

Electronic Supplementary Information for

**Ammonia-Modulated Reversible Gel-Solution Phase
Transition and Fluorescence Switch for a Salicylhydrazide-
Based Metal-Organic Gel**

**Shu-Mei Lu,^a Jian-Cai Huang,^a Guo-Ting Liu,^a Zhi-Wei Lin,^b Yan-Tong Li,^a Xi-He
Huang,^a Chang-Cang Huang,^a Shu-Ting Wu^{*a,c}**

a. Institute of Optical Crystalline Materials, College of Chemistry, Fuzhou University, Fuzhou, 350116, PR China. E-mail: shutingwu@fzu.edu.cn

b. College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China.

c. State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China.

Part I. Experimental section

1.1 Synthesis of the ligand H₆L

1.2 Preparation of Gel2/1

1.3 Dye adsorption tests

1.4 Cycling experiments of the fluorescence sensing for NH₃

1.5 Measurement details

Part II. Spectral data of the H₆L and Gel2/1

2.1 ¹H NMR, mass spectra and thermal analysis of H₆L (Fig. S1-3)

2.2 IR spectrum of Gel2/1 (Fig. S4)

2.3 Dynamic rheology of Gel2/1 (Fig. S5)

2.4 UV-Vis adsorption spectra of Gel2/1 dealt with ammonia vapor (Fig. S6)

2.5 HRMS-ESI spectra (Fig. S7-S9)

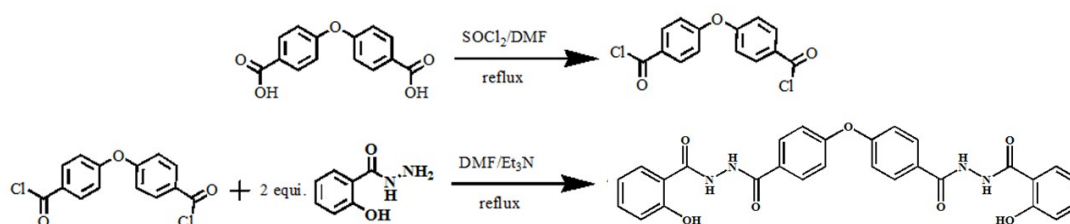
1. EXPERIMENTAL SECTION

1.1 Synthesis of **H₆L**

4,4'-oxydibenzoyl chloride: 4,4'-oxybisbenzoic acid (2.58 g, 10 mmol) was refluxed with SOCl₂ (20 mL) and DMF (N,N-dimethylformamide, 40 μ L) for 9 hours. After reaction, excess solvent and reactants were removed with rotary evaporation, leaving light yellow solid of 4,4'-oxydibenzoyl chloride.

4,4'-oxybis(N'-(2-hydroxybenzoyl)benzohydrazide) (H₆L**):** 10 mL DMF solution of 4,4'-oxydibenzoyl chloride (2.95 g, 10 mmol) and 10 mL DMF solution of Et₃N (triethylamine, 1.4 mL) and salicylhydrazide (3.65 g, 24 mmol) were mixed with ice-bath. The mixture was warmed to room temperature and refluxed for 9 h. The solvent was removed with reduced pressure distillation to get the crude product as a brown solid. After washed with ethanol for several times, white product was obtained with ~80% yield. The product was characterized by ¹H-NMR and mass spectrum. ¹H NMR (400 MHz, DMSO-d₆, ppm, Fig. S1): δ H 11.95 (s, 2 H, OH), 10.71 (s, 4 H, NH), 8.01 (d, J = 35.4 Hz, 4 H, Ar-H), 7.94 (d, J = 35.4 Hz, 2 H, Ar-H), 7.48 (t, J = 7.2 Hz, 2 H, Ar-H), 7.25 (d, J = 8.7 Hz, 4 H, Ar-H), 6.99 (q, 4 H, Ar-H). ESI-MS (Fig. S2): 525.1426(Exp.), 526.1488(Calc. for H₅L⁻). Elemental analysis: N: 10.24% (Cald. 10.64%), C: 62.74% (Cald. 63.87%), H: 4.23% (Cald. 4.21%).

Scheme S1. The synthesis of **H₆L**.



1.2 Preparation of Gel2/1

Fresh gel for Gel2/1: Typical preparation is to mix two 0.5 mL DMF solution that contains Zn(CH₃COO)₂·9H₂O (0.0250 mmol, 0.0055g) and **H₆L** (0.0125 mmol, 0.0066g) separately together. Ultrasonic oscillate the mixture to make a uniform solution. The solution is allowed to stand for two days to obtain fresh gel of **Gel2/1**.

Xerogel for Gel2/1: The xerogel was prepared by leaving the fresh **Gel2/1** in the air to

dry naturally for 1 week.

1.3 Dye adsorption tests

Four kinds of dye molecules were chosen to study the adsorption capacity of the xerogel for **Gel2/1**: methyl violet, methylene blue, phenyl red and methylene orange. The dyes were dissolved in water to make the aqueous dye solution in $1.67 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. 2.5 mg xerogel was added into 1 mL dye solution, mixing for 1 hour by ultrasonic oscillation to run the adsorption test. The resultant was centrifuged to obtain upper clear liquid which is recorded by UV-Vis absorption spectra to evaluate the adsorption capacity.

1.4 Cycling experiments of the fluorescence sensing for NH_3

The fluorescence sensing for NH_3 along with phase transformation experiment detail is as follows. An open glass bottle that contains 1 mL fresh gel of **Gel2/1** (labeled as **Gel⁰**) was placed in a sealed vessel that contains ammonia aqueous for a few minutes. The ammonia vapor was allowed to diffuse into the glass bottle to react with the fresh gel inside. The transformation from gel to solution would be observed during the diffusion. The resultant was light yellow solution (labeled as **Solution^{C1}**). If the above procedure was conducted in dark room under UV light, the fluorescent gel could be observed to transform to dark solution along with the ammonia diffusion. After the phase transformation was completed, the light yellow solution was allowed to stand open for two days to evaporate the ammonia gas. Transparent gel phase would be obtained (labeled as **Gel^{C1}**). Cycling experiments for this phase transformation was conducted repeatedly for 7 times. The corresponding samples of **Gel⁰**, **Solution^{C1-C7}**, **Gel^{C1-C7}** were tested by fluorescence spectrometer to assess their fluorescence sensing behavior.

1.5 Measurement details.

Rheological measurements were performed on a stress controlled rheometer (AR2000ex, TA instruments) with a cone-plate sensor. The cone is made of standard ETC steel with a diameter of 20 mm and a cone angle of 2 degree. The gap between the center of the cone and the plate is 50 mm. Each sample was kept for 5 min on the plate to reach equilibrium before testing. The ^1H NMR spectrum was recorded on BRUKER AVANCE III 400 MHz spectrometer. High Resolution Mass spectrum was carried out by using Thermo Fisher Scientific 1100 LC/MSD Trap XCT spectrometer. MALDI-MS (Matrix Assisted Laser

Desorption Ionization mass) spectrum was taken on MicroFlex MALDI-TOF-MS spectrometer with Micro SCOUT Plate (MSP) for 96 sample points, a cassette N₂ laser, laser wavelength at 337 nm and frequency at 60 Hz, and the matrix molecule is 2,5-dihydroxy benzoic acid (DHB). IR, UV-Vis absorption and fluorescence spectroscopy were recorded by FT-IR spectrum 2000 (4000–400 cm⁻¹), Perkin-Elmer Lambda 900 and Edinburgh FL-FS 920 TCSPC spectrometer, respectively. The photos of photoluminescence were taken under a WD-9403E hand-held ultraviolet lamp. The FESEM and TEM images were obtained on Nova NanoSEM 230 Microscopy and TECNAI G2F20 Field Emission Transmission Electron Microscopy, respectively. KQ-100E ultrasonic cleaner was used for ultrasonic oscillation. The elemental analysis was performed on Vario EL Cube. The thermal analysis was recorded on STA 448C TGA/DSC 3+ HT/1600 (25-1000 °C, Ar, 10 °C/min).

2. Spectral data of the H₆L and Gel2/1

2.1 ¹H NMR and mass spectra of H₆L

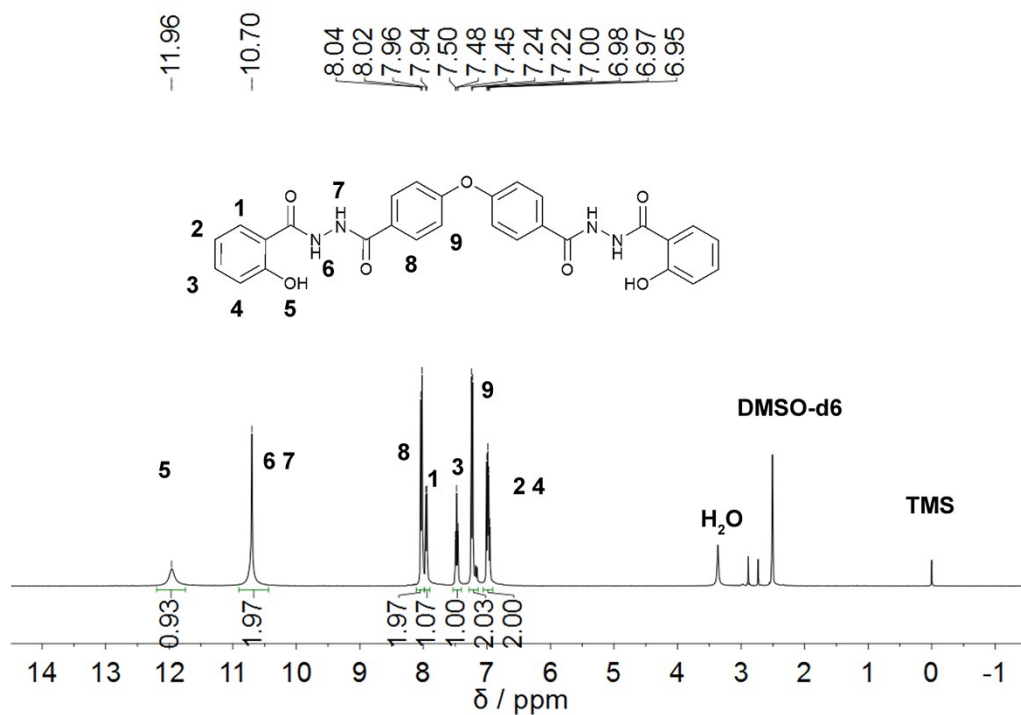


Fig. S1 the ¹H NMR of H₆L (DMSO-d₆).

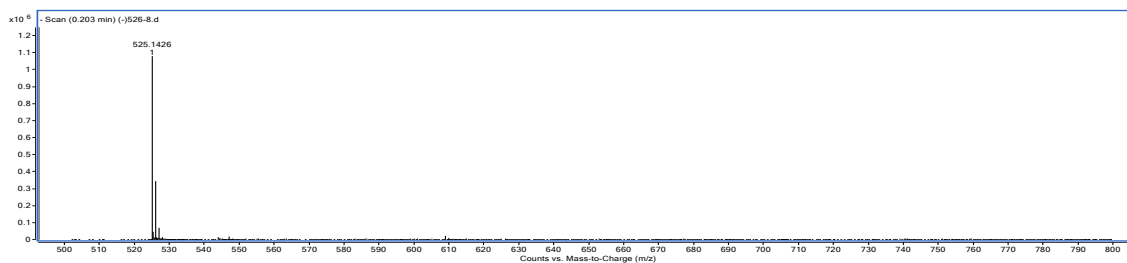


Fig. S2 Mass spectrum for the solution of H₆L in negative ion mode, with the range of 490.00-800.00. The m/z signals 525.1426, could be attributed to H₅L⁻ (Calc. 526.1488).

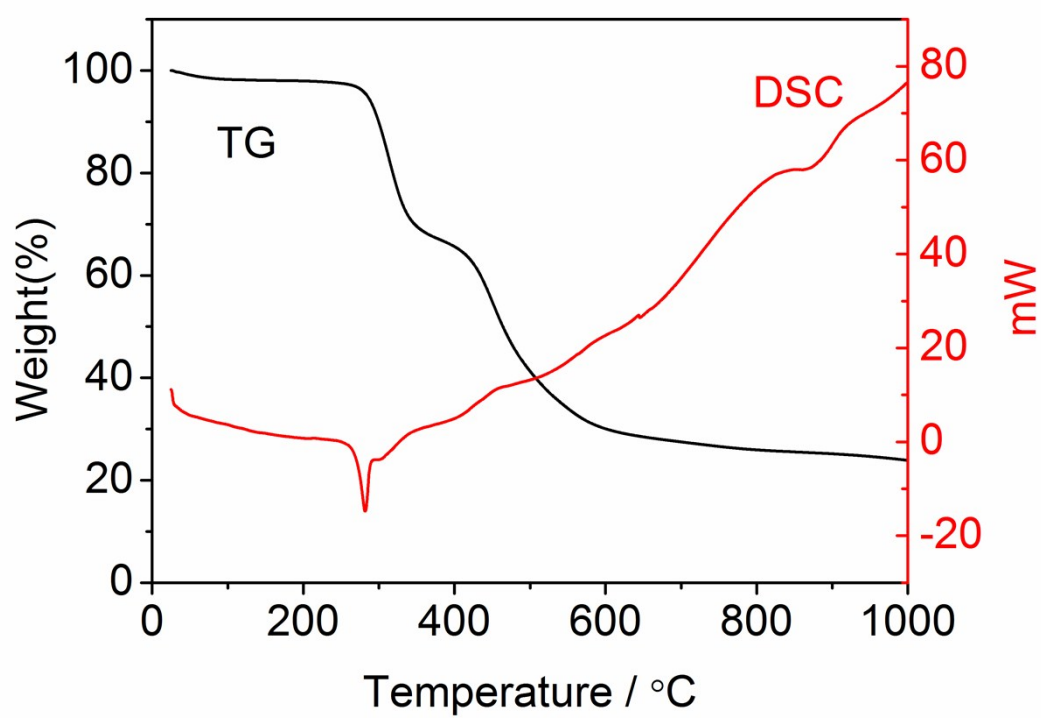


Fig. S3 Thermal analysis of H₆L.

2.2 IR spectrum of Gel2/1

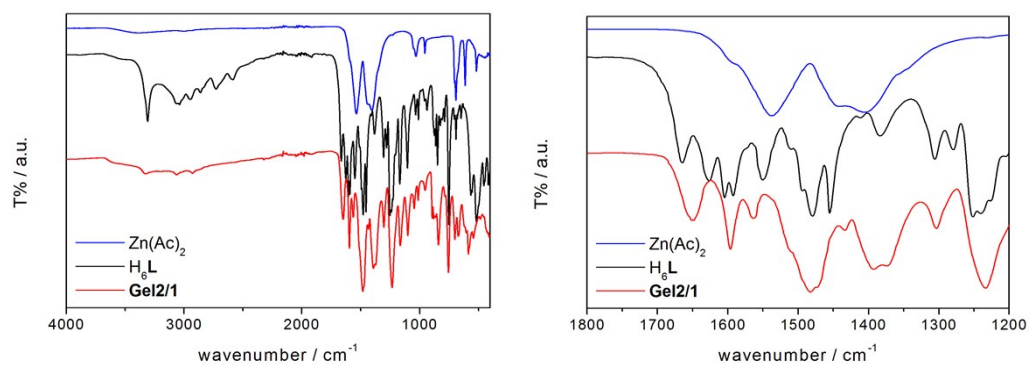


Fig.S4 IR spectra of zinc acetate, H₆L and the xerogel of **Gel2/1**, left:4000-400 cm⁻¹, right: 1800-1200 cm⁻¹.

2.3 Dynamic rheology of Gel2/1

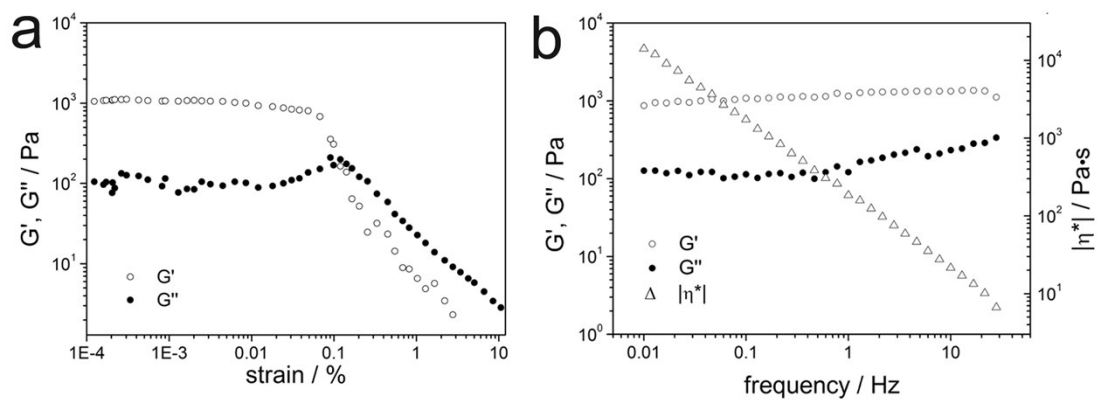


Fig. S5 a) Strain sweep at a frequency of 1 rad·s⁻¹ of **Gel2/1**. b) Frequency sweep of G' and G'' for **Gel2/1** at a strain of 0.01%.

2.4 UV-Vis adsorption spectra of Gel2/1 dealt with ammonia vapor

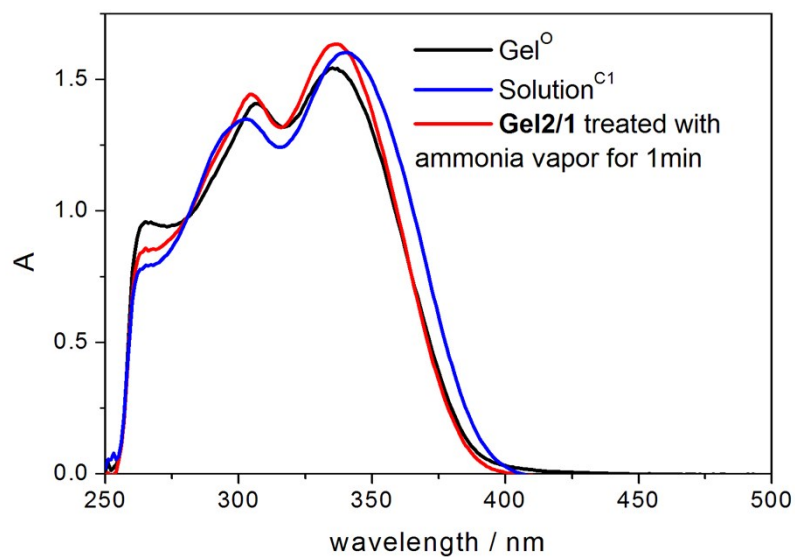


Fig. S6 The UV-Vis adsorption spectra for three different cases as follows: (1) Gel⁰: the original Gel2/1; (2) Solution^{C1}: the gel to solution phase transition after ammonia treatment for 5 min; (3) the intermediate soft colloidal sol phase for the Gel2/1 treated with ammonia vapor for 1min.

2.5 HRMS-ESI spectra

HJC-2_170413104133 #155-175 RT: 1.36-1.53 AV: 21 NL: 1.13E7
T: FTMS - p ESI Full ms [600.00-3000.00]
661.0070

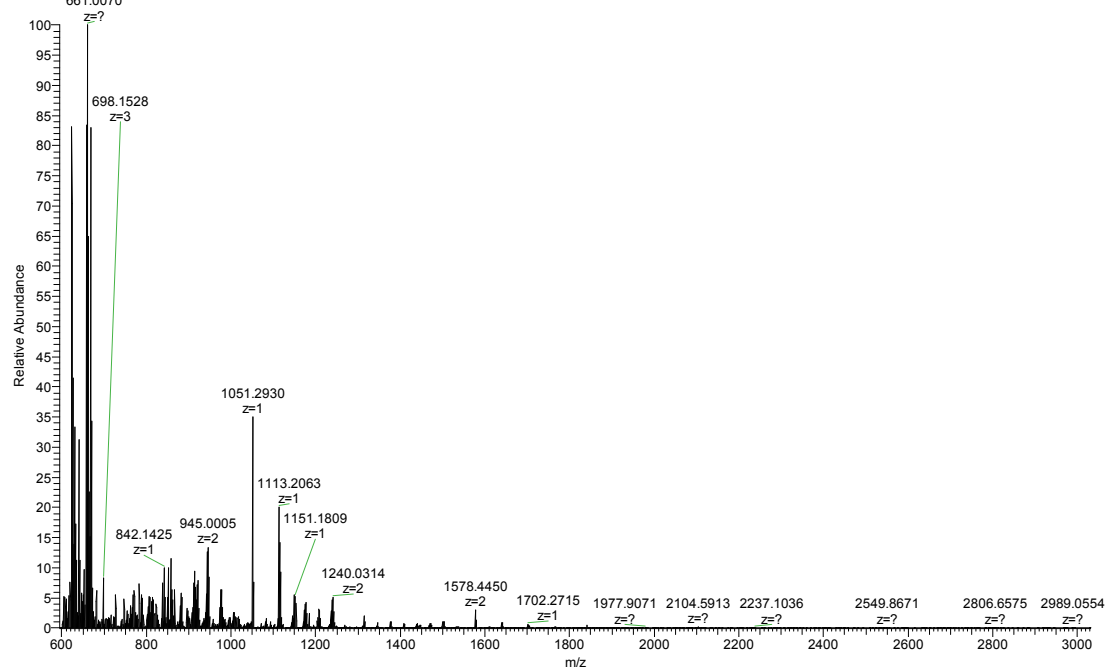


Fig. S7 The HRMS-ESI spectrum for the solution after complete ammonia treatment, negative mode, 600-3000.

H-2_170510144739 #38-47 RT: 0.33-0.41 AV: 10 NL: 5.76E6
T: FTMS + p ESI Full ms [700.00-3000.00]
738.5198

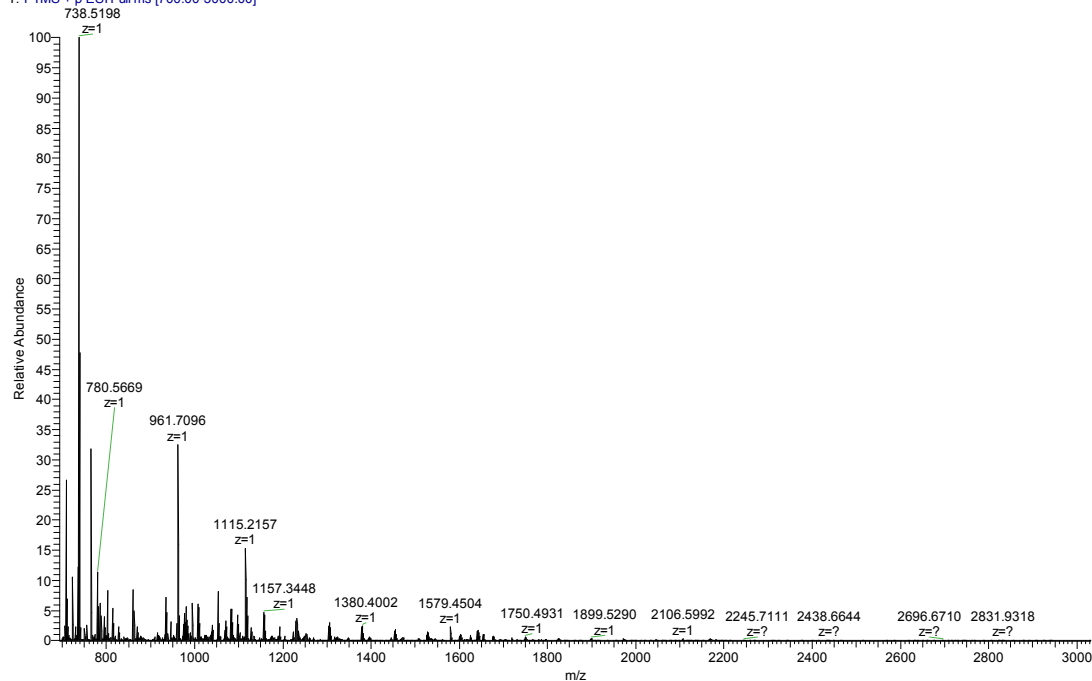


Fig. S8 The HRMS-ESI spectrum for the gel solution (5 min after mixing reactants) in acetonitrile, positive mode, 700-3000.

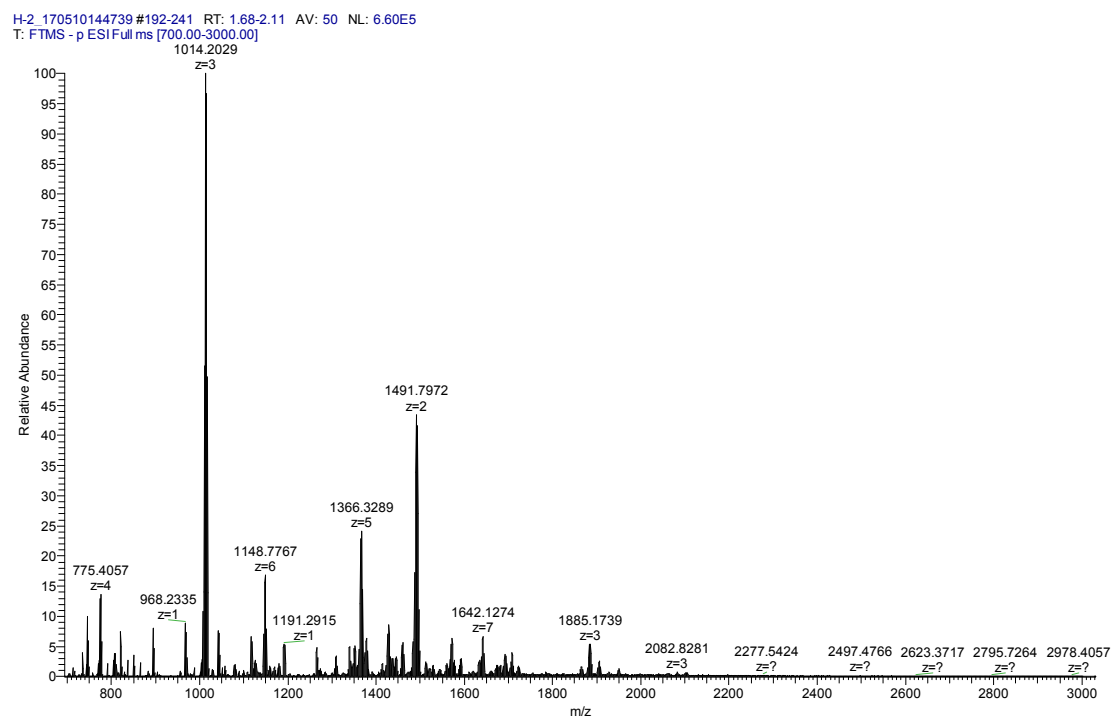


Fig. S9 The HRMS-ESI spectrum for the gel solution (5 min after mixing reactants) in acetonitrile, negative mode, 700-3000.