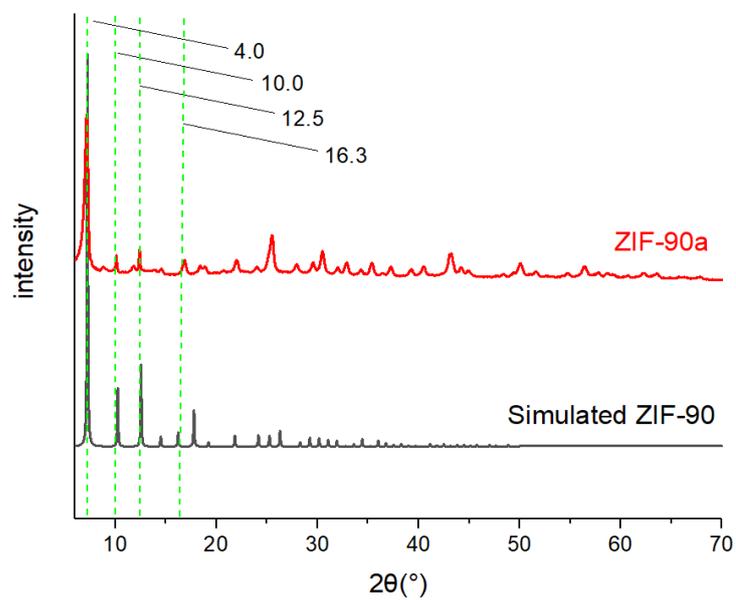
# Mechanism of FA sensing:



**Figure S6.** PXRD data of product **ZIF-90a** and simulated pattern of ZIF-90.
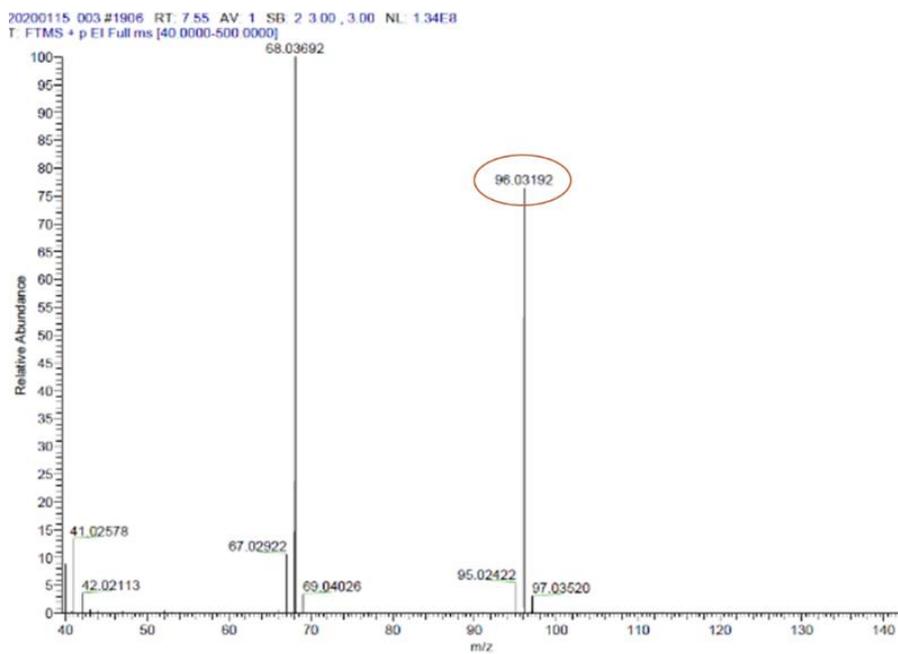


**Figure S7.** ESI mass spectra of ICA.

To support the turn-on mechanism of **ZIF-90-LW**, we tested the fluorescence change of **Ligand 1** before and after the reaction with FA. It's proved that FA reacted with **ZIF-90-LW** according to the mechanism of 2-aza-Cope rearrangement and caused fluorescence to turn on.
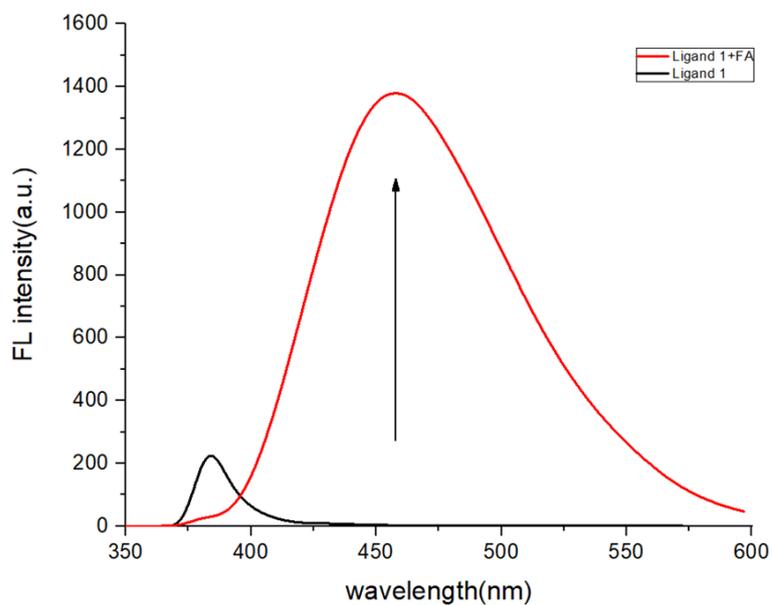


**Figure S8.** The fluorescence spectra of Ligand 1 with and without FA. **Ligand 1** is 25 mM, FA is 25 mM, in a mixture of DMF and Tris buffer solution (7 : 3, v/v), pH = 7.0. $\lambda_{ex}$= 380 nm, $\lambda_{em}$= 438 nm.

## Applications of ZIF-90-LW:

The detection applications of **ZIF-90-LW** were studied by self-made experimental devices (Figure S9-S11).



**Figure S9.** Device-1 for FA gas detection by **ZIF-90-LW** test paper.

Another device for detecting FA is designed as follows.10 ml 25 mM (0.4 mg/mL) of **ZIF-90-LW** suspension was added to the conical flask, and the cuvette containing 25 mM FA solution was placed in the conical flask to ensure that the two solutions were not in contact (Figure S10).



**Figure S10.** Device-2 for FA gas detection by **ZIF-90-LW** suspension

The flask was sealed at room temperature and **ZIF-90-LW** will respond as soon as the FA molecules diffuse and enter the suspension. The experimental results are shown in the Figure S10. The color of the conical flask changed from colorless to blue under the 365 nm UV lamp, indicating that **ZIF-90-LW** has potential application in detecting FA gas.
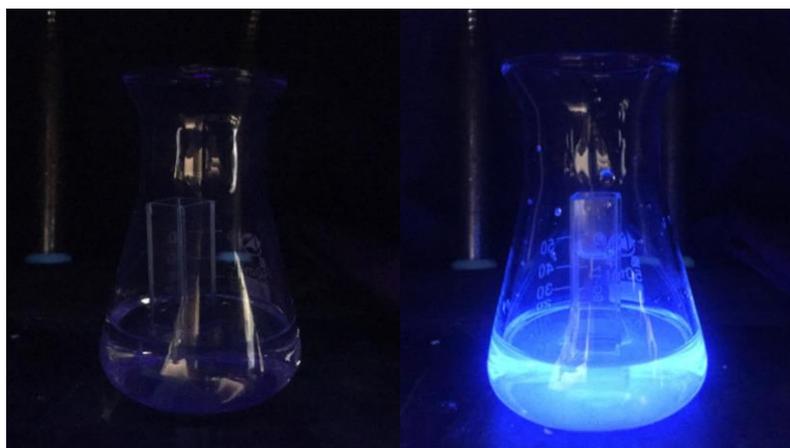


**Figure S11.** Fluorescence response of **ZIF-90-LW** suspension after exposure to FA gas under 365 nm UV lamp.
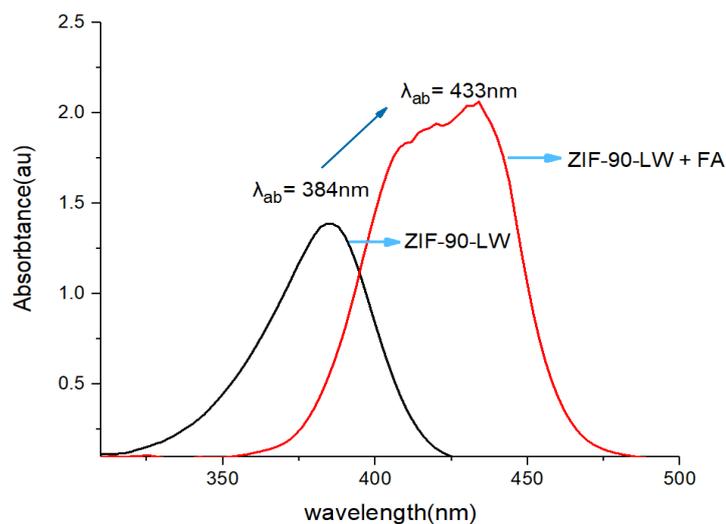
**Fig. S12.** UV-vis spectra of **ZIF-90-LW** in the absence and presence of FA. **ZIF-90-LW** is 25 mM

(0.4mg/mL), FA is 25 mM, in a mixture of DMF and Tris buffer solution (7 : 3, v/v), pH = 7.0. $\lambda_{ex}$ = 380 nm, $\lambda_{em}$ =
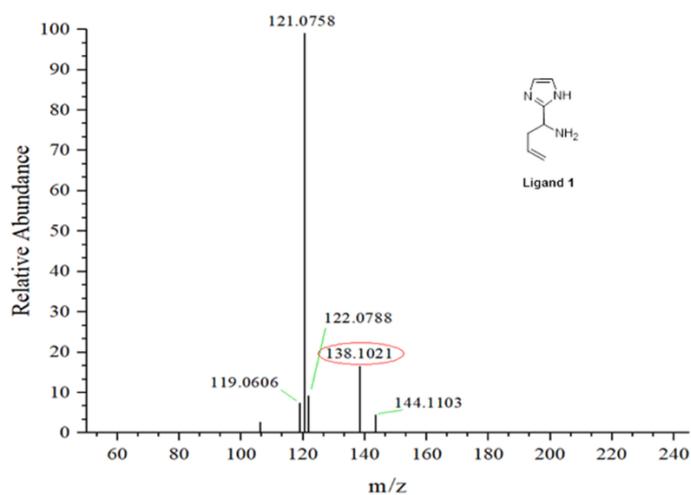
438 nm.



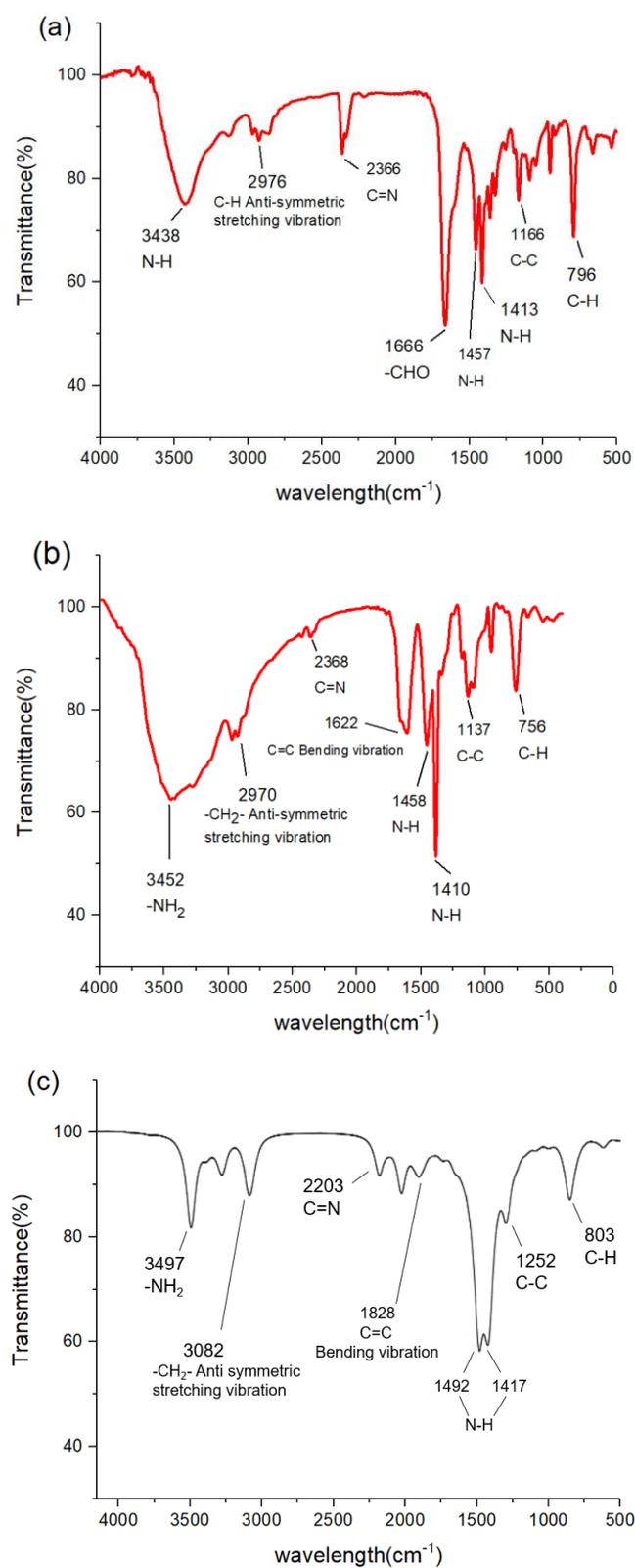**Figure S13.** Mass spectrum of **Ligand 1** obtained after disintegration of **ZIF-90-LW**.

**Figure S14.** (a)FT-IR of ZIF-90. (b) FT-IR of **ZIF-90-LW**. (c) FT-IR of **Ligand 1**.