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Synthesis and structures of two mononuclear iron(II) complexes derived from polypyridine ligands

Hongqiao Wang, Nan Wu, Jing Zheng, Chunyang Zheng and Dunjia Wang

Experimental

Materials and methods

All chemicals were commercial and purified according to standard procedures. All organic solvents were dried and freshly distilled before use. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 300 MHz spectrometers using $CDCl_3$ as the solvent. Chemical shifts are reported relative to tetramethylsilane TMS (internal standard), and chemical shifts are expressed in δ (ppm). Mass spectra were measured on a LCQ Advantage MAX (ESI-MS). Magnetic susceptibility measurements were carried out on a Quantum Design MPMS XL-7 magnetometer at a sweeping rate of 2 K/min.

Single-crystal structure determination

Single Crystal structural data for **Py$_5$**, **1** and **2** were collected on a Bruker Apex-II CCD diffractometer using graphite-collimated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXL97) and completed by difference Fourier methods (SHELXL97). Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL97) and empirical absorption corrections (SADABS) were applied. Hydrogen atoms were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Synthesis of 1-methyl-2,2'-bipyridin-1-ium iodide

2,2'-Bipyridine (5.0 g, 32 mmol) was dissolved in acetonitrile (40 mL). Methyl iodide (13.6 g, 96.0 mmol) was added. The solution was heated to 45 °C and stirred for 3 days. The solid precipitated was filtered off, washed with acetonitrile and dismissed. Diethyl ether (20 mL) was added to the mother liquor, which led to precipitation of a solid that was filtered off and rinsed once more with diethyl ether. The process was repeated two times after concentration of the mother liquor. The resulting solid was dried in vacuum to give a light tan powder 6.8 g (yield 72 %).

Synthesis of 1-methyl-2,2'-bipyridin-6(1*H*)-one

Potassium hexacyanoferrate(III) (15.8 g, 48 mmol) was dissolved in water (50 mL) and cooled to 0 °C. Solutions of sodium hydroxide (16 g, 400 mmol) in water (50 mL) and 1-methyl-2,2'-bipyridinium iodide (6 g, 20 mmol) in water (50 mL) cooled to 0 °C were simultaneously added *via* dropping funnel within 1.5 h. The resulting solution was stirred for 4 h at 0 °C and then warmed to room temperature overnight. The mixture was extracted several times with dichloromethane, and the combined organic extracts were dried over $MgSO_4$ and filtered, and the solvent was removed. The residue was dissolved in ethyl acetate/methanol (8:2) and filtered through aluminum oxide. The solvent was removed and the resulting dark brown oil was crystallized overnight to give a dark brown solid 2.8 g (yield 75 %).

Synthesis of 6-bromo-2,2'-bipyridine

Triphenylphosphine (4 g, 14 mmol) was dissolved in acetonitrile (20 mL). The solution was cooled to 0 °C, and bromine (2.2 g, 14 mmol) was added dropwise. After stirring for 30 min, a yellow precipitate formed. A cooled solution (0 °C) of 1-methyl-2,2'-bipyridin-6(1*H*)-one (2 g, 10.8 mmol) in acetonitrile (5 mL) was added quickly. The reaction mixture was heated under reflux for 2 days and then poured onto ice. A white solid formed, which was filtered off and rinsed with dichloromethane. The aqueous phase was neutralized with $NaHCO_3$ solution and extracted three times with dichloromethane. The combined organic extracts were dried over $MgSO_4$ and filtered, and the solvent was removed, Purification by column chromatography to give a colourless power 1.8 g (yield 71 %). ESI-MS: m/z = 235.01, 236.91 ($[M+H]^+$). ^1H NMR (300 MHz, $CDCl_3$): δ ppm: 8.68 (d, J_2 = 4.7 Hz, 1H), 8.37-8.42 (m, 2H), 7.83 (t, J = 7.8 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H).

Synthesis of (2,2'-bipyridin-6-yl)di(2-pyridyl)methane (Py_4)

A solution of 2-methylpyridine (1.21 g, 13 mmol) in THF (100 mL) was cooled to –78 °C, and a solution of *n*-butyllithium (2.2 *M* in hexane, 5.5 mL, 12 mmol) was slowly added to the stirring solution within 30 min. The resulting deep red solution was stirred at −78 °C for 30 min. The temperature was then raised to –20 °C, at which point 2-fluoropyridine (0.58 g, 6 mmol) was added dropwise. After raising the temperature to ambient within 20 min, the mixture was refluxed for 1 h and cooled to room temperature. 6-Bromo-2,2'-bipyridine (1.41 g, 6 mmol) was added, and the solution was refluxed for 48 h. After cooling to room temperature, the mixture was quenched with water (30 mL) and the organic and aqueous layers were separated. The aqueous layer was extracted with ethyl acetate, the organic layers were combined and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure to leave yellow oil. The residue was dissolved in CH_2Cl_2 (3 mL) and layered with 10 mL diethyl ether prior to cooling to -25 °C. The yellow product separated after one day, and collected by filtration and washed with diethyl ether (5 mL) to afford 1.52 g (yield 78%) of pure product. ESI-MS: m/z = 325.22 ($[M+H]^+$), 671.00 ($[2M+Na]^+$).

^{1}H NMR (300 MHz, $CDC1_3$): δ ppm: 8.59-8.65 (m, 3H), 8.26-8.30 (m, 2H), 7.62-7.80 (m, 5H), 7.36-7.40 (m, 3H), 7.15-7.19 (m, 2H), 6.12 (s, 1H).

Synthesis of tri(2-pyridyl)methane (Py_3)

A solution of 2-methylpyridine (4.84 g, 52.0 mmol) in THF (100 mL) was cooled to –78 °C, and a solution of *n*-butyllithium (2.2 *M* in hexane, 22.7 mL, 50 mmol) was slowly added to the stirred solution within 30 min. The resulting deep red solution was stirred at −78 °C for 30 min. The temperature was then raised to –20 °C, at which point 2-fluoropyridine (2.43 g, 25 mmol) was added dropwise. After raising the temperature to ambient within 20 min, the mixture was refluxed for 1 h and cooled to room temperature. Another portion of 2-fluoropyridine (2.43 g, 25 mmol) was added, and the solution refluxed for 48 h. After cooling to room temperature, the mixture was quenched with water (100 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with ethyl acetate, the organic layers were combined and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure to leave yellow oil. The residue was dissolved in CH_2Cl_2 (5 mL), and layered with diethyl ether (20 mL) prior to cooling to -25 °C. The yellow crystalline product separated after one day, it was collected by filtration and washed with diethyl ether (40 mL) to afford 5.3 g (yield 86%) of pure product. ESI-MS: m/z = 248.15 ($[M+H]^+$), 516.93 ($[2M+Na]^+$). ^{1}H NMR (300 MHz, $CDC1_3$): δ ppm: 8.57-8.60 (m, 3H), 7.59-7.65 (m, 3H), 7.33 (d, 3H), 7.15 (t, 3H), 6.00 (s, 1H).

Synthesis of 2,6-Bis[di(2-pyridyl)methyl]pyridine (Py_5)

A solution of 2-methylpyridine (4.84 g, 52.0 mmol) in THF (100 mL) was cooled to –78 °C, and a solution of *n*-butyllithium (2.2 *M* in hexane, 22.7 mL, 50 mmol) was slowly added to the stirred solution within 30 min. The resulting deep red solution was stirred at −78 °C for 30 min. The temperature was then raised to –20 °C, at which point 2-fluoropyridine (2.43 g, 25 mmol) was added dropwise. After raising the temperature to ambient within 20 min, the mixture was refluxed for 1 h and cooled to room temperature. 2,6-Difluoropyridine (1.38 g, 12 mmol) was added, and the solution was refluxed for 48 h. After cooling to room temperature, the mixture was quenched with water (100 mL), and the organic and aqueous layers were separated. The aqueous layer was extracted with ethyl acetate, the organic layers were combined and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure to leave yellow solid which was recrystallized from methanol to afford slightly yellow crystals; yield: 4.1 g (82%). ESI-MS: m/z = 416.33 ($[M+H]^+$), 438.18 ($[M+Na]^+$). ^{1}H NMR (300 MHz, $CDC1_3$): *δ* ppm: 8.53 (dd, *J* = 4.8 and 0.8 Hz, 4H). 7.47-7.61 (m, 5H), 7.17-7.21 (m, 6H), 7.07-7.12 (m, 4H), 5.93 (s, 2H).

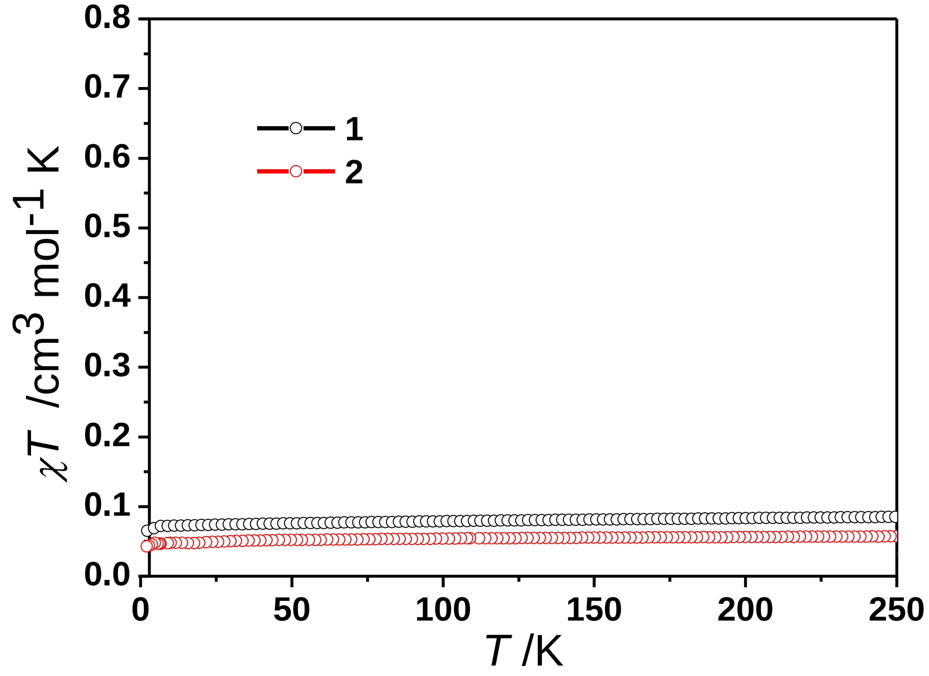

Figure S1. Temperature dependence of $\chi_M T$ plots for **1** and **2**

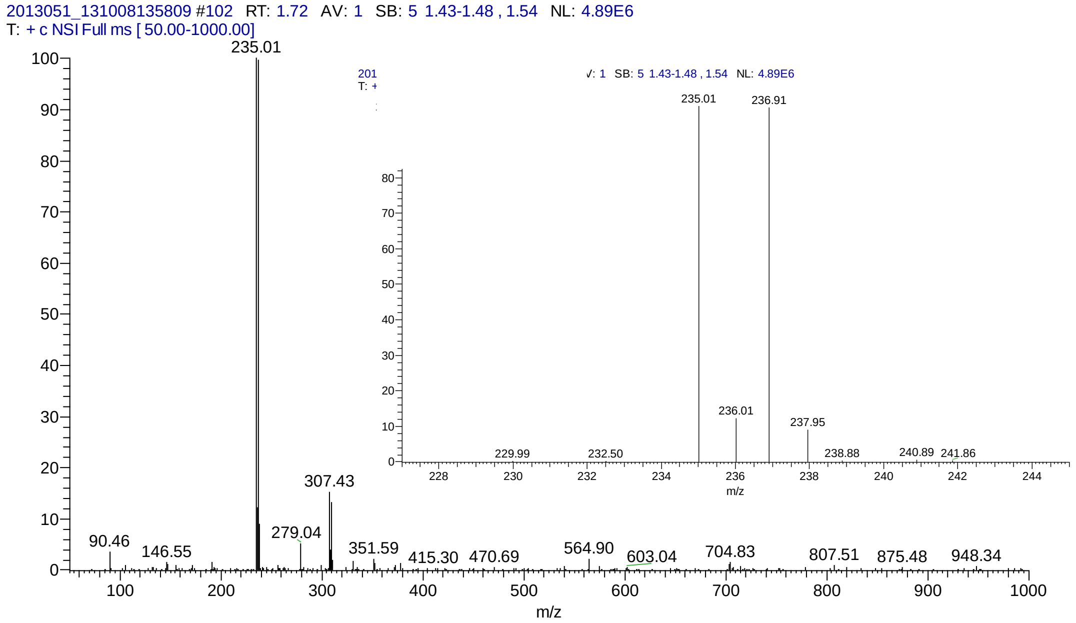

Figure S2 ESI-MS spectrum for 6-bromo-2,2'-bipyridine in CH_3OH

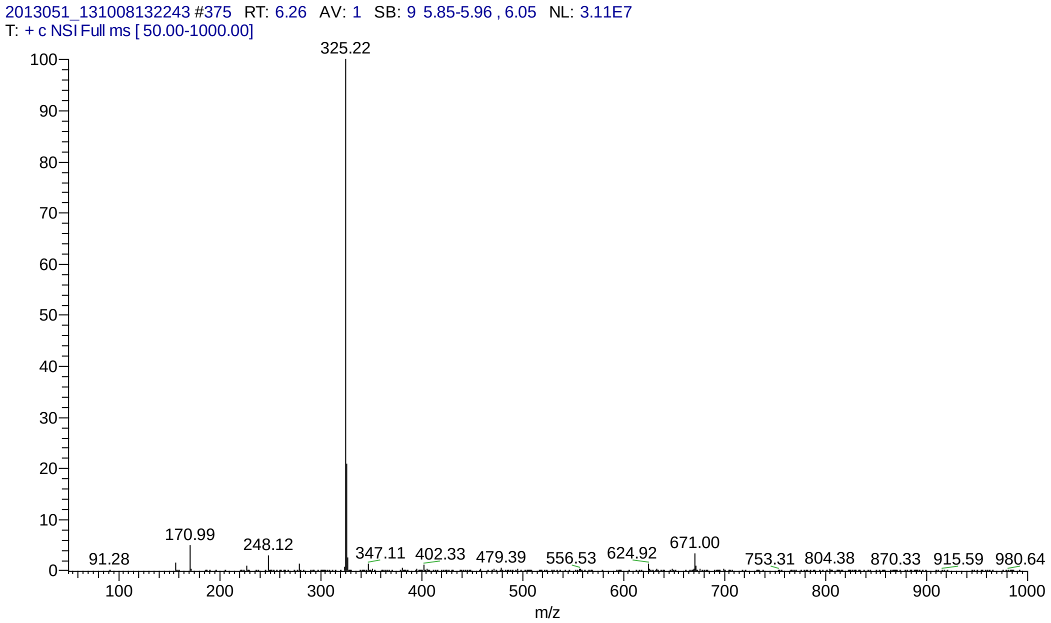

Figure S3 ESI-MS spectrum for **Py_4** in CH_3OH

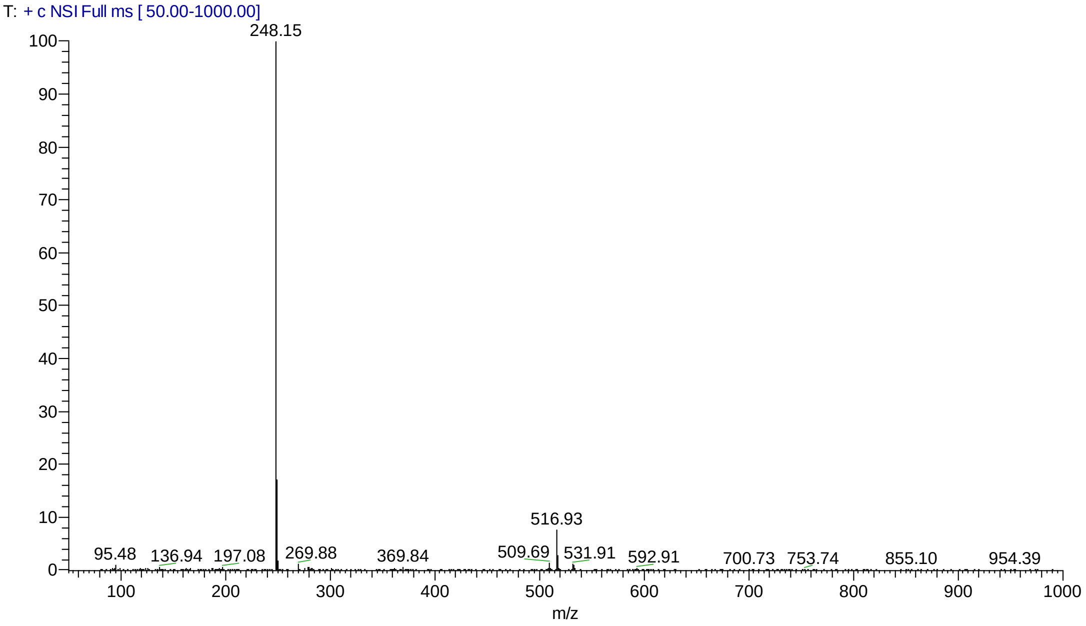

Figure S4 ESI-MS spectrum for **Py$_3$** in CH$_3$OH

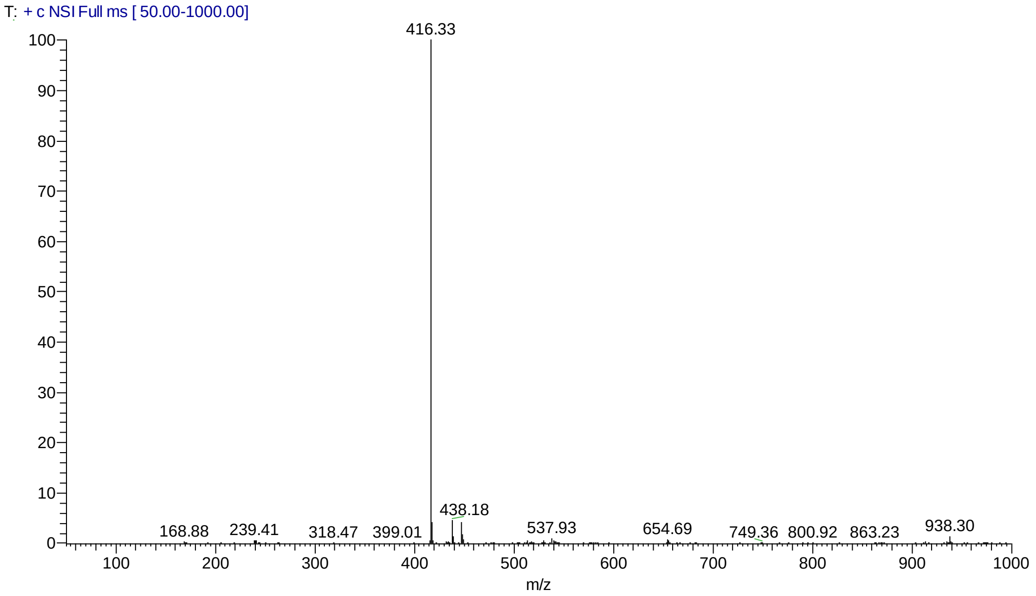

Figure S5 ESI-MS spectrum for **Py$_5$** in CH$_3$OH

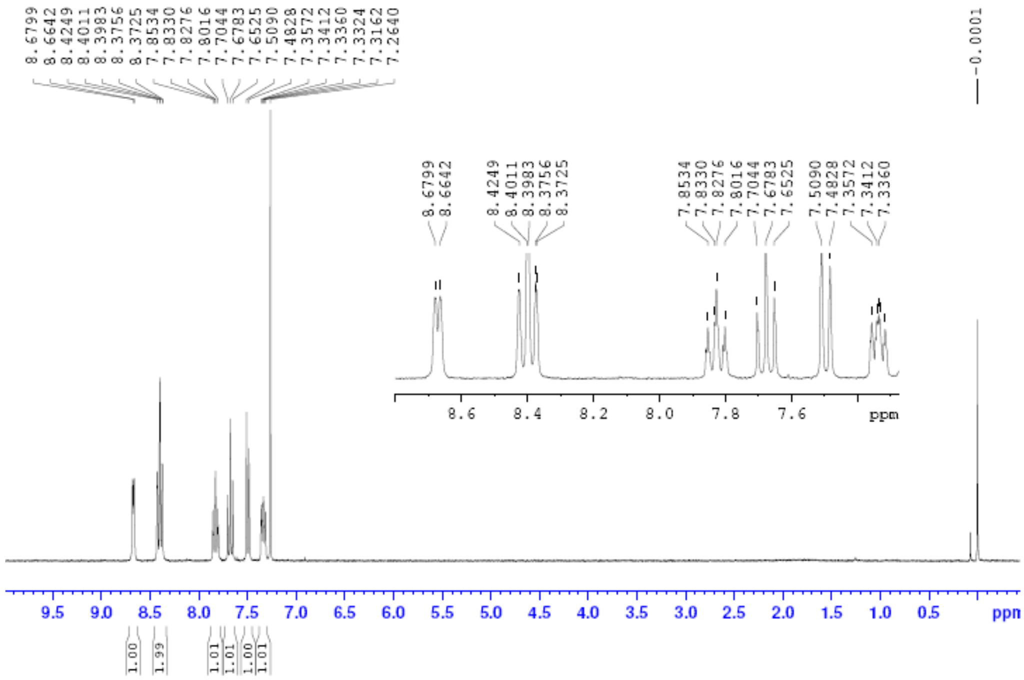

Figure S6 ^{1}H NMR (300 MHz, CDCl$_3$) of 6-bromo-2,2'-bipyridine

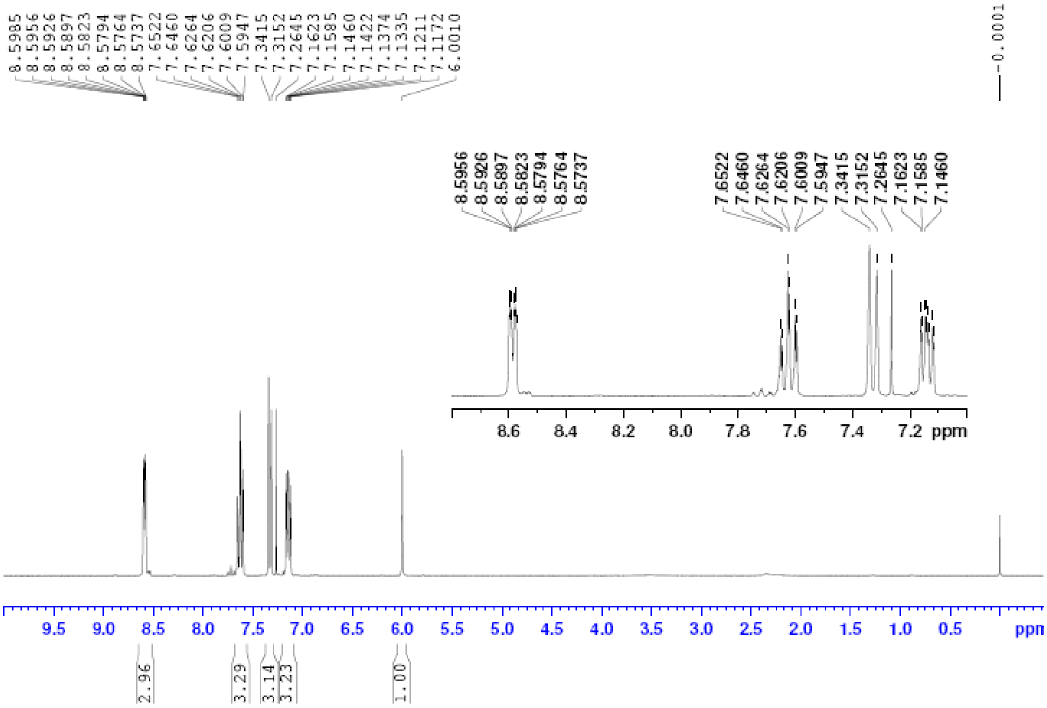

Figure S7 ^{1}H NMR (300 MHz, CDCl$_3$) of **Py$_3$**

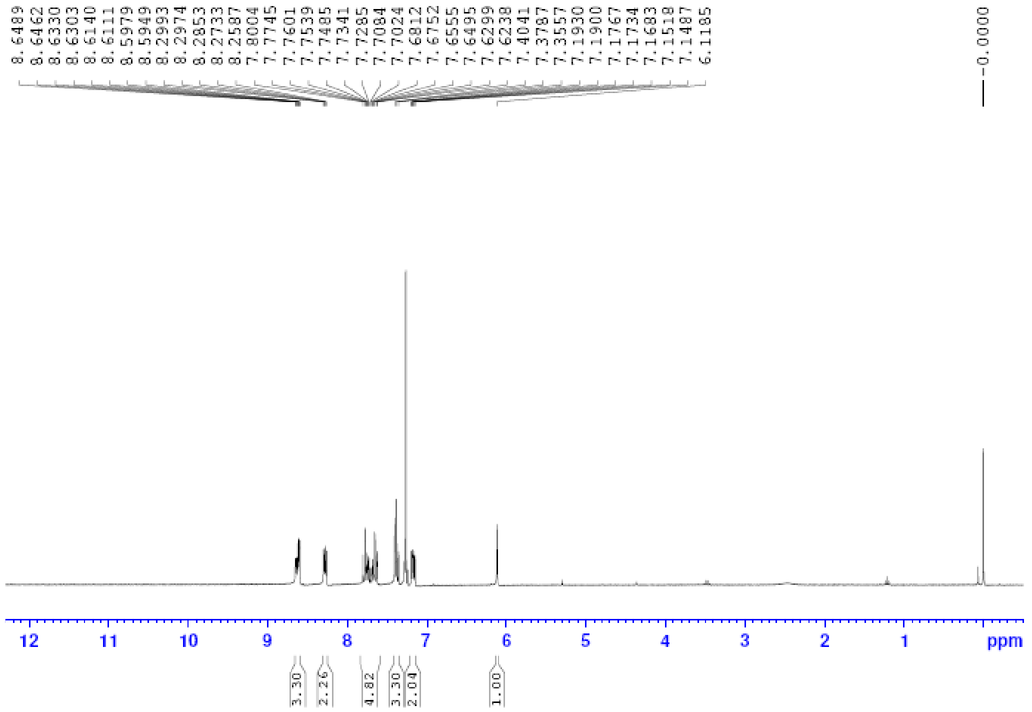

Figure S8 ^{1}H NMR (300 MHz, CDCl$_3$) of **Py$_4$**

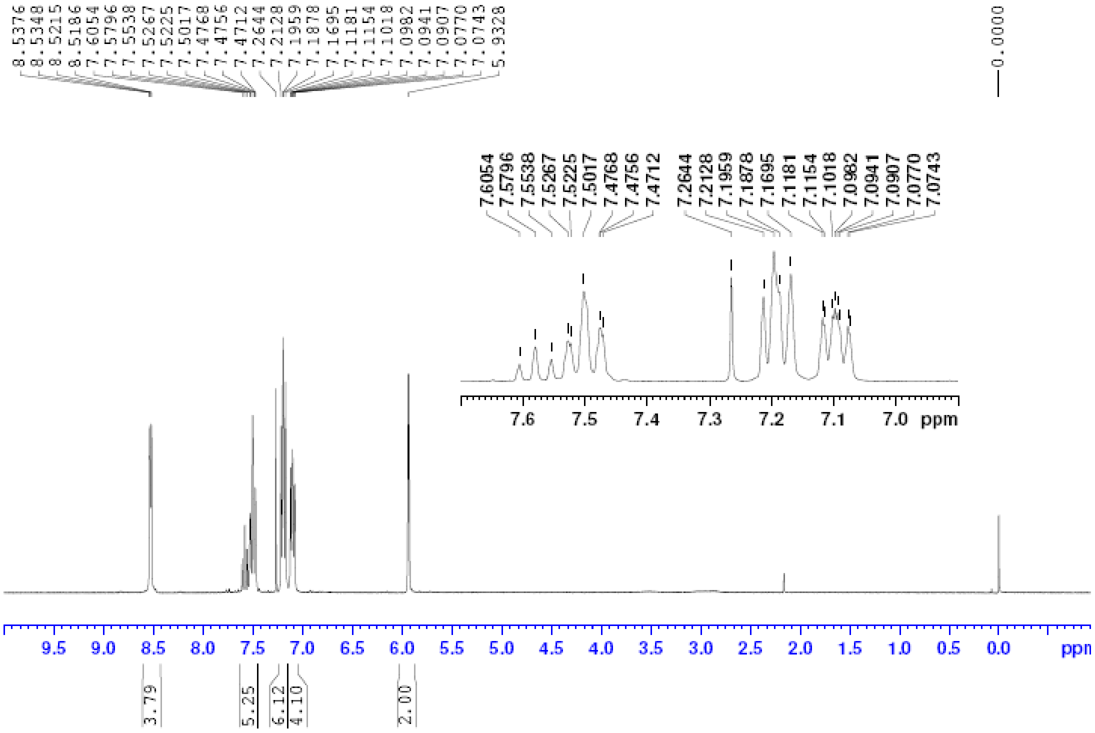

Figure S9 ^{1}H NMR (300 MHz, CDCl$_3$) of **Py$_5$**