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Electronic Supplementary Information

for

High Molecular Weight Organometallic Conjugated Polymer Incorporated with Hg (II)

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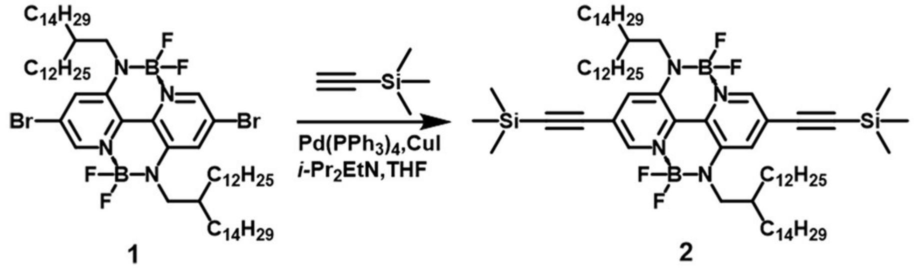
Contents

1.Experimental details

General. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AV-500 (500 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer in $CDCl_3$, C_6D_6 at 25 ^oC and in 1,2-dichlorobenzene-d4 at 100 ^oC. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a PL-GPC 220-type at the temperature of 150 ^oC. 1,2,4-Trichlorobenzene (TCB) was used as the eluent and monodisperse polystyrene was used as the standard. Thermal gravimetric analysis (TGA) was performed under an N_2 flow at a heating rate of 10 ^oC/min with a Perkin-Elmer-TGA 7 system. The temperature of degradation (T_d) was corresponding to a 5% weight loss. The grazing incident X-ray diffraction (GI-XRD) measurement was performed using a Bruker D8 Discover reflector. UV-vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer. Cyclic voltammetry (CV) was performed on an CHI660a electrochemical workstation using tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile as electrolyte solution and ferrocene as an internal reference at a scan rate of 50 mV s^{-1}. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The polymer was spin-casted on the working electrode for measurements. The redox potentials were calibrated with ferrocene as an internal standard. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: $E_{\mathrm{HOMO/LUMO}} = -(4.80 + E_{\mathrm{onset}}^{\mathrm{ox}}/E_{\mathrm{onset}}^{\mathrm{red}})$ eV. Polymers were dissolved in tetrahydrofuran and poured into a glass petri dish, then dried at room temperature for 24 h. Red polymer films were then obtained. The polymer self-supported smooth film thickness were measured by the scanning electron microscopy (SEM) operating on a Hitachi S-4800 SEM analyzer. The tensile test of polymer films were carried out by INSTRON 1121.

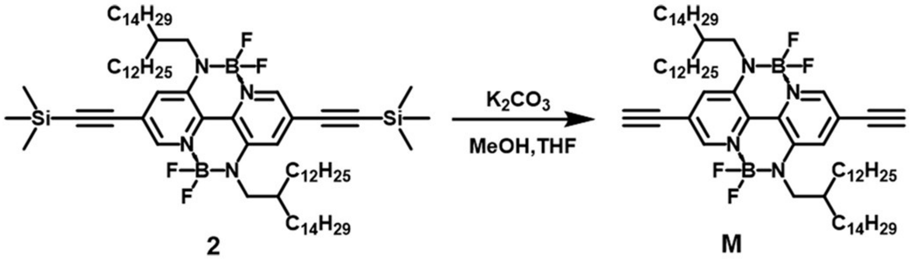
Materials and reagents. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Dry diisopropylethylamine, diisopropylamine, dichloromethane, tetrahydrofuran, diethylether and triethylamine were distilled via standard methods. 5,5'-dibromo-N3,N3'-di-2-dodecylhexadecyl-[2,2'-bipyridine]-3,3'-diamine (1) was prepared according to the literature methods.[1]

2. Syntheses and characterizations



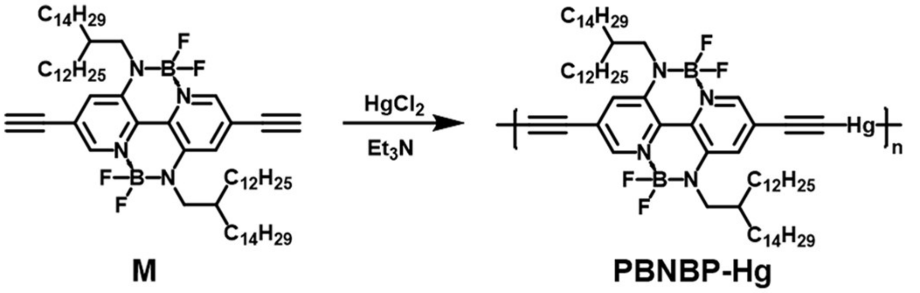
5,5'-ditrimethylsilylethynyl-N3,N3'-di-2-dodecylhexadecyl-[2,2'-bipyridine]-3,3'-diamine (2).

5,5'-dibromo-N3,N3'-di-2-dodecylhexadecyl-[2,2'-bipyridine]-3,3'-diamine**1** (1 g, 0.82 mmol), $Pd(PPh_3)_4$ (47.2 mg, 0.041 mmol), CuI (12.4 mg, 0.065 mmol) were combined in anhydrous THF (3 mL) to yield a orange solution under argon atmosphere, and then diisopropylethylamine (1.2 ml, 7.35 mmol) and trimethylsilylacetylene (0.35 ml, 2.45 mmol) were added to the mixture. The mixture was stirred at 70 ^{o}C for 2 h and extracted with petroleum ether for several times. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed by rotary evaporation. the crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane = 3:1). **2** was obtained as a red solid. (750.0 mg, yielded 73%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ (ppm) 8.19 (2H, d), 7.50 (2H, d), 3.49 (4H, d), 1.72 (2H, s), 1.32-1.22 (96H, m), 0.88 (12H, t), 0.29 (18H, s). ^{13}C NMR(100 MHz, $CDCl_3$, 25 ^{o}C): δ (ppm) 143.81, 130.83, 125.84, 125.28, 122.82, 102.40, 99.95, 48.39, 36.11, 32.31, 32.16, 30.46, 30.08, 30.04, 29.75, 23.07, 14.50.



5,5'-diethynyl-N3,N3'-di-2-dodecylhexadecyl-[2,2'-bipyridine]-3,3'-diamine (M).

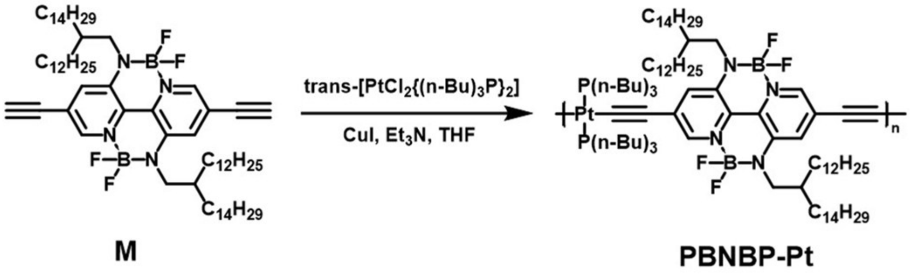
A mixture of **2** (400 mg, 0.32 mmol), K_2CO_3 (439 mg, 3.18 mmol), anhydrous THF (8 ml) and MeOH (8 ml) were stirred at room temperature for 1 h. Then, the reaction mixture was extracted by water and petroleum ether for three times. The separated organic layer was dried over anhydrous Na_2SO_4 and the solvent was then removed by rotary evaporation. The crude product was purified by silica gel chromatography (CH_2Cl_2) to give **M** (360 mg, yielded 86%) as a red solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ (ppm) 8.23 (2H, d), 7.58 (2H, d), 3.50 (4H, d), 3.39 (2H, s), 1.73 (2H, s), 1.32-1.22 (96 H, m), 0.88 (12H, t). ^{13}C NMR(100 MHz, $CDCl_3$, 25 ^{o}C): *δ* (ppm) 143.53, 130.28, 125.78, 125.48, 121.54, 83.37, 78.73, 48.14, 35.72, 31.93, 31.70, 30.06, 29.72, 29.67, 29.65, 29.38, 26.48, 22.70, 14.12.



Synthesis of PBNBP-Hg with different number-average molecular weight (M_n).

A two-necked flask was charged with $HgCl_2$ (24.3 mg, 0.090 mmol), **M** (100 mg, 0.090 mmol), and then anhydrous solvent (Et_2O (2 ml) for **P-L**; THF (5 ml) for **P-H**) was added to the mixture. After the solids are fully dissolved, anhydrous triethylamine (0.12 ml, 0.086 mmol) for **P-L**; (0.62 ml, 4.75 mmol) for **P-H** was added to the mixture. The mixture was stirred at room temperature for 36 h. Then, the reaction mixtures were precipitated into methanol and purified by silica gel chromatography using THF as eluent to give **P-L** (105 mg, yielded 89%), **P-H** (110 mg, yielded 93%) as red solids. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ (ppm) 8.22-8.11 (2H, m), 7.64-7.50 (2H, d), 3.51 (4H, s), 1.76 (2H, s), 1.58-1.10 (96H, m), 0.86 (12H, s). Anal. Calcd for $C_{70}H_{118}B_2F_4HgN_4$: C, 63.99; H, 9.05; N, 4.26. Found: C, 62.75; H, 9.08; N, 4.09. $HgCl_2$ is highly toxic and easily sublimates, so direct contact or inhalation of $HgCl_2$ should be avoided. Weighing $HgCl_2$ needs to be done quickly in the fume hood.

After the experiment is completed, the experimental instruments that are in contact with $HgCl_2$ need to be cleaned with ethanol. The experimental supplies (gloves, weighing paper, etc.) that are in contact with $HgCl_2$ should be treated with sodium sulfide, and then add ferrous sulfate for co-precipitation.



Synthesis of PBNBP-Pt.

A two-necked flask was charged with trans-[$PtCl_2\{(n\text{-}Bu)_3P\}_2$] (30.0 mg, 0.045 mmol), **M** (49.9 mg, 0.045 mmol), CuI (1.0 mg, 0.005 mmol), and then anhydrous diisopropylamine (7ml), dichloromethane (7ml) were added to the mixture. The mixture was stirred at 40 ^{o}C for 32 h. Then, the reactions mixtures were precipitated into methanol and purified by silica gel chromatography using dichloromethane as eluent to give **PBNBP-Pt** (71.0 mg, yielded 93%) as a yellow solid. ^{1}H NMR (500 MHz, CDCl3, 25 ^{o}C): δ(ppm) 7.98 (2 H, s), 7.27 (2 H, s), 3.46 (4 H, s), 2.13 (12 H, s), 1.78 (2 H, s), 1.62 (12 H, s), 1.49 (12 H, m), 1.34-1.24 (108 H, m), 0.95 (18 H, t), 0.87 (12 H, t).

3. Thermalgravimetric Analysis

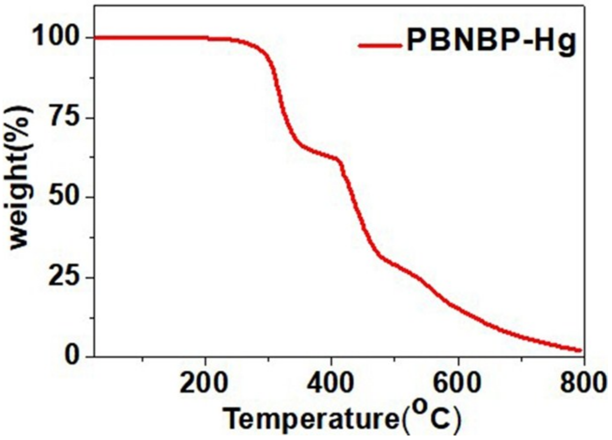


Fig. S1. The thermal properties of **PBNBP-Hg** were determined by thermogravimetric analysis (TGA) using **P-H** testing. TGA analysis shows that **PBNBP-Hg** have good thermal stability with decomposition temperature (T_d) at 5% weight loss of 294 °C under N_2.

4. Molecular packing

The GI-XRD pattern of the **PBNBP-Hg** film shows the (100) diffraction at 2Θ = 3.2° and (010) diffraction at 2Θ = 25.9°, indicating a lamellar packing distance of 2.76 nm and a π–π stacking distance of 0.34 nm, respectively. The (200) diffraction peak can be observed, suggesting good crystallinity of **PBNBP-Hg**.

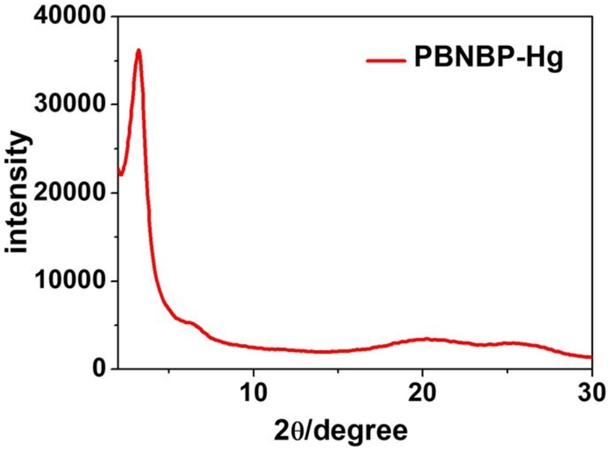


Fig. S2. The GI-XRD pattern of the **PBNBP-Hg** film.

5. Absorption spectra

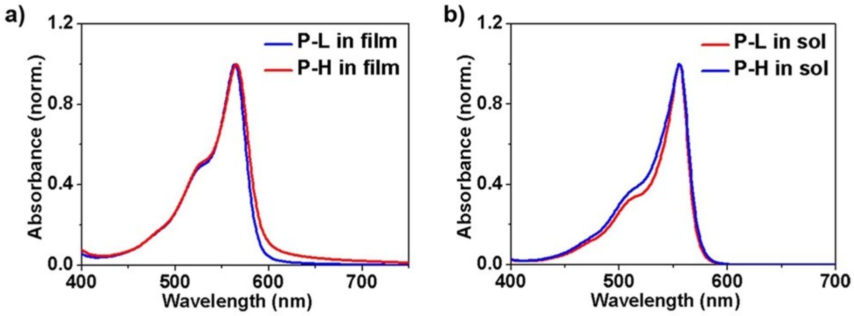


Fig. S3. UV/Vis absorption spectra of **P-H** and **P-L** a) in film and b) in THF solution. **PBNBP-Hg** with different molecular weights exhibit similar absorption spectra either in solution or in film.

6. Cyclic voltammograms

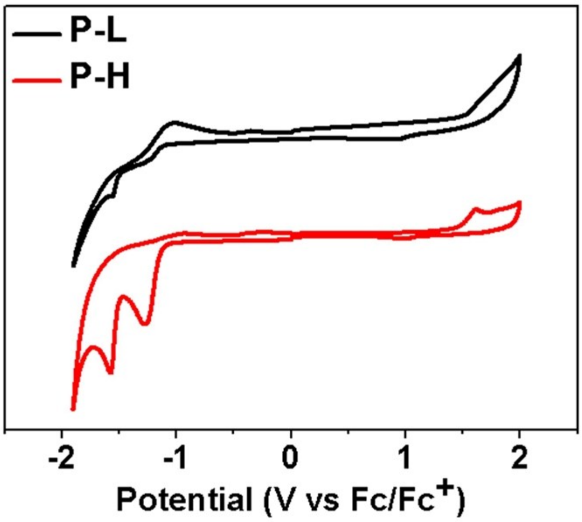


Fig. S4. The cyclic voltammograms of **P-H** and **P-L** films. **P-H** and **P-L** shows the similar onset oxidation potential of 1.12 V and onset reduction potential of -1.46 V. Therefore, the LUMO/HOMO energy levels of **P-H** and **P-L** are estimated to be -3.34 eV/-5.92 eV. The molecular weight does not affect the LUMO/HOMO energy levels of the organometallic conjugated polymers.

7. Film-forming properties of PBNBP-Hg as a function of M_n

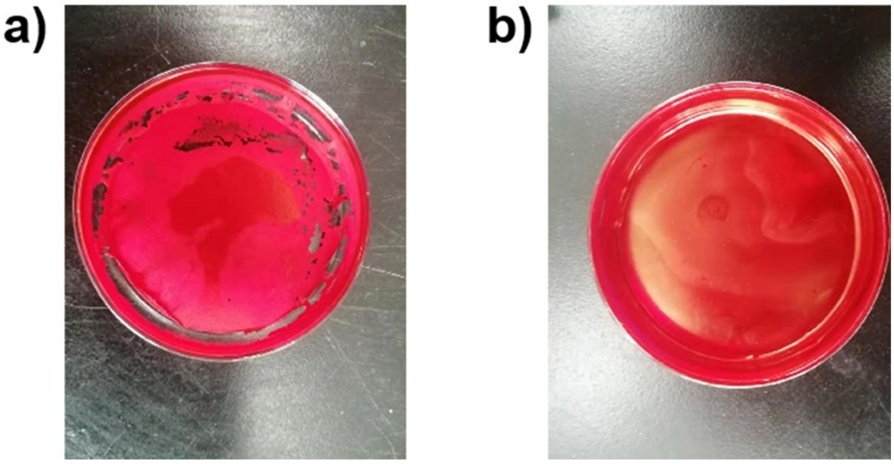


Fig. S5. a) **P-L** self-supported smooth film, b) **P-H** self-supported smooth film. **P-H** and **P-L** are dissolved in THF at a concentration of 5 mg/ml, then dried at room temperature for 24 h. **P-H** clearly shows better film-forming properties than **P-L**, which shows that an increase in M_n can improve the film-forming properties of polymers.

8. Tensile properties of PBNBP-Hg films as a function of M_n

The polymer self-supported smooth films were frozen in liquid nitrogen at -78 ^{o}C and then broken. After that, polymer film thickness were measured by measuring the intersecting surface of the film with SEM. The tensile test was performed with a film of 10 mm gauge length, and 5 mm width at a stretching speed of 5 mm min^{-1}.

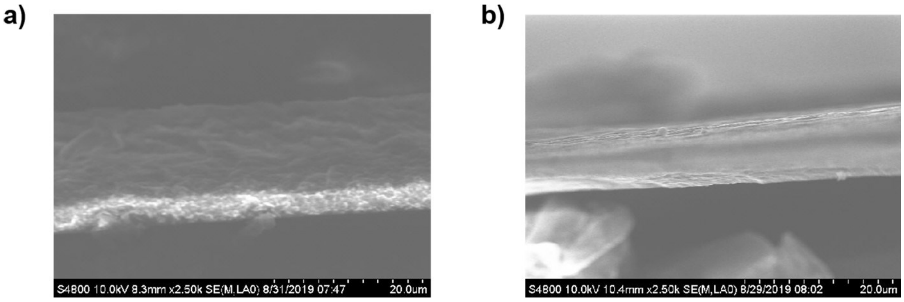


Fig. S6. SEM images of the intersecting surface of a) **P-L** film and b) **P-H** film.

9. Gel permeation chromatography curves of Pt-containing conjugated polymer

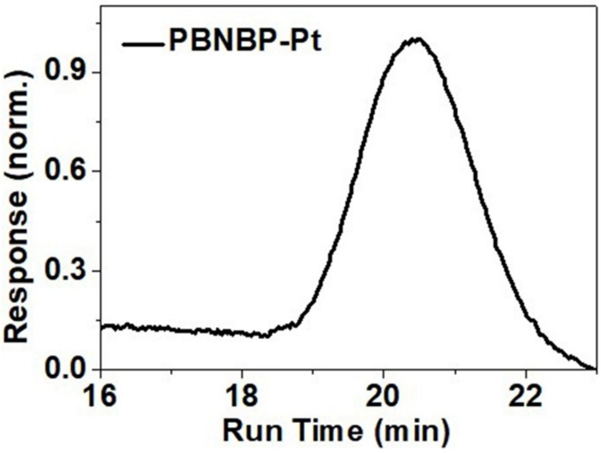


Fig. S7. Gel permeation chromatography (GPC) curves of Pt-containing conjugated polymer (M_n = 70 000, PDI = 1.49)

10. ^{1}H NMR and ^{13}C NMR spectra

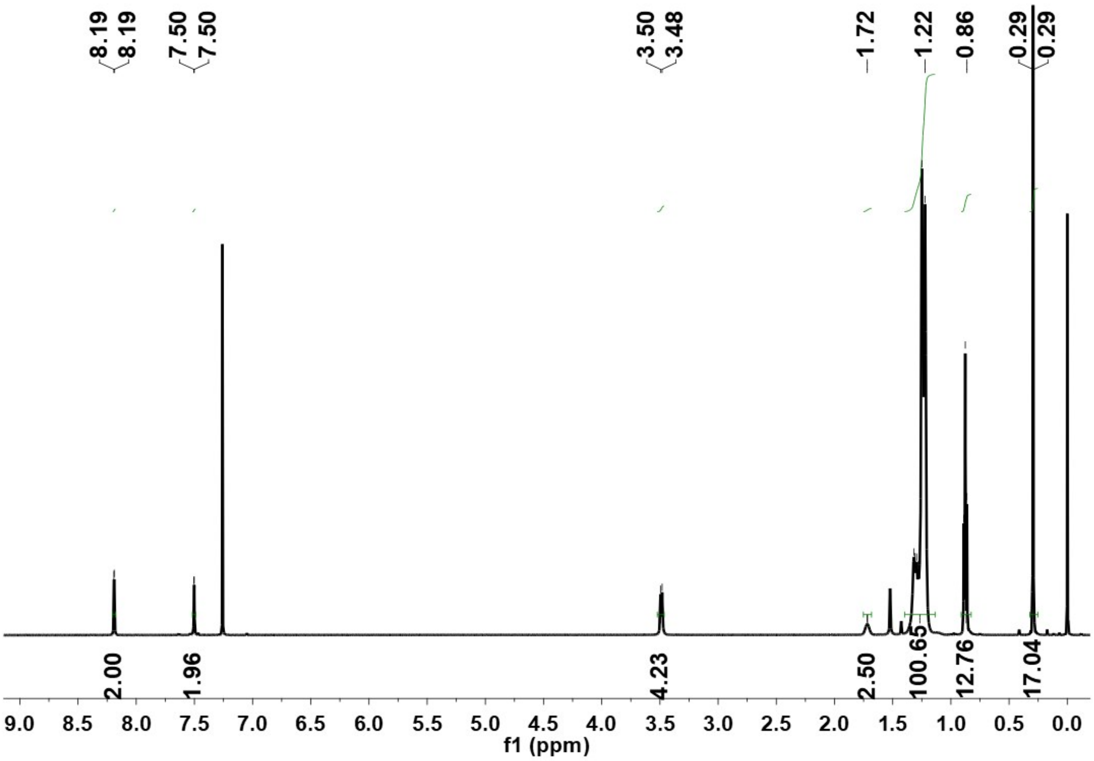


Fig. S8. ^{1}H NMR spectrum of **2** in $CDCl_3$.

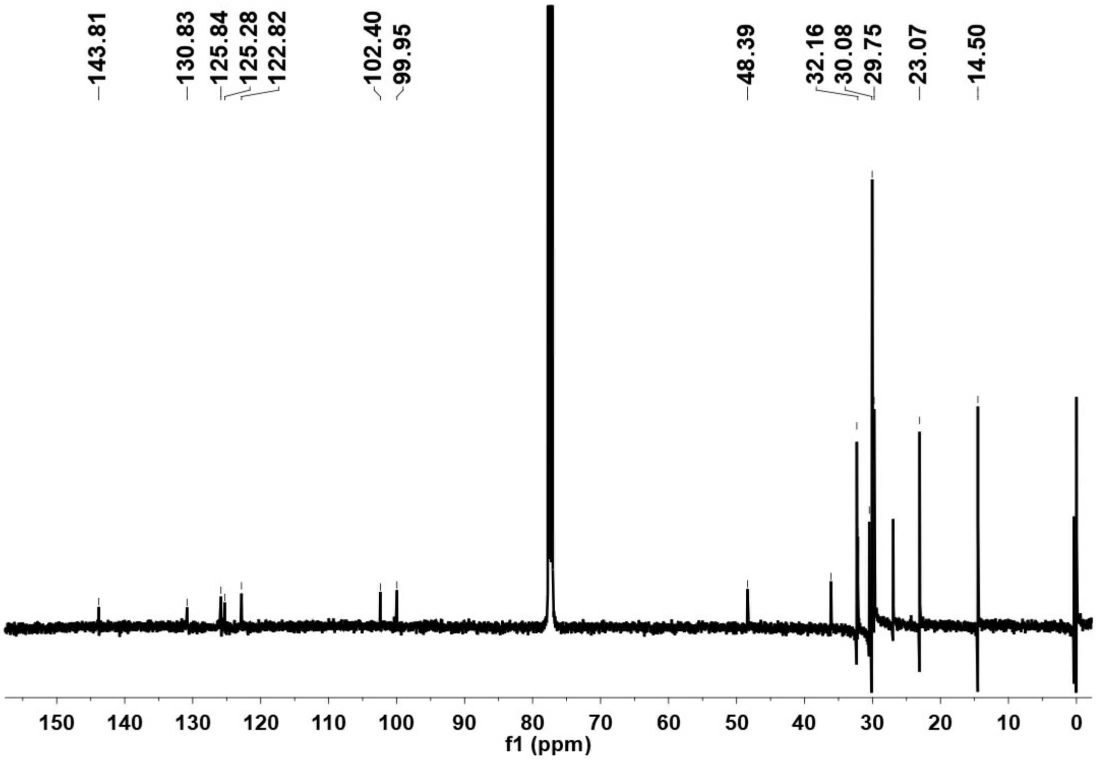


Fig. S9. ^{13}C NMR spectrum of **2** in CDCl$_3$.

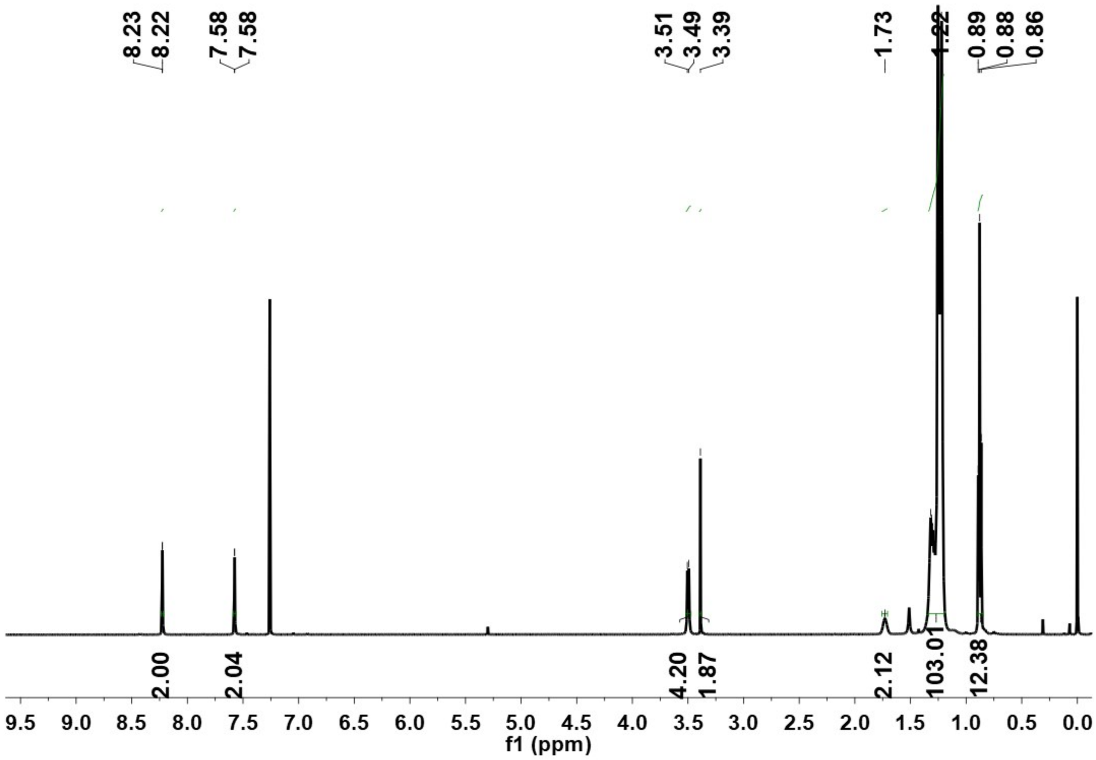


Fig. S10. ^{1}H NMR spectrum of **M** in CDCl$_3$

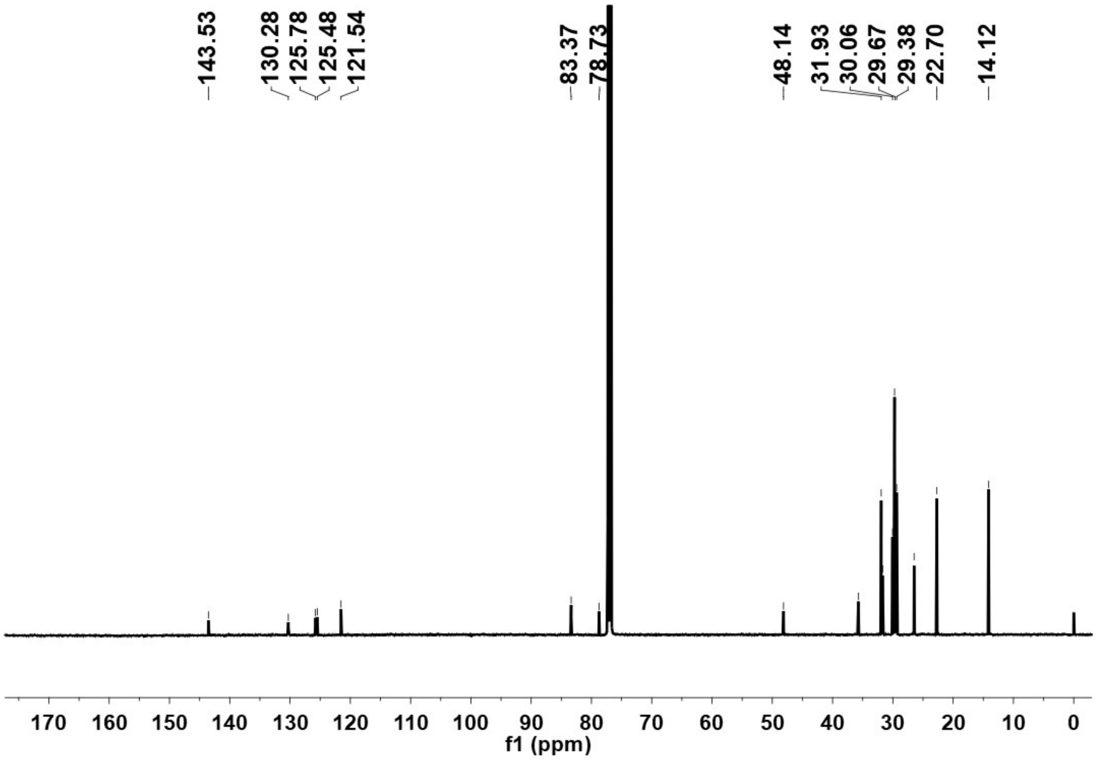


Fig. S11. ^{13}C NMR spectrum of **M** in CDCl$_3$.

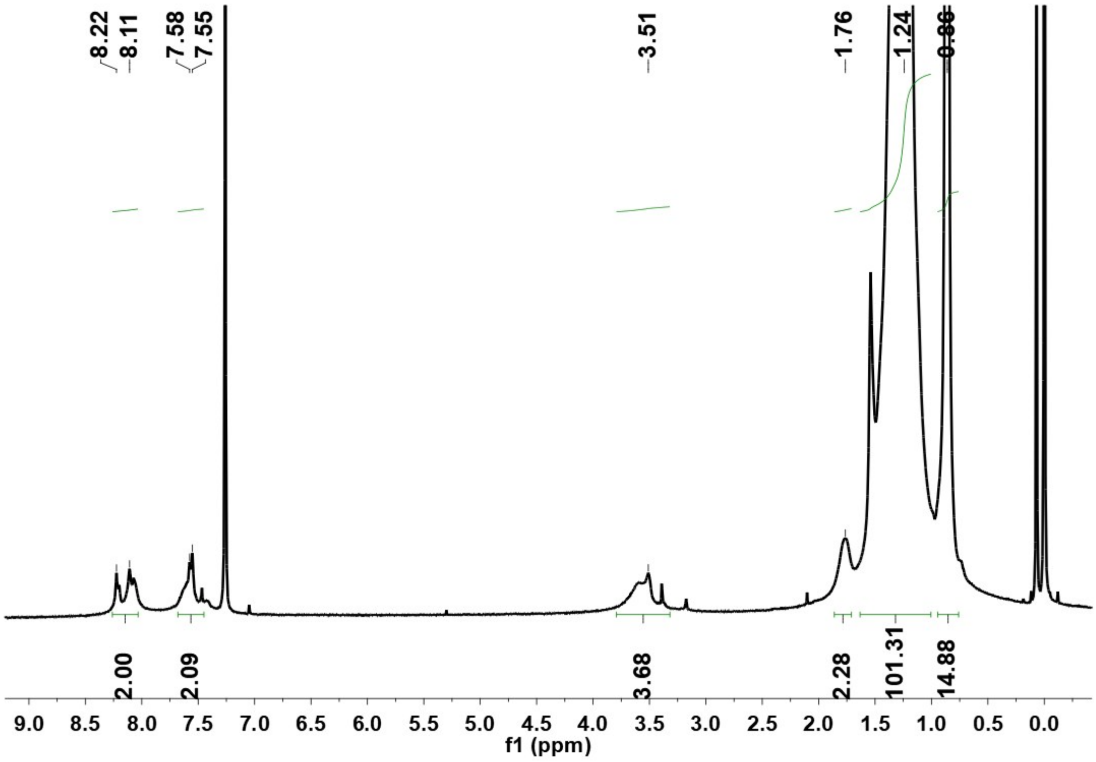


Fig. S12. ^{1}H NMR spectrum of **PBNBP-Hg** in CDCl$_3$.

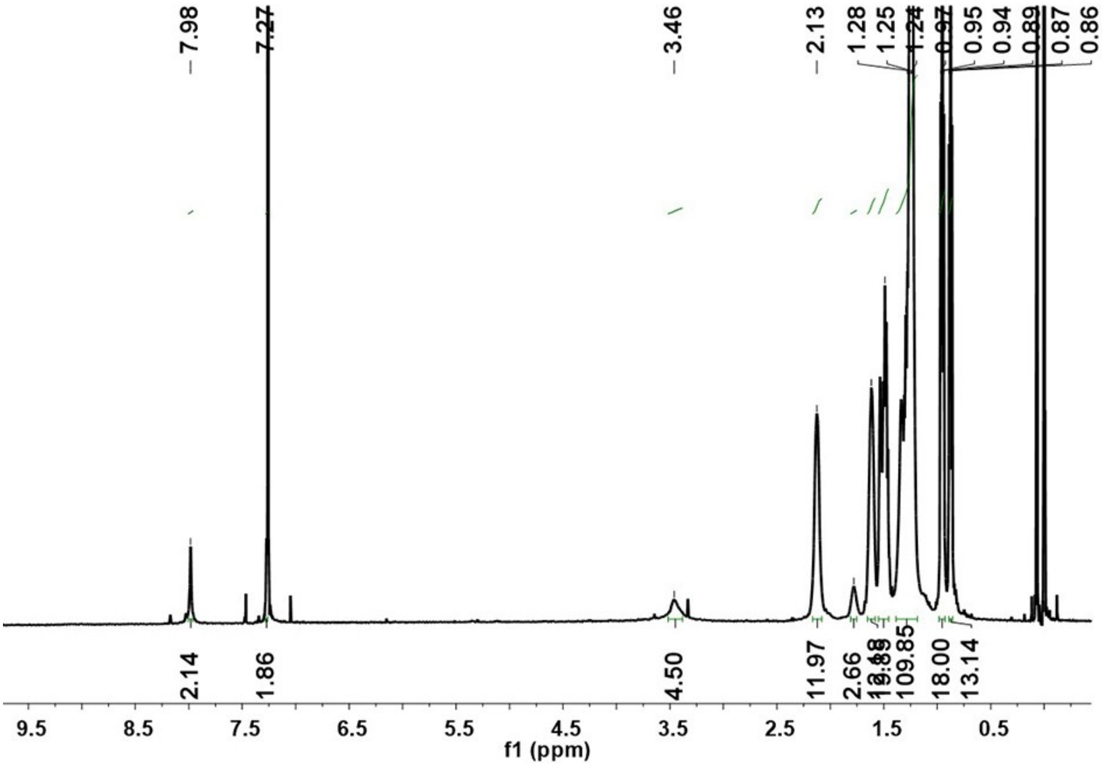


Fig. S13. ^{1}H NMR spectrum of **PBNBP-Pt** in $CDCl_3$.

11. Reference

1. C. Dou, X. Long, Z. Ding, Z. Xie, J. Liu and L. Wang, *Angewandte Chemie International Edition*, 2016, **55**, 1436-1440.