Electronic Supplementary Information

Preparing highly-dispersed noble metal supported mesoporous silica catalysts by reductive amphiphilic molecules

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Contents

Measurement of the critical micellar concentration (CMC) of the amphiphile $FcC_{11}PyBr$

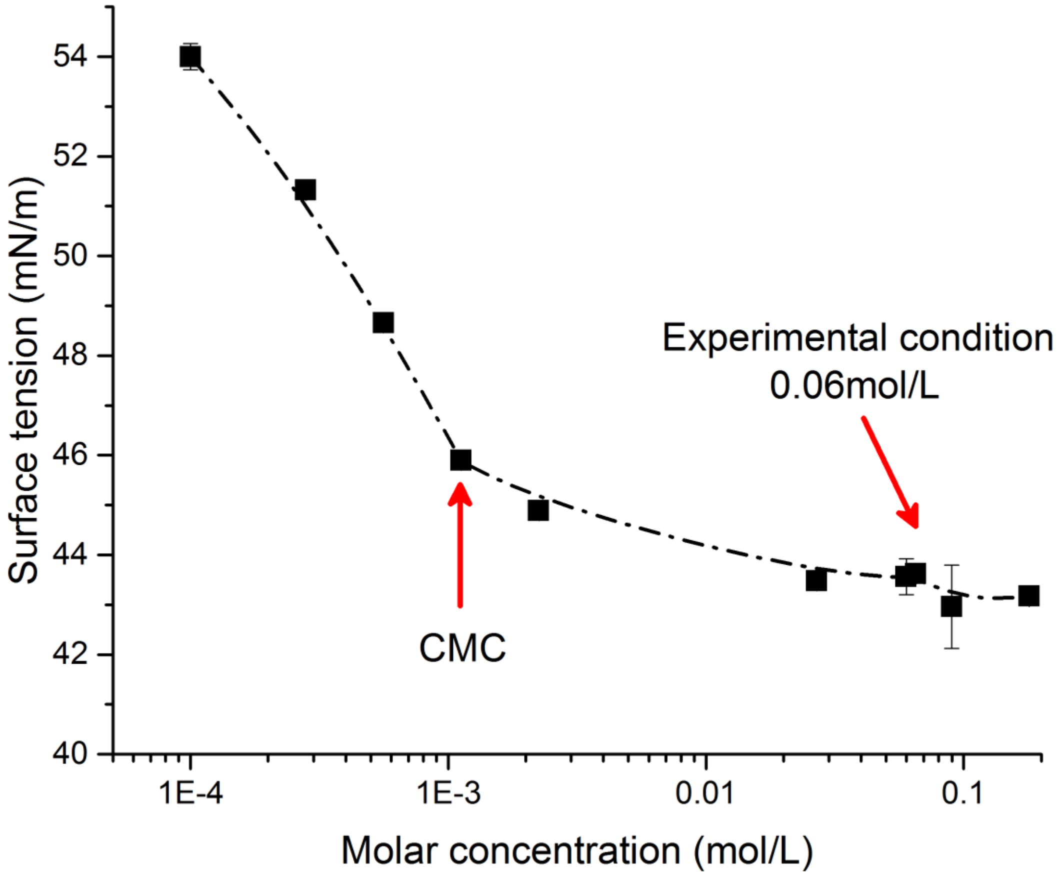

Fig. S1 The plot of the surface tension of the water-ammonia solution of the amphiphile versus the molar concentration of $FcC_{11}PyBr$.

From the measurement we can infer that the CMC of $FcC_{11}PyBr$ is 0.001mol/L, while the experimental concentration is 0.06mol/L, indicating that the amphiphile did form micellar during the assembly process.

Analysis of the redox reaction between $[PdCl_4]^{2-}$ and $FcC_{11}PyBr$

According to the literature[1],

$$PdCl_4^{-} + 2e^{-} = Pd + 4Cl^{-} \qquad E_1^{\ominus} = 0.591V \ ,$$

From the cyclic voltammograms,

$$FcC_{11}Py^{2+} + e^{-} = FcC_{11}Py^{+} \qquad E_2^{\ominus} = 0.687V \ ,$$

At standard state, for a cell using the following reaction

$$PdCl_4^{-} + 2FcC_{11}Py^{+} = Pd + 2FcC_{11}Py^{2+} + 4Cl^{-} \ ,$$

Its electromotive force $\mathscr{E}^{\ominus}$ is

$$\mathscr{E}^{\ominus} = E_1^{\ominus} - E_2^{\ominus} = 0.591V - 0.687V = -0.096V < 0 \ .$$

Thus, the reaction won’t happen at standard state.

However, according to the experiment, we obtained Pd@MS via the redox reaction between $PdCl_4^{2-}$ and $FcC_{11}PyBr$.

Despite system in the experiment is a non-aqueous solvent system (methanol/dichloromethane), the order of corresponding electrode potentials should be consistent with that in aqueous solution. Consequently, the estimation from the aqueous solution could still be a reference. Owing to the small difference of the two electrode potentials (|-0.096 V| < 0.1 V), the reaction is possible to be reversed. And according to the calculation given by Nernst Equation, it can be confirmed that the reaction is possible under the same experimental concentration in aqueous solution. The calculations are as follows.

1) First, we calculate the electrode potential of the redox couple $[PdCl_4]^{2-}/Pd$.

The mother solution of H_2PdCl_4 was prepared as follows: 1 mmol $PdCl_2$ was dissolved in 1 ml hydrochloric acid and then the solution was diluted with the mixture solvent (methanol/dichloromethane=3:1) to 10 ml. When preparing Pd@MS, 350 μl of mother solution was added into 5 ml solvents. Thus, in the final system,

$$c\left(\mathrm{PdCl_4^-}\right)=7\times10^{-3}\mathrm{mol/L}, c\left(\mathrm{Cl^-}\right)=0.084\mathrm{mol/L}$$

From the Nernst Equation, let the temperature $T = 298\mathrm{K}$, then we have

$$\begin{aligned} E_1 &= E_1^{\ominus} + \frac{RT}{zF}\ln\frac{c\left(\mathrm{PdCl_4^-}\right)/c^{\ominus}}{\left[c\left(\mathrm{Cl^-}\right)/c^{\ominus}\right]^4} \\ &= 0.591\mathrm{V} + \frac{0.0592}{2}\lg\frac{7\times10^{-3}}{0.084^4}\mathrm{V} \\ &= 0.655\mathrm{V} \end{aligned}$$

2) Next, we calculate the electrode potential of the redox couple $\mathrm{FcC_{11}Py^{2+}/FcC_{11}Py^{+}}$

According to the thermogravimetric analysis, the mass fraction of $\mathrm{FcC_{11}PyBr}$ in MS is $w_1 = 38\%$[2]. The reaction happened in the mesoporous channels, so let the mass of MS is m_1 g, the pore volume per grams of MS is V mL/g. Then, at the beginning of the reaction, the concentration of $\mathrm{FcC_{11}PyBr}$ is

$$c\left(\mathrm{FcC_{11}Py^+}\right) = \frac{\dfrac{m_1 \cdot w_1}{M\left(\mathrm{FcC_{11}PyBr}\right)}}{m_1 \cdot V}$$

Suppose after calcination, let the mass of MS be changed to m_2 g. According to the ICP data, the mass fraction of Pd in Pd@MS is $w_2 = 0.3231\%$. Thus, when we terminated the reaction, it can be inferred that the concentration of $\mathrm{FcC_{11}Py^{2+}}$ is

$$c\left(\mathrm{FcC_{11}Py^{2+}}\right) = \frac{\dfrac{m_2 \cdot w_2}{M\left(\mathrm{Pd}\right)} \cdot 2}{m_2 \cdot V}$$

From the Nernst Equation, let the temperature $T = 298\text{K}$, then we have

$$
\begin{aligned}
E_2 &= E_2^{\ominus} + \frac{RT}{zF}\ln\frac{c\left(\text{FcC}_{11}\text{Py}^{2+}\right)/c^{\ominus}}{c\left(\text{FcC}_{11}\text{Py}^{+}\right)/c^{\ominus}} \\
&= E_2^{\ominus} + \frac{RT}{zF}\ln\frac{\dfrac{\dfrac{m_1\cdot w_2}{M\left(\text{Pd}\right)}\cdot 2}{m_1\cdot V}}{\dfrac{\dfrac{m_2\cdot w_1}{M\left(\text{FcC}_{11}\text{PyBr}\right)}}{m_2\cdot V}-\dfrac{\dfrac{m_1\cdot w_2}{M\left(\text{Pd}\right)}\cdot 2}{m_1\cdot V}} \\
&= E_2^{\ominus} + \frac{RT}{zF}\ln\frac{2\cdot w_2\cdot M\left(\text{FcC}_{11}\text{PyBr}\right)}{w_1\cdot M\left(\text{Pd}\right)-2\cdot w_2\cdot M\left(\text{FcC}_{11}\text{PyBr}\right)} \\
&= 0.687\text{V} + 0.0592\lg\frac{2\times 0.3231\%\times 542.34}{38\%\times 106.42 - 2\times 0.3231\%\times 542.34}\text{V} \\
&= 0.626\text{V}
\end{aligned}
$$

3) To sum up, the electrode potentials under the experimental concentrations are

$$\text{PdCl}_4^{-} + 2\text{e}^{-} = \text{Pd} + 4\text{Cl}^{-} \qquad E_1 = 0.655\text{V}$$

$$\text{FcC}_{11}\text{Py}^{2+} + \text{e}^{-} = \text{FcC}_{11}\text{Py}^{+} \qquad E_2 = 0.626\text{V}$$

The electromotive force of such cell is

$$\mathscr{E} = E_1 - E_2 = 0.655\text{V} - 0.626\text{V} = 0.029\text{V} > 0$$

Consequently, when we terminated the reaction, the equilibrium hasn’t been established.

The characterization data for FcC$_{11}$Br

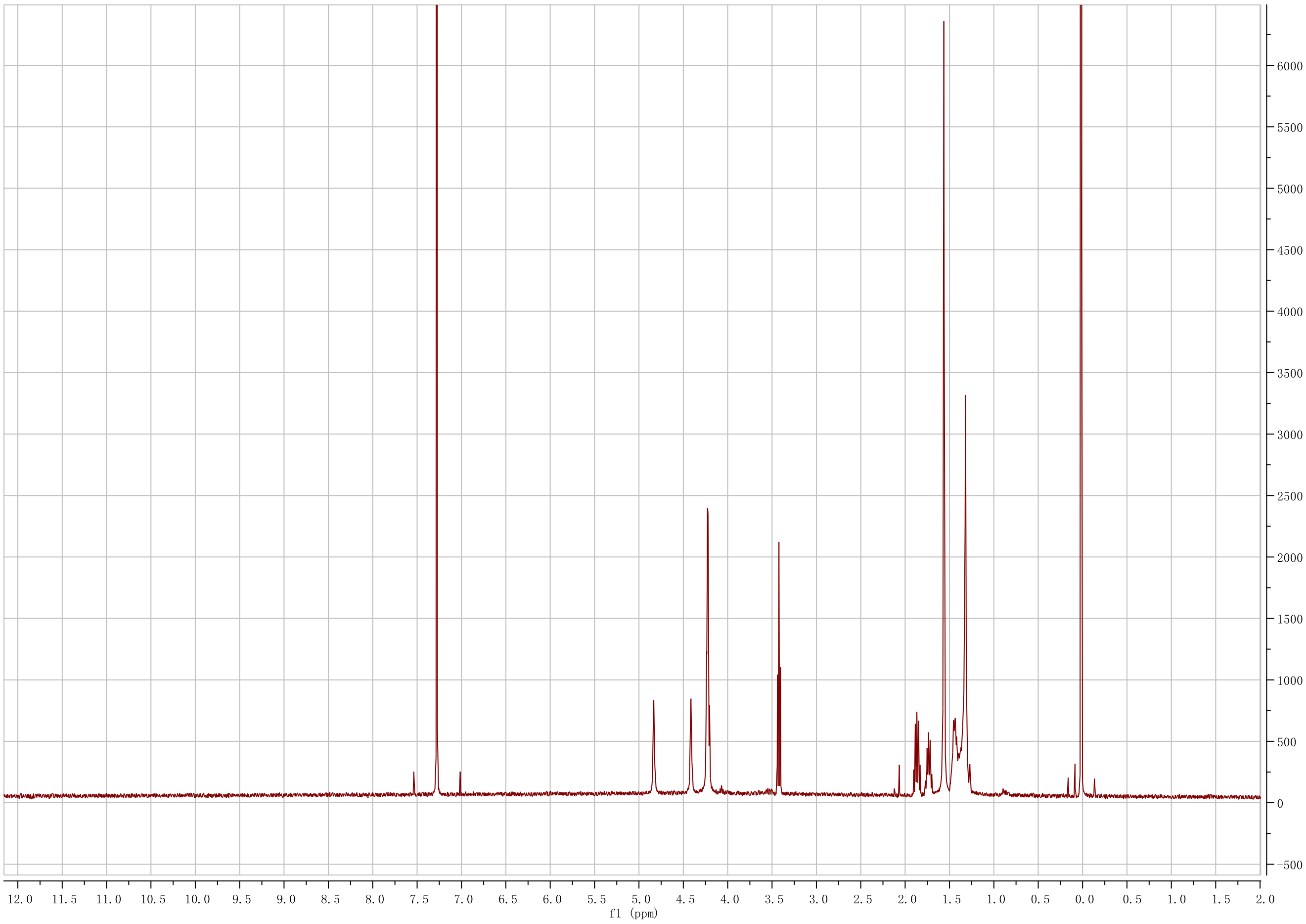

Fig. S2.1 ^{1}H NMR spectra of FcC$_{11}$Br.

^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm) = 4.82 (s, 2H), 4.40 (s, 2H), 4.16 (m, 7H), 3.41 (t, 2H), 1.92 – 1.79 (5, 2H), 1.77 – 1.64 (5, 2H), 1.49 – 1.22 (m, 14H).

In the spectra, δ = 7.26 ppm for $CDCl_3$, δ = 1.56 ppm for H_2O.

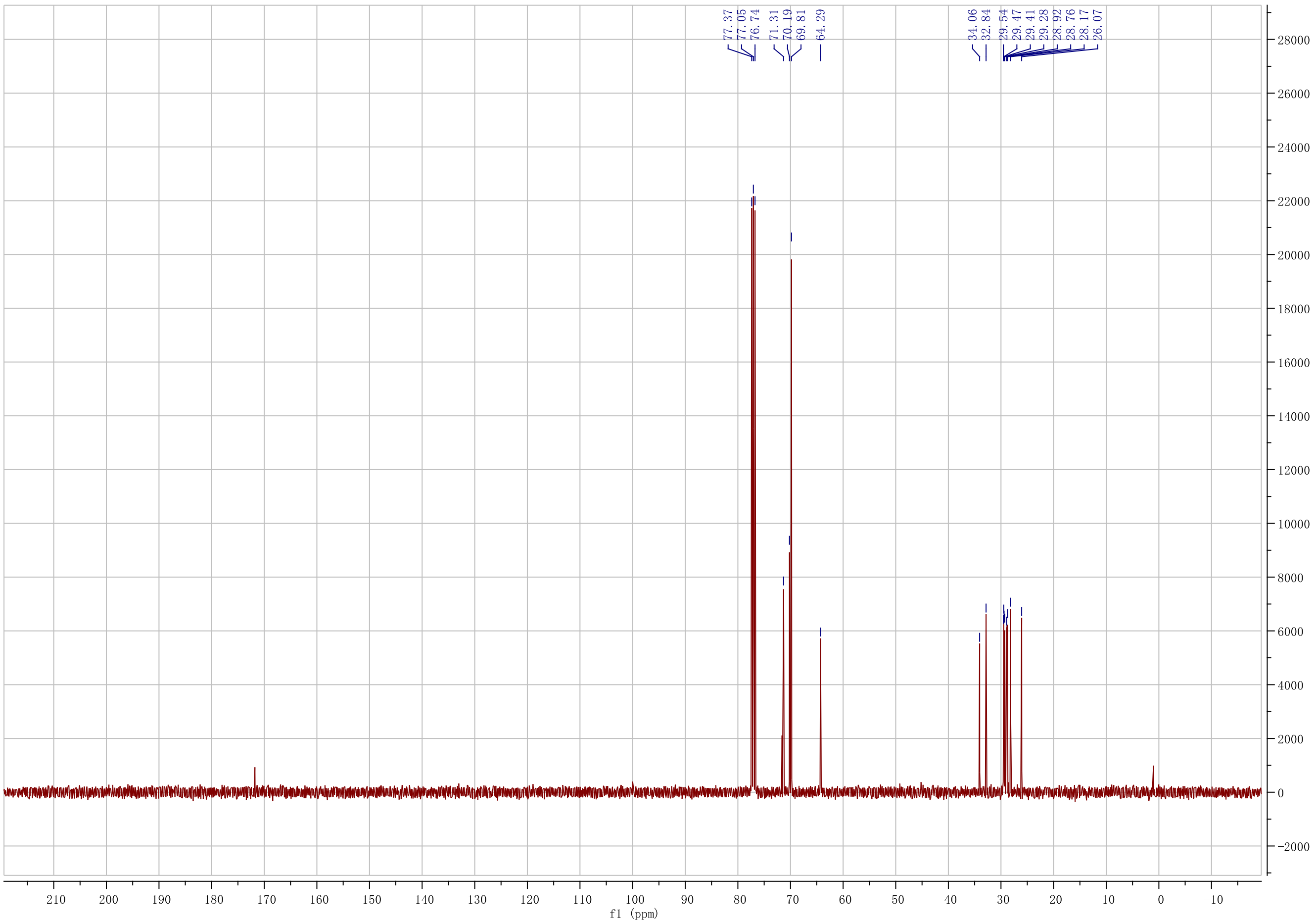

Fig. S2.2 ^{13}C NMR spectra of $FcC_{11}Br$.

^{13}C NMR (400 MHz, $CDCl_3$) δ(ppm) = 77.37, 77.05, 76.74, 71.31, 70.19, 69.81, 64.29, 34.06, 32.84, 29.54, 29.47, 29.41, 29.28, 28.92, 28.76, 28.17, 26.07.

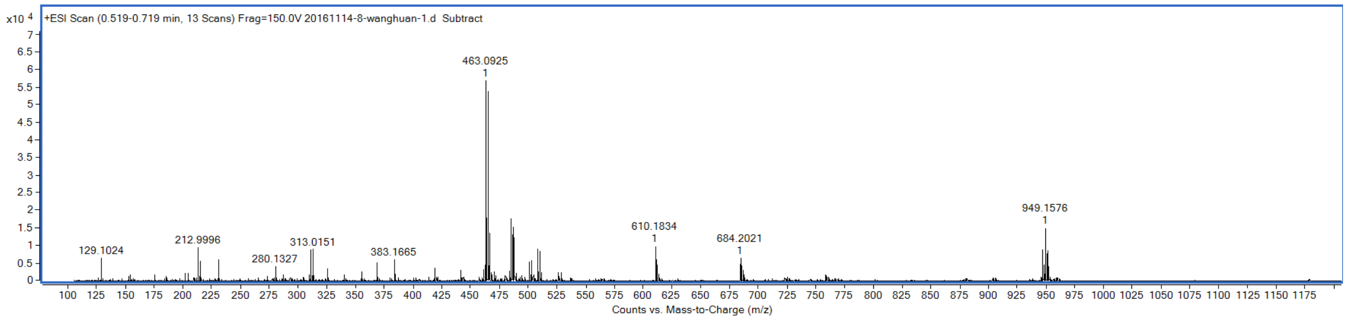

Fig. S2.3 HRMS spectra of $FcC_{11}Br$.

HRMS: m/z = 463.0925

The characterization data for $FcC_{11}PyBr$

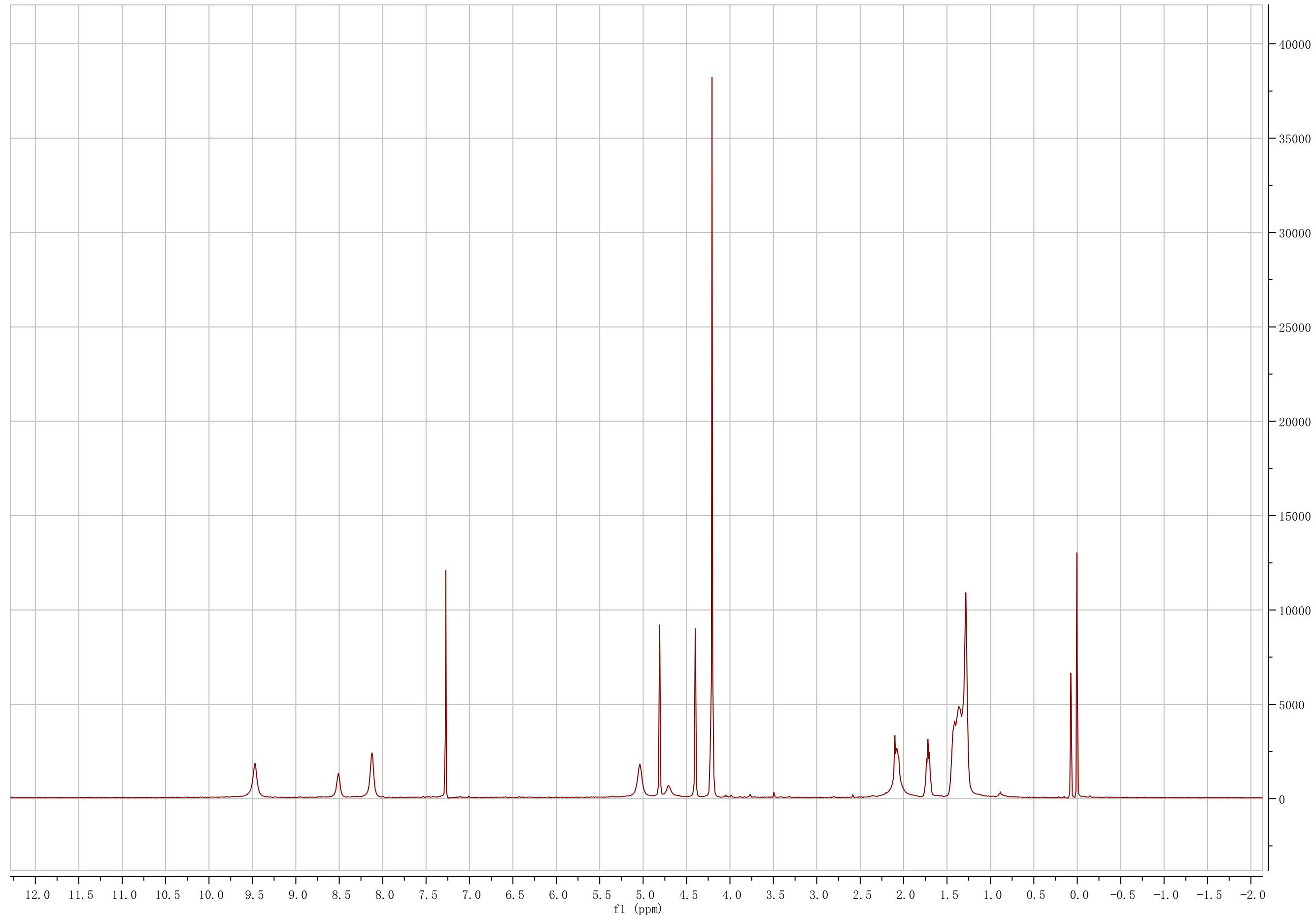

Fig. S3.1 ^{1}H NMR spectra of $FcC_{11}PyBr$.

^{1}H NMR (400 MHz, $CDCl_3$) : δ(ppm) = 9.47 (s, 2H), 8.50 (s, 1H), 8.12 (s, 2H), 5.03 (s, 2H), 4.81 (s, 2H), 4.40 (s, 2H), 4.21 (m, 7H), 2.09 (m, 2H), 1.83 – 1.60 (m, 2H), 1.54 – 1.19 (m, 14H).

In the spectra, δ = 7.26 ppm for $CDCl_3$.

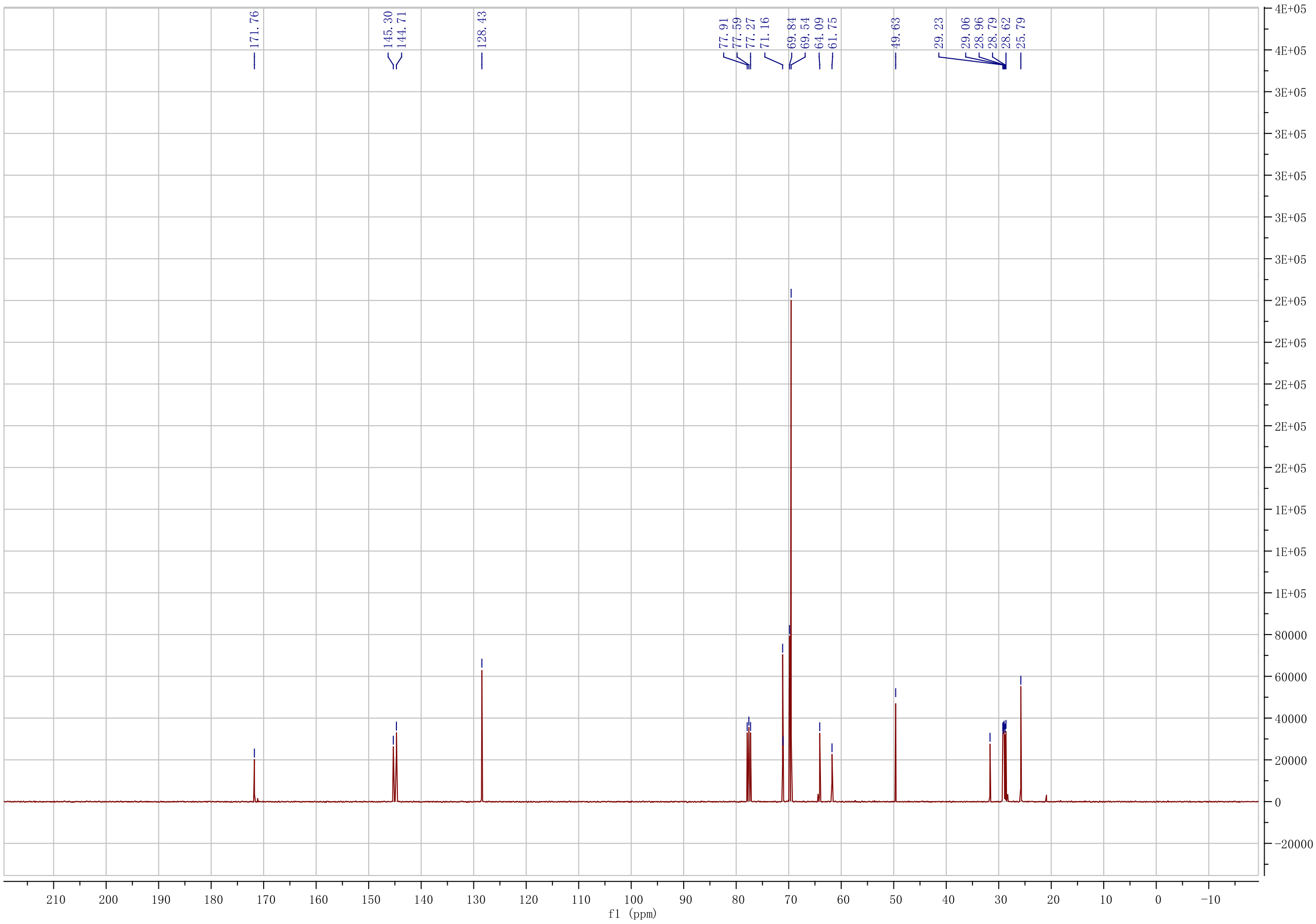

Fig. S3.2 ^{13}C NMR spectra of FcC$_{11}$PyBr.

^{13}C NMR (400 MHz, CDCl$_3$) δ(ppm) = 171.76, 145.30, 144.71, 128.43, 77.91, 77.59, 77.27, 71.16, 71.08, 69.84, 69.54, 64.09, 61.75, 49.63, 31.66, 29.23, 29.16, 29.06, 28.96, 28.79, 28.62, 25.79.

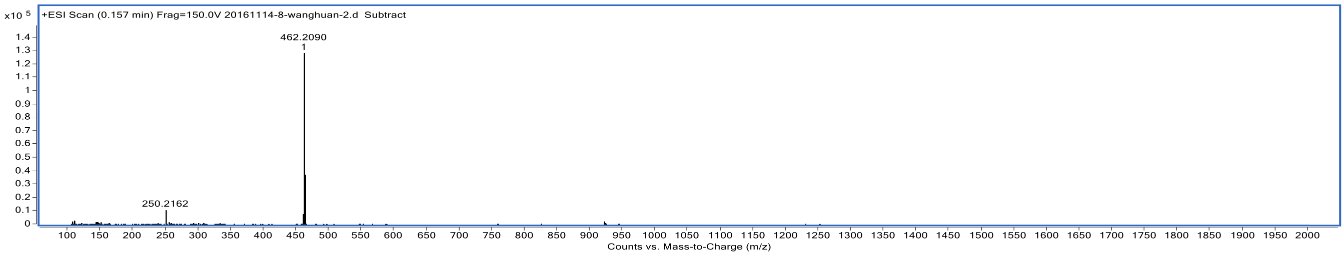

Fig. S3.3 HRMS spectra of FcC$_{11}$PyBr.

HRMS: m/z = 462.2090

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1. V. I. Kravtsov, and M. I. Zelenskii., *Elek trokhimiya*, 1966, **2**, 1138-1143.
2. C. Wang, S. Tao and C. Meng, *J. Mater. Chem.*, 2012, **22**, 7179-7186.