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Supporting Information

Coplanar Angle Change Inspired Liquid Polarity Sensing Based on Pyrene Boned Graphene Nanoribbon

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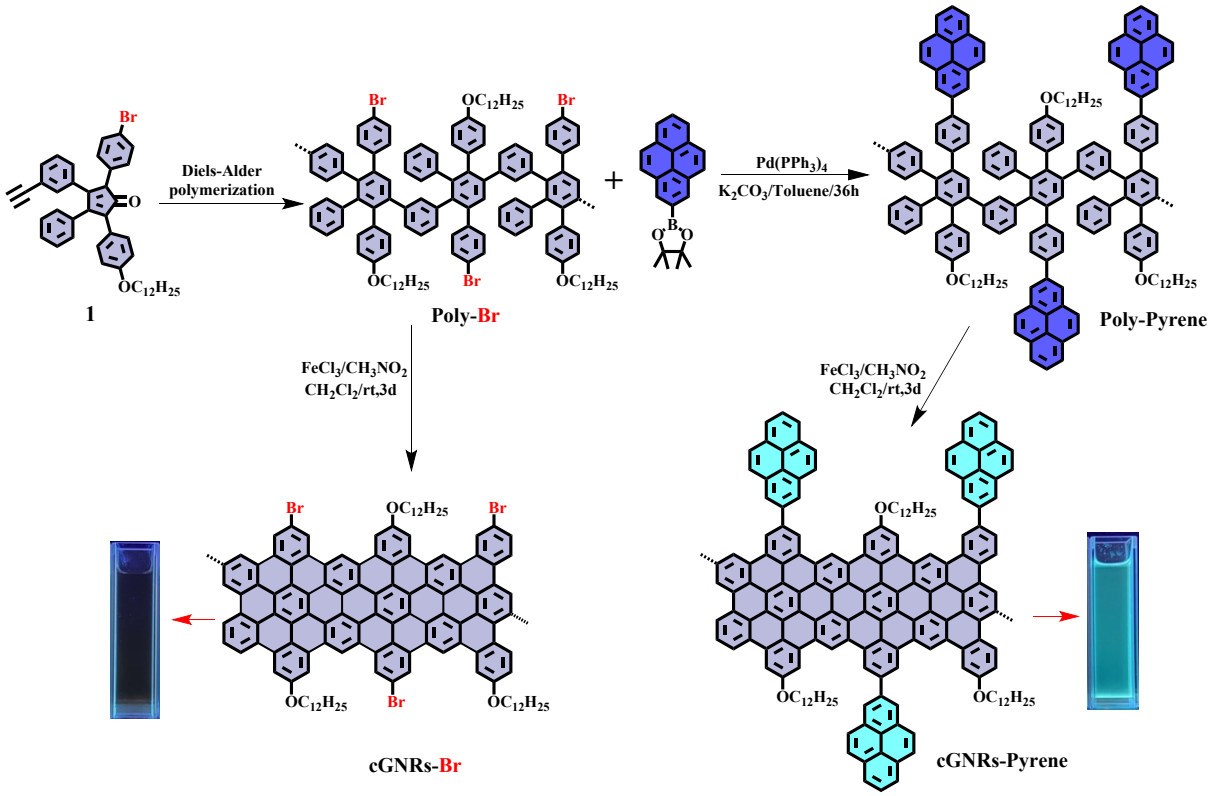
Supplementary Methods

Materials and methods

All reagents (including anhydrous reagents) and drugs (analytical purity) used for synthesis are purchased from Aladdin without further purification. 1-(3-ethynyl phenyl)-2-phenylethane-1,2-dione[1] were prepared following the reported procedures. H and ^{13}C NMR spectra were recorded on a Bruker AVANCE NEO 400 NMR spectrometer at room temperature using TMS as an internal standard. High resolution ransmission electron microscopy (HRTEM) was performed using an FEI Talos-F200S G2 transmission electron microscope (FEI, Netherland). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB250Xi spectrometer (ThermoFisher Scientific). UV-vis absorption spectra were recorded on a BioTek Microplate Reader (ELx800, USA). Fluorescence measurements were obtained by using an FLS1000 fluorescence spectrometer (Edinburgh). Fourier transforms infrared (FTIR) spectra were recorded on a Nicolet 380 FTIR spectrometer. Analytical size exclusion chromatography (SEC) was performed on LC20 High-Performance Liquid Chromatograph (Shimadzu, Japan) using THF as eluent at a temperature of 303 K. The samples were referenced with respect to standard polystyrene (PS) calibration curves. The high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) was performed on Bruker Daltonics flexAnalysis. The DFT calculations were performed using Gaussian16[2] at the B3LYP/6-31G(d)[3] level with the D3(BJ) empirical dispersion correction [4]. The fluorescence imaging of cells was performed with TSC-SP8 (Leica, Wetzler, Germany) confocal laser scanning microscope.



Scheme 1. Synthetic route of **cGNRs-Pyrene** and **cGNRs-Br**

We prepared cGNRs-Pyrene according to our previous research report[17], and the preparation process is shown in **Scheme 1**. Firstly, we prepared precursor **1** with bromine atoms and alkyl carbon chains at the edges and then converted precursor **1** into **Poly-Br** with one bromine and one dodecyl chain per repeat unit based on the Diels-Alder polymerization reaction. Due to the existence of edge alkyl carbon chains, the dispersibility of the polymer graphitized into graphene nanoribbons in the solution can be effectively improved. At the same time, the bromine atoms on the edge of the **Poly-Br** enable the polymer to continue to modify other compounds in situ. After that, 4,4,5,5-Tetramethyl-2-(2-pyrenyl)-1,3,2-dioxaborolane(2-Pyrenyl)boronic acid pinacol ester was displaced for the bromine position on the edge of **Poly-Br** by Suzuki coupling reaction to obtain **Poly-Pyerene** functionalized with pyrene group. Finally, referring to the literature scheme, the oxidative cyclization dehydrogenation was started

with anhydrous $FeCl_3$ in anhydrous dichloromethane and anhydrous nitromethane, and **Poly-Pyrene** was graphitized into **cGNRs-Pyrene** [13, 18].

Synthesis of Poly-Br

Compound **9** (800 mg, 1.19 mmol) was added into a 50 ml round bottom flask and heated with a heating hood under nitrogen at 260-270 ℃ for 3 hours. The purple disappeared and turned to light yellow, indicating that the polymerization was completed. After the reaction was completed and cooled to room temperature, the obtained polymer was dissolved in tetrahydrofuran by ultrasound, filtered, the filtrate was collected, the solvent was removed under reduced pressure, the polymer solid was collected. The polymer was treated with methanol/tetrahydrofuran (5:1) extracted by Soxhlet extractor to obtain gray solid (400 mg, yield: 51%; PS standard was used for GPC analysis and characterization. M_w=367.267 kg/mol, PDI = 1.09, percentage was 16.27%, M_w = 54.337 kg/mol, PDI = 2.45, percentage was 70.83%, M_w = 3.189 kg/mol, percentage was 9.71%, PDI = 1.09, M_w = 0.774 kg/mol, PDI = 1.13, percentage was 3.19%).

Synthesis of Poly-Pyrene

To a solution of **Poly-Br** (100 mg) and 2-(Pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5 equivalents per one bromo group of Poly-Br) in toluene (15 mL) was added an aqueous solution of K_2CO_3 (1 M, 7.5 mL) and EtOH (2 mL). The reaction mixture was degassed and then the catalyst, tetrakis(triphenylphosphine)palladium(37 mg, 10 mol% to one bromo group of **Poly-Br**) was added under the nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 48 hours under a nitrogen atmosphere. After cooling down to room temperature methanol was added. The precipitates were collected by filtration with a membrane filter (PTFE, 200-nm pores) to obtain a crude product. The crude material was

dispersed in 20 ml of ethanol and sonicated, and the solid was collected by centrifugation, repeated 5 times, and the brown solid was collected to obtain 210 mg of **Poly-Pyrene** (**PP**).

Synthesis of cGNRs-Pyrene (or cGNRs-Br)

A solution of Poly-Pyrene (368mg, or 300mg Poly-Br) in unstabilized dichloromethane (350 mL) was degassed by nitrogen bubbling for 15 min. To the degassed solution was added a suspension of $FeCl_3$ (7.0 eq. for one hydrogen to be removed) in nitromethane (15 mL). After stirring at room temperature for 48 h under continuous bubbling with nitrogen pre-saturated by dichloromethane, the reaction was quenched by the addition of methanol to form black precipitates. The precipitate was collected by centrifugation and washed with methanol. The crude product was Soxhlet extracted with methanol/tetrahydrofuran (3/1) solution to obtain black solid (320mg, yield 87% for **cGNRs-Pyrene**; 270mg, yield 90% for **cGNRs-Br**).

Cell culture

Cultured HepG2 cells in DMEM (Dulbecco's modified Eagle's medium), supplemented with 10% FBS, 1% streptomycin sulfate, 1% penicillin in a humidified 5% CO_2/ 95% air incubator at 37 ℃. Replace the growth medium every two days. When the cells had grown to 80%, they were digested with trypsin and then subcultured before experiments.

Cytotoxicity test

The cytotoxicity of the **cGNRs-Pyrene** sensor to HepG2 cells was studied by standard MTT assays. About 1.5×10^4 cells/mL HepG2 cells were incubated with various concentrations of **cGNRs-Pyrene** sensor (0-40 μM) in 96-well plates for 24 h. Subsequent remove the culture medium, wash each well three times with PBS, add 10% CCK8 culture medium at 100 μL/well, and culture in a 37°C incubator with 5% CO_2 for 2 h. Detect the absorbance at 450 nm with an enzyme-labeled instrument.

$$\text{Cell viability} = \frac{OD_{sample} - OD_{blank}}{OD_{control} - OD_{blank}} \times 100\%$$

OD_{sample} denotes cells treated with various concentrations of **cGNRs-Pyrene** sensor; OD_{blank} denotes the plates with DMEM; $OD_{control}$ denotes cells without being treated with **cGNRs-Pyrene** sensor.

Cell fluorescence imaging

With moderate amounts of cells were cultured in DMEM（Dulbecco's modified Eagle's medium）supplemented with 10% FBS (fetal calf serum) in the air with 5% CO_2 at 37 ℃. Then the cultured cells were seeded into glass culture dishes and cultured to a density of 4×10^5 cells/mL before fluorescence imaging. Afterward, cell experiments were performed as follows:

Cell imaging

HepG2 cells were cultured had been associated with the above methods. After that HepG2 cells were first incubated with **cGNRs-Pyrene** sensor (10 μM) for 1 h, then were stimulated with different concentrations (0 μM, 20 μM, 50 μM, 100 μM, 200 μM and 400 μM) of oleic acid for 60 min; **cGNRs-Pyrene** sensor was excited at 405 nm, and emission range at 510 nm.

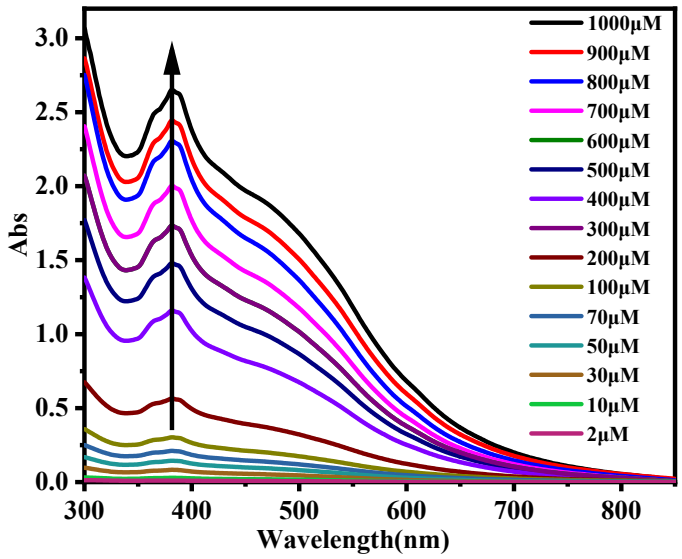


Fig. S1 UV-Vis absorption curve of **cGRNs-Pyrene** in NMP solvent

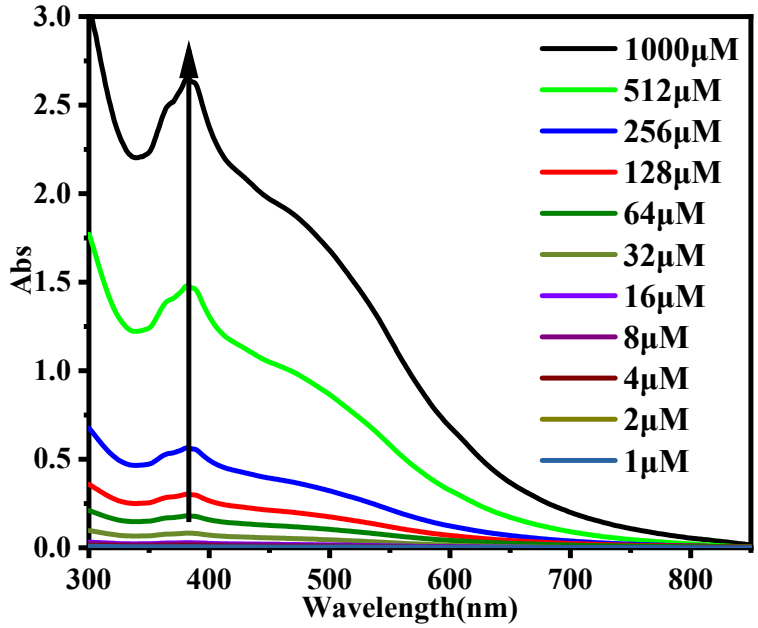


Fig. S2 UV-Vis absorption curve of **cGNRs-Pyrene** in TCB solvent

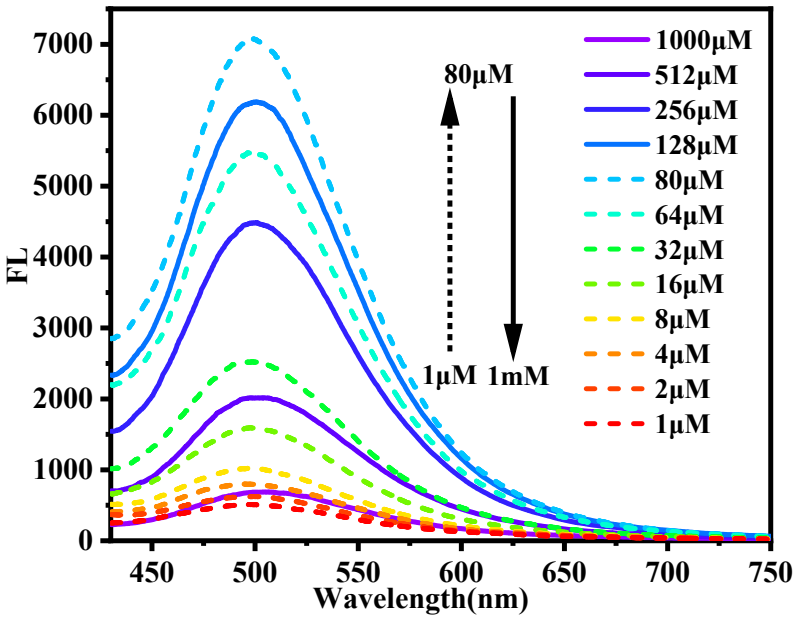


Fig. S3 Fluorescence spectra of **cGNRs-Pyrene** in TCB solvent at different concentrations.

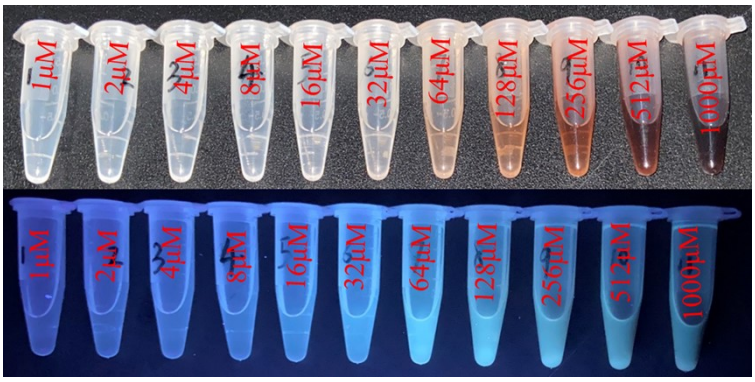


Fig. S4 Optical images of **cGNRs-Pyrene** under different concentrations of sunlight and 365 nm UV lamp in TCB solvent.

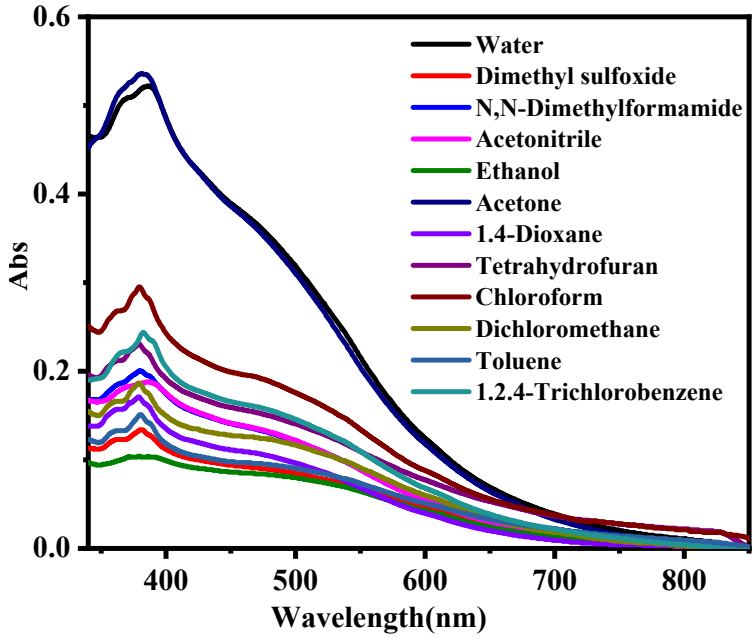


Fig. S5 UV-Vis absorption curve of **cGNRs-Pyrene** in different solvents

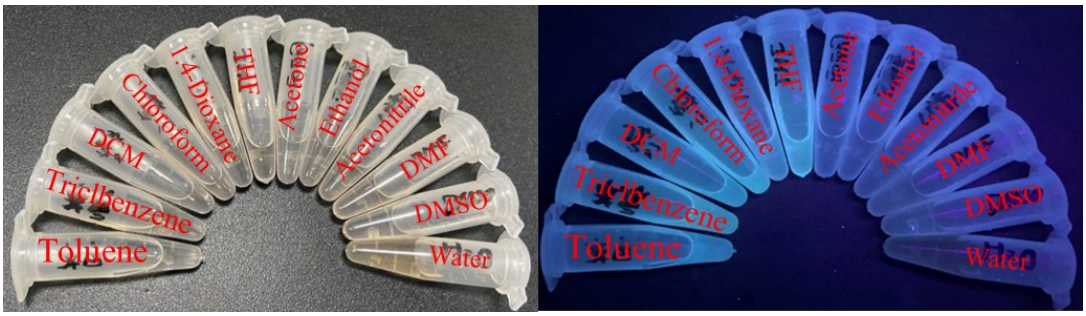


Fig.S6 Optical images of **cGNRs-Pyrene** under sunlight and 365 nm UV lamp in different solvents

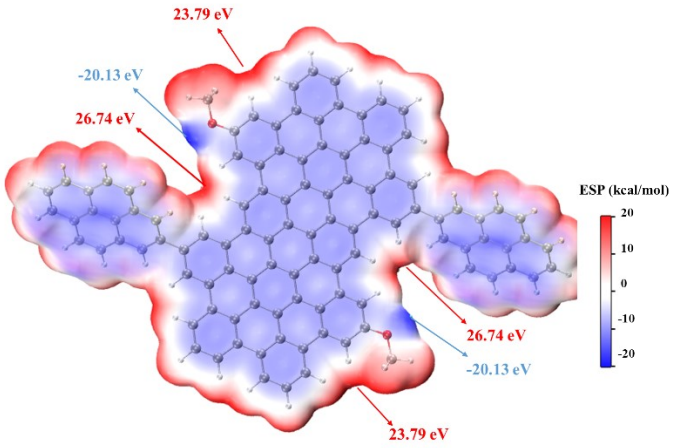


Fig. S7 Molecular electrostatic potential surface of dimer of **cGNRs-Pyrene**

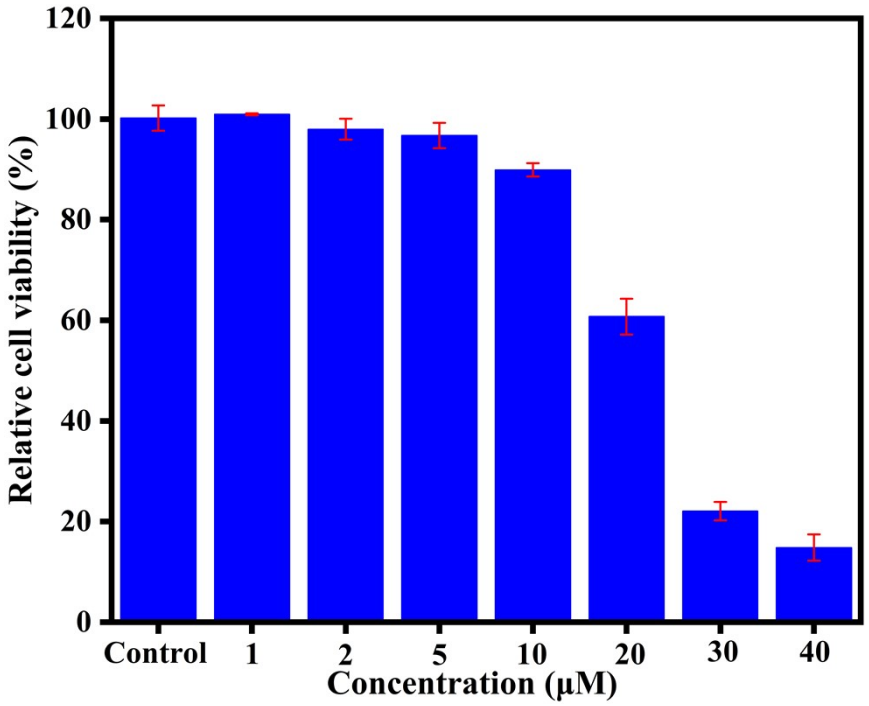


Fig. S8 Percentage of viable HepG2 cells treated with various concentrations of **cGNRs-Pyrene** after 24 hours.

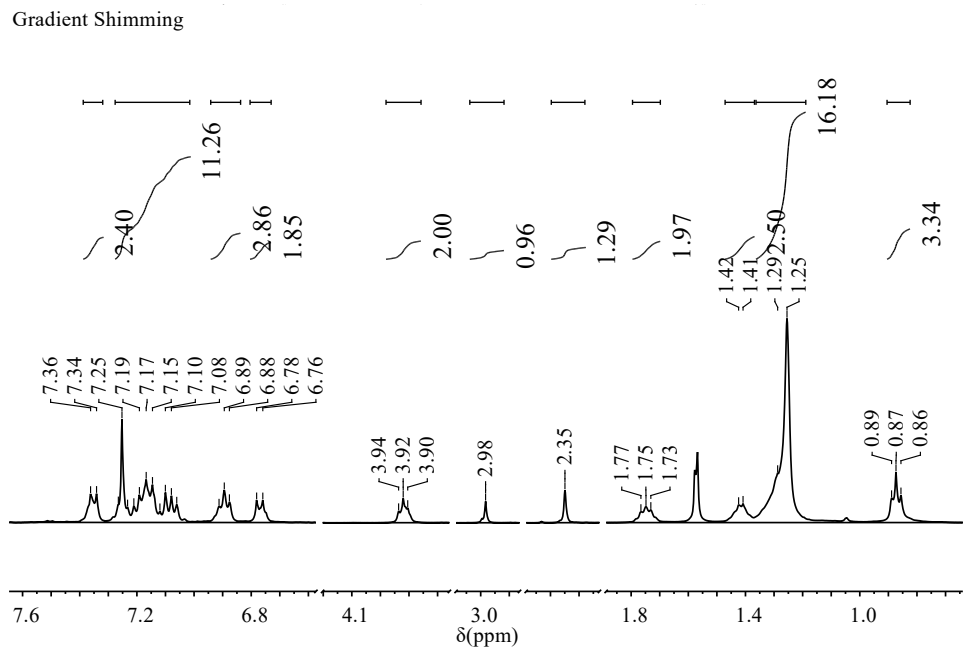


Fig. S9 ^{1}H NMR spectrum of compound **1** (400 MHz, $CDCl_3$).

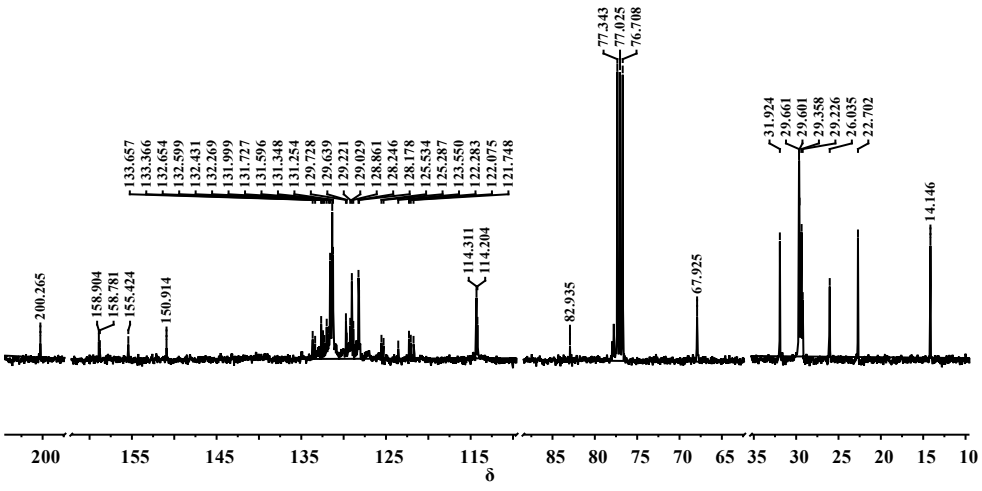


Fig. S10 ^{13}C NMR spectrum of compound **1** (400 MHz, $CDCl_3$).

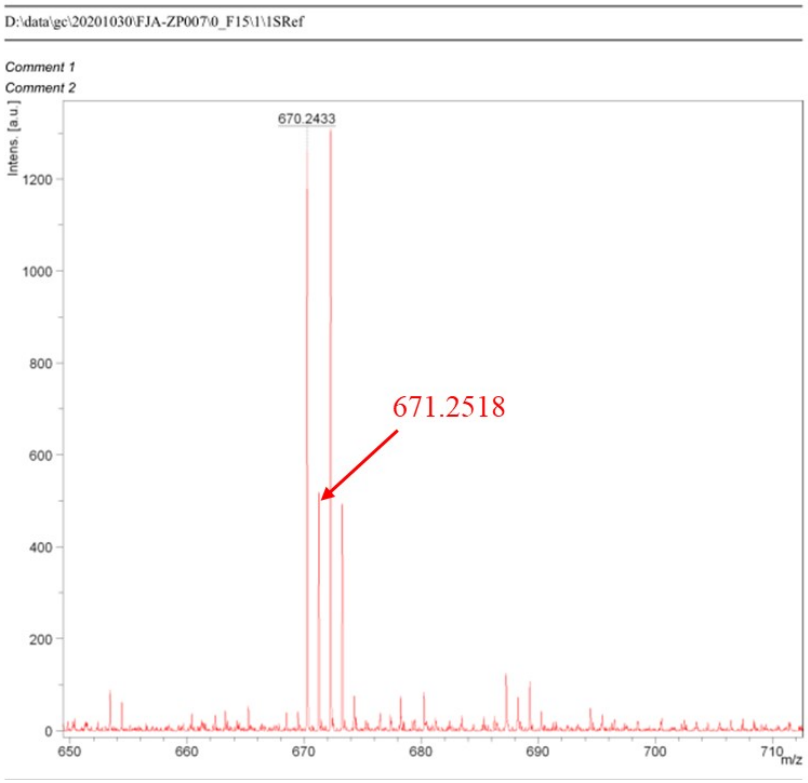


Fig. S11 HR-ESI-MS of compound **1**

Supplementary References

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