New Journal of Chemistry, 2015

Supporting Information

Conjugated Aromatic Asymmetrical Terpyridine Analogues *via* Step-wise Photocyclization and Their Ruthenium Complexization

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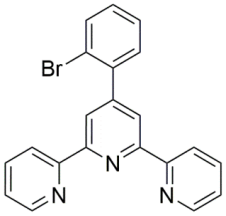
Experiment section:

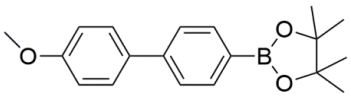
Melting points was taken on an electro-thermal melting point apparatus. The UV irradiation source (PLS-LAM250) was purchased from Beijing Perfect-Light company, ^{1}HNMR and ^{13}CNMR spectrum are recorded on a Bruke NMR (500 MHz, 400 MHz, 300 MHz), ESI-MS and UPLC were obtained on a Agilent 2100 MS spectrometer. UV-vis spectra were recorded on SHIMADZU UV-2041 spectrometer. High-resoluton MS spectrum was recorded on Waters Q-Tof MS spectrumer. Photoluminescence spectrum was recorded on HITACHI F-7000 spectrometer. Starting materials and solvents purchased from Sigma-Aldrich, Chemicalenergy and Acros used without further purification. Column chromatography was conducted using basic Al_2O_3 (200-300 mesh) or SiO_2 (200-300 mesh).

1. Synthesis of Br-Tpy[S1]:



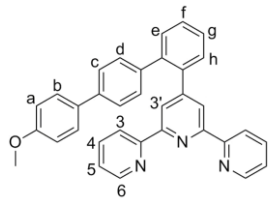
To a solution of NaOH (1.6g, 40mmol) in 100ml EtOH, 2-bromobenzaldehyde (3.67 g, 20 mmol) and 2-acetylpyridine (4.84g, 40mmol) was added. After stirring at 25 ℃ for 10 h, aqueous $NH_3.H_2O$ (30 mL) was added and the mixture was refluxed overnight. After cooling to room temperature, the solvent was evaporated in vacuo. The residue was added in MeOH and then filtrated, washed with water and methanol, then dried on oven at 80 ℃. 4.2g white powder was obtained pure enough for the next step (yield: 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71-8.68 (m, 4H), 8.58 (s, 2H), 7.87-7.84 (m, 2H), 7.72-7.70 (d, J=10Hz, 1H), 7.48-7.47 (d, J=5Hz, 1H), 7.41-7.38 (m, 1H), 7.33-7.30 (m, 2H), 7.27-7.24 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.09, 155.38, 150.82, 149.22, 140.48, 136.88, 133.22, 130.97, 129.73, 127.55, 123.87, 121.96, 121.68, 121.35. ESI-MS: 389.2 [M+H].

2. Synthesis of 4'-Methoxybiphenyl-4-boronic acid pinacol ester[S2]:



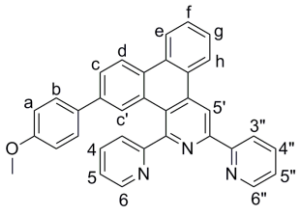
4-bromo-4'-methoxybiphenyl (2.61g, 10mmol) was dissolved in 100mL THF, then degassed 3 minutes under vacuum, then $Pd(PPh_3)_4$ (77mg, 0.5mmol) and 1M NaOH aqueous solution (20mL) was added, the mixture was refluxed overnight under argon atmosphere, then the solvent was evaporated in vacuo, the residue was purified on silica gel column (DCM/Petrol 1:10), 1.5g (50%) desired product was obtained. ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.89-7.87 (d, J=8Hz, 2H), 7.60-7.59 (d, J=4Hz, 2H), 7.58-7.57 (d, J=4Hz, 2H), 7.01-6.99 (d, J=8Hz, 2H), 3.88 (s, 3H), 1.38(s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.42, 143.48, 135.25, 133.53, 128.26, 125.98, 114.24, 83.77, 55.06.

3. Synthesis of tpy 1:



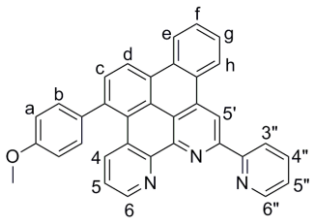
Br-Tpy (1.95g, 5mmol) and 4'-Methoxybiphenyl-4-boronic acid pinacol ester (1.62g, 5mmol) was dissolved in THF, after degassed under argon atmosphere for 5 minutes, $Pd(PPh_3)_4$ (77 mg, 0.5 mmol) and 1M NaOH aqueous solution (20mL) were added in, then the mixture was refluxed for 12 hours under argon atmosphere. After cooling to room temperature, the solvent was evaporated in vacuo, the residue was purified on Al_2O_3 column to obtain tpy **2** (1.25g, 52%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65-8.64 (d, J=5Hz, 2H, 6), 8.56- 8.55 (d, J=5Hz, 2H, 3), 8.33 (s, 2H, 3'), 7.84-7.80 (m, 2H, 4), 7.64-7.62 (d, J=10Hz, 1H, h), 7.56-7.47 (m, 3H, e, f, g), 7.44-7.41 (m, 4H, b, c), 7.33-7.28 (m, 5H, d, 5,5"), 6.93-6.91 (d, J=10Hz, 2H, a), 3.83 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.05, 156.21, 155.20, 151.80, 149.13, 140.36, 139.15, 139.09, 138.34, 136.72, 133.27, 130.60, 130.43, 130.31, 128.61, 127.97, 127.56, 126.35, 123.63, 122.16, 121.24, 114.09, 55.32. ESI-MS: 492.8 [M+H], Melting point: 197-200 ℃.

4. Synthesis of tpy 2:



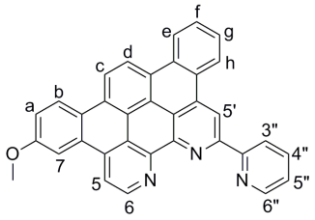
Tpy **1** (122mg, 0.25mmol) was dissolved in 100 ml toluene, the reaction vessel was exposed to ultraviolet lamp for 2 hours, keep the temperature below 10 ℃ (reaction was monitored by TLC), after the raw material disappeared, the mixture was poured into a round-neck bottle and the solvent was evaporated in vacuo, then purified on Al_2O_3 column chromatography to obtain tpy **2** as a pale-yellow solid (60 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H, 5'), 8.97-8.95 (d, J=8Hz, 1H, 3), 8.82-8.81 (d, J=4Hz, 1H, 4), 8.78-8.77 (d, J=4Hz, 1H, 6), 8.69-8.67 (d, J=8Hz, 1H, 3"), 8.65-8.64 (d, J=4Hz, 1H, e), 8.64-8.61 (d, J=12Hz, 1H, d), 8.04 (s, 1H, c'), 8.03-8.01 (d, J=8Hz, 1H, 4), 7.90-7.86 (m, 1H, 4"), 7.83-7.74 (m, 4H, h, g, g, c), 7.53-7.50 (m, 1H, 5), 7.38-7.36 (m,1H, 5"), 7.13-7.11 (d, J=8Hz, 2H, b), 6.90-6.88 (d, J=4Hz, 2H, a), 3.87 (s, 3H, OCH_3).^{13}C NMR (126 MHz, $CDCl_3$): δ 162.24, 159.24, 156.71, 156.04, 151.05, 149.83, 149.25, 139.09, 137.62, 137.55, 136.91, 132.79, 131.77, 129.99, 129.51, 128.42, 128.25, 127.94, 127.47, 127.35, 126.04, 124.71, 123.90, 123.66, 123.19, 122.99, 121.66, 114.04, 113.00, 55.35. ESI-MS: 490.8. [M+H], Melting point: >250 ℃.

5. Synthesis of tpy 3:



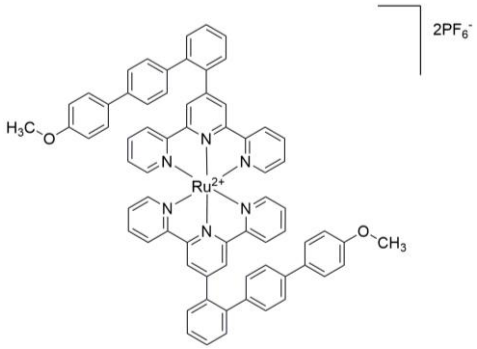
Tpy **2** (60mg, 0.12mmol) was dissolved in 100mL $CHCl_3$ and CH_3CN (1:1), and exposed in ultraviolet for 2 hours, the reaction was monitored by TLC. The solvent was evaporated in vacuo and purified on prepared TLC (Al_2O_3) to obtain tpy **3** as a yellow solid (10%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.12-10.11 (d, J=5Hz, 1H, 6), 9.97 (s, 1H, 5'), 9.71-9.70 (d, J=5Hz, 1H, 4), 9.10-9.09 (d, J=5Hz, 1H, h), 9.00-8.97 (m, 1H, g), 8.93-8.92 (d, J=5Hz, 2H, d, e), 8.85-8.84 (d, J=5Hz, 1H, 6"), 8.82-8.81 (d, J=5Hz, 1H, 3"), 8.25-8.23 (d, J=10Hz, 1H, c), 8.10-8.04 (m, 2H, 4", f), 7.96-7.93 (m, 1H, 5), 7.90-7.87(m, 1H, 5"), 7.53-7.52 (d, J=5Hz, 1H, b), 7.15-7.14 (d, J=5Hz, 1H, a), 3.98 (s, 3H, OCH_3). ESI-MS: 489.1 [M+H]. Melting point: >250 ℃.

6. Synthesis of tpy 4:



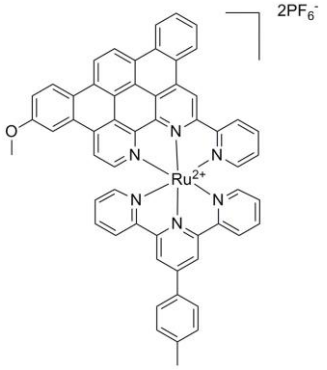
Tpy **3** (60mg, 0.12mmol) was dissolved in 100mL DCM solvent, the mixture was exposed in ultraviolet for 2 hours, the reaction was monitored by TLC, after all the starting material disappeared. The solvent was removed under vacuum and purified with Al_2O_3 column chromatography to obtain tpy **4** (30 mg, 50%). ^{1}H NMR (300 MHz, DMSO) δ: 10.12-10.09 (d, J=9Hz, 1H, 6), 9.86-9.83 (d, J=9Hz, 1H, 5), 9.67 (s, 1H, 5'), 9.32-9.30 (d, J=6Hz, 1H, 6"), 9.22-9.21 (d, J=3Hz, 1H, 3"), 9.02-8.79 (m, 5H, h, g, f, e, d), 8.47 (s, 1H, 7), 8.18-8.10 (m, 1H, 4"), 7.96-7.91 (m, 2H, c, b), 7.84-7.81(d, J=9Hz, 1H,a), 7.69-7.65 (m, 1H, 5"), 4.22 (s, 3H, OCH_3).^{13}C NMR (126 MHz, DMSO) δ 180.18, 161.66, 149.92, 131.62, 126.39, 125.89, 125.52, 125.34, 124.87, 124.18, 122.23, 121.94, 108.73, 56.94, 40.53, 40.45, 40.36, 40.29, 40.20, 40.03, 39.86, 39.69, 39.53, 0.57. HR Tof-MS: 486.1604 [M+H], Melting point: >250 ℃.

7. Synthesis of Ru-Dimer with tpy 1:



Tpy **1** (49.2mg, 0.1mmol) was suspended in EtOH with 3 drops of N-Ethylmorpholine as a catalyst, $RuCl_3$ (13mg, 0.05 mmol) was added into the solvent, then the mixture was refluxed for 12 hours and the solvent was removed under vacuum, the residue was purified on Al_2O_3 column chromatography, the precipitate was dissolved in MeOH and NH_4PF_6 was added in, then a red solid was obtained by filtration (50mg, 82%). ^{1}H NMR (300 MHz, CD_3CN): δ 8.49 (s, 4H), 8.22-8.20 (d, J=6.02Hz, 4H), 8.01-7.98 (m, 2H), 7.86-7.76 (m, 10H), 7.62-7.52 (m, 8H), 7.43-7.40 (d, J=9.03Hz, 4H), 7.26-7.24 (d, J=6.02Hz, 4H), 7.16-7.12 (m, 4H), 6.91-6.88 (d, J=9.03Hz, 4H). ^{13}C NMR (126 MHz, CD3CN) δ 159.50, 158.01, 154.46, 151.99, 149.29, 141.11, 139.70, 138.61, 138.03, 136.72, 132.27, 131.07, 130.76, 130.17, 128.53, 127.83, 127.35, 126.31, 124.84, 124.05, 114.22, 54.97. ESI-MS: 541.9 [M^{2+}]. Melting point: >250 ℃.

8. Synthesis of Ru-Dimer with tpy 4 and *4*-methylbezenylterpyridine:



Tpy **4** (24.4mg, 0.05 mmol) was suspended in glycol with 3 drops N-Ethylmorpholine as a catalyst, *4*-methylbenzenyltepyridine mono $RuCl_3$ complexes (28 mg, 0.05mmol) was added into the solvent, then the mixture was refluxed for 12 hours and the solvent was removed under vacuum, the residue was purified on Al_2O_3 column chromatography, the precipitate was dissolved in MeOH and NH_4PF_6 was added in, then a red solid was obtained by filtration (12 mg, 25%). ^{1}H NMR (500 MHz, CD3CN): δ 10.01 (s, 1H), 9.56-9.54 (d, J=10Hz, 1H), 9.45-9.44 (d, J=5Hz, 1H), 9.33-9.31 (d, J=10Hz, 1H), 9.29-9.28 (d, J=5Hz, 1H), 9.08-9.07 (m, 3H), 8.89-8.87 (d, J=10Hz, 1H), 8.69-8.66 (m, 3H), 8.24-8.15 (m, 5H), 8.08-8.07 (d, J=5Hz, 1H), 7.91-7.90 (d, J=5Hz, 1H), 7.86-7.83 (m, 1H), 7.80-7.78 (d, J=5Hz, 1H), 7.68-7.66 (d, J=10Hz, 1H), 7.64-7.62 (d, J=10Hz, 1H), 7.49-7.47 (m, 1H), 7.36-7.33 (m, 3H),

7.27-7.24 (m, 1H), 6.96-6.94 (m, 2H), 4.04(s, 3H), 2.58 (s, 3H).ESI-MS: 541.9 [M^{2+}]. Melting point: >250 ℃.

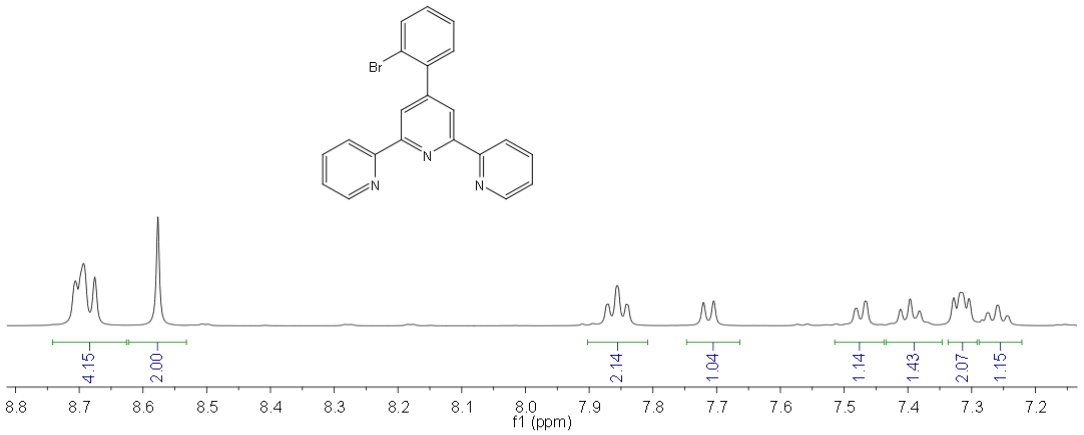


Fig.S1. ^{1}H NMR of Br-Tpy.

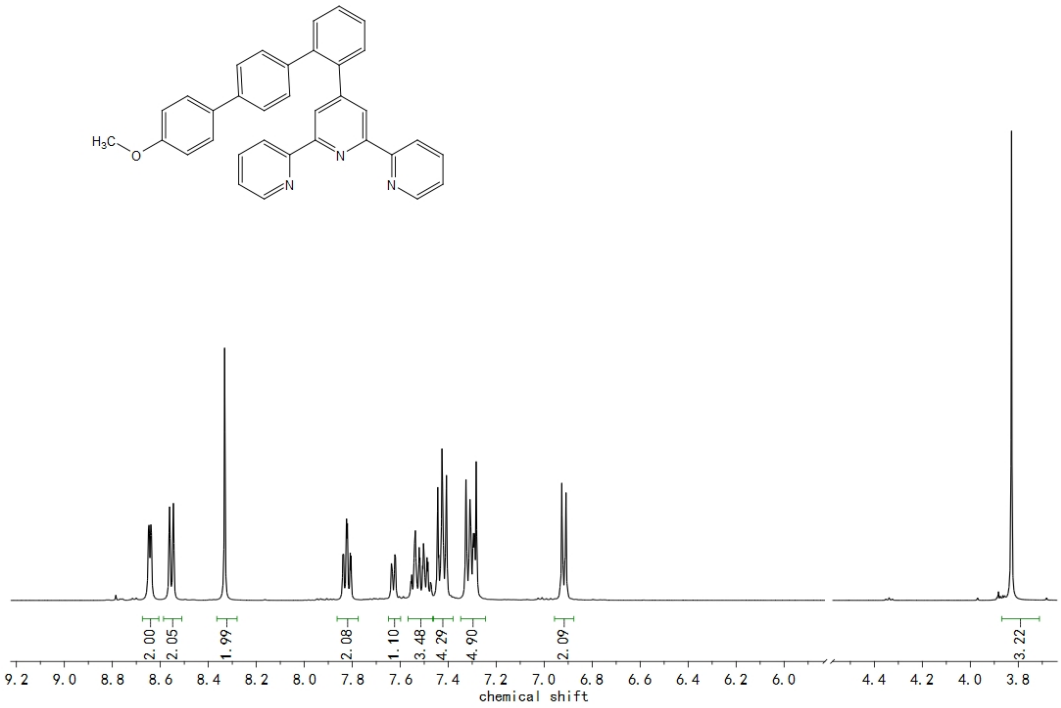


Fig.S2. ^{1}H NMR of tpy **1**.

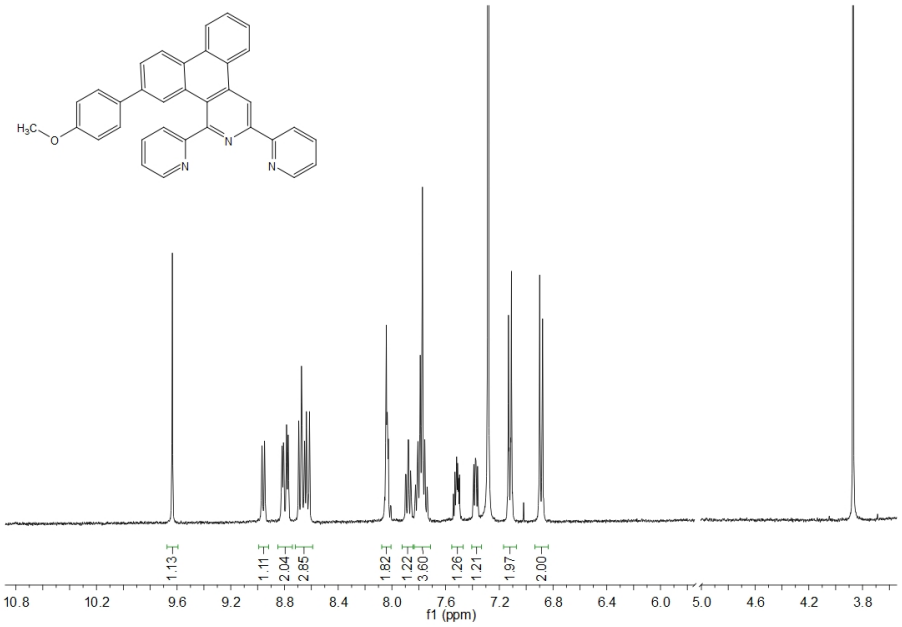


Fig.S3. ^{1}H NMR of tpy **2**.

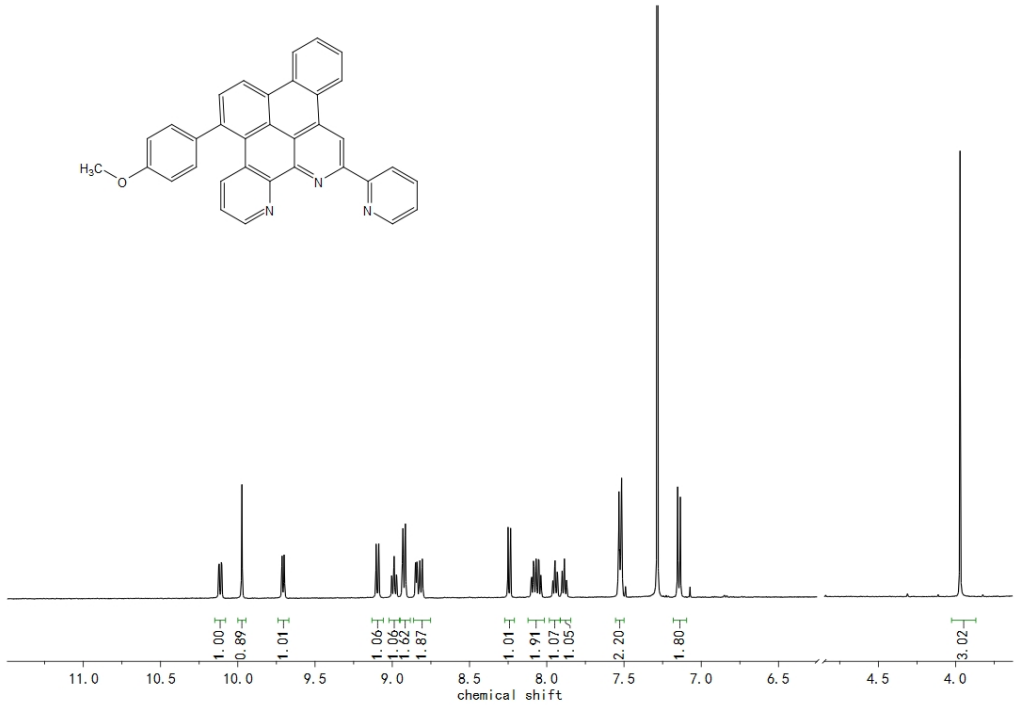


Fig. S4. ^{1}H NMR of tpy **3**.

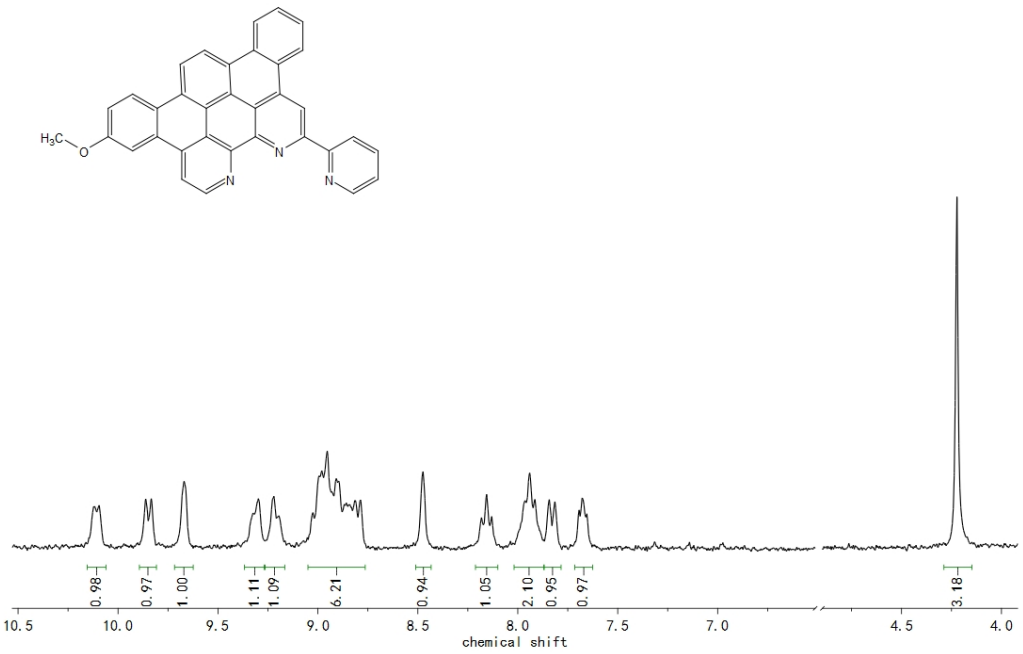


Fig. S5. ^{1}H NMR of tpy **4**.

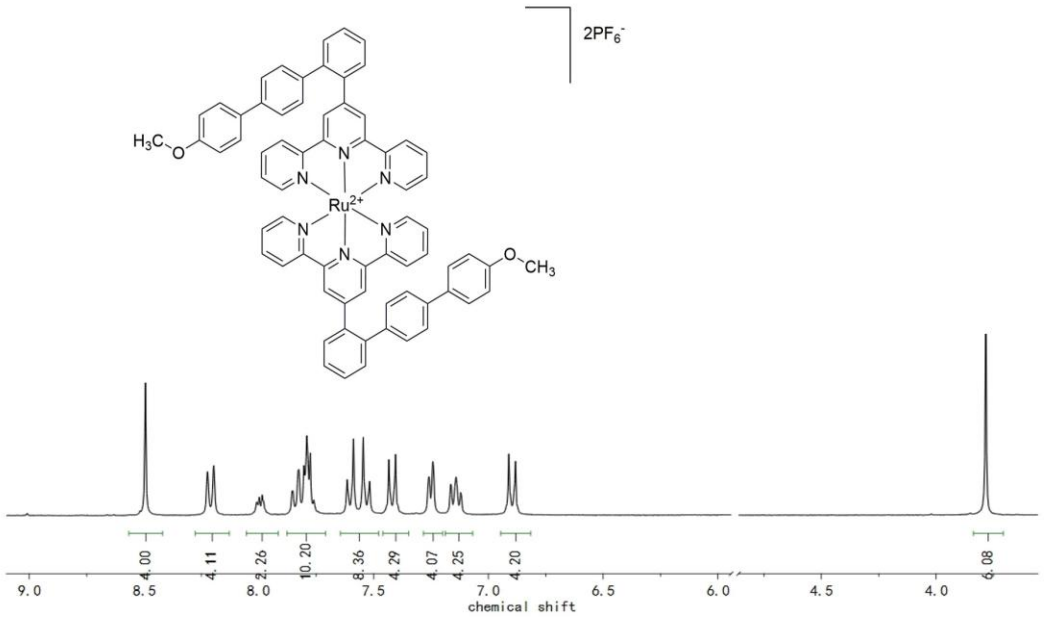


Fig. S6. ^{1}H NMR of Ru-Dimer **5**.

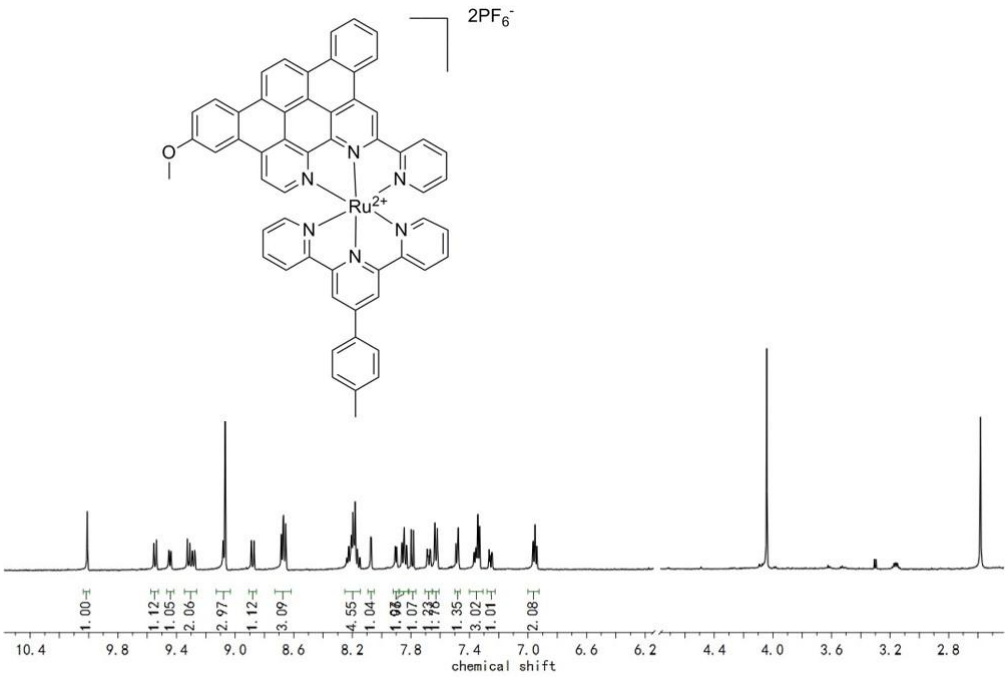


Fig. S7. ^{1}H NMR of hetero Ru-Dimer **7**.

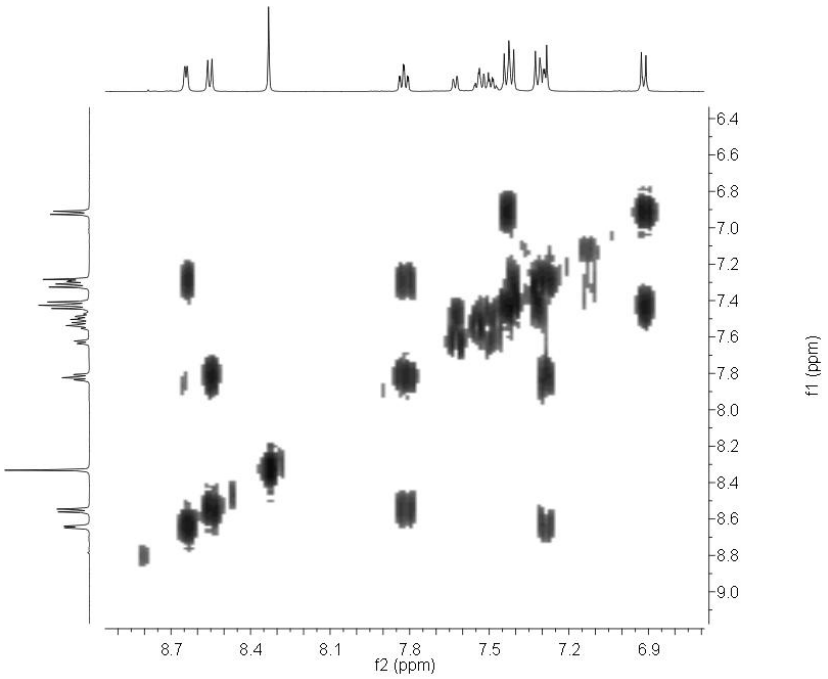


Fig.S8. H-H COSY of Tpy **1**.

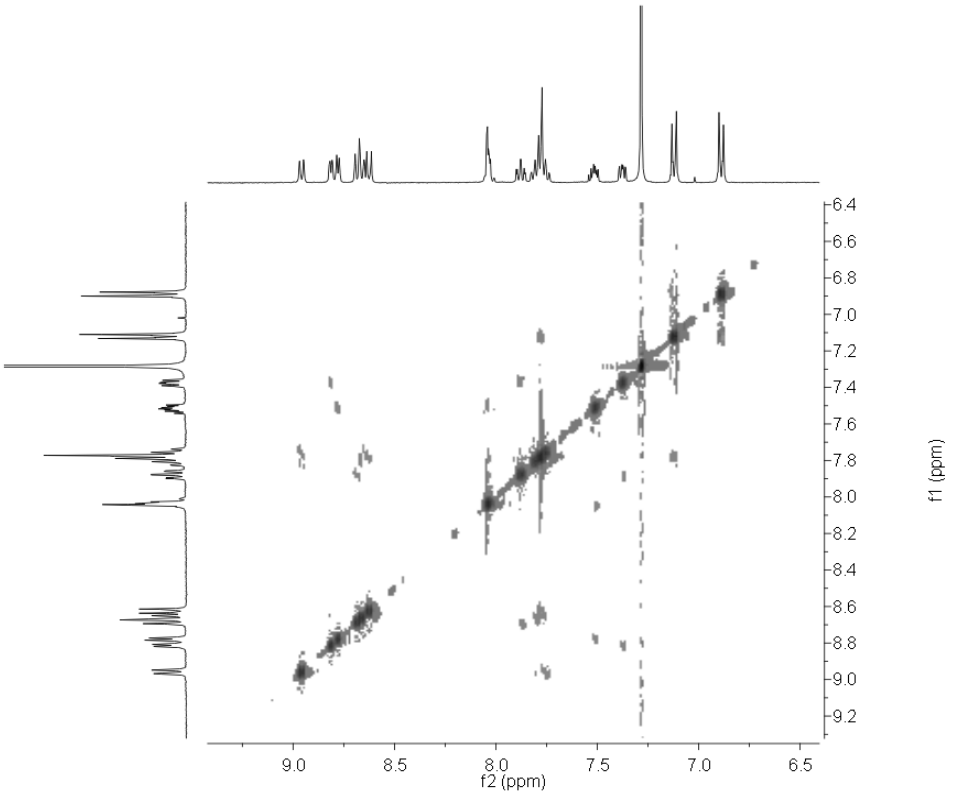


Fig. S9. ROESY of Tpy **2.**

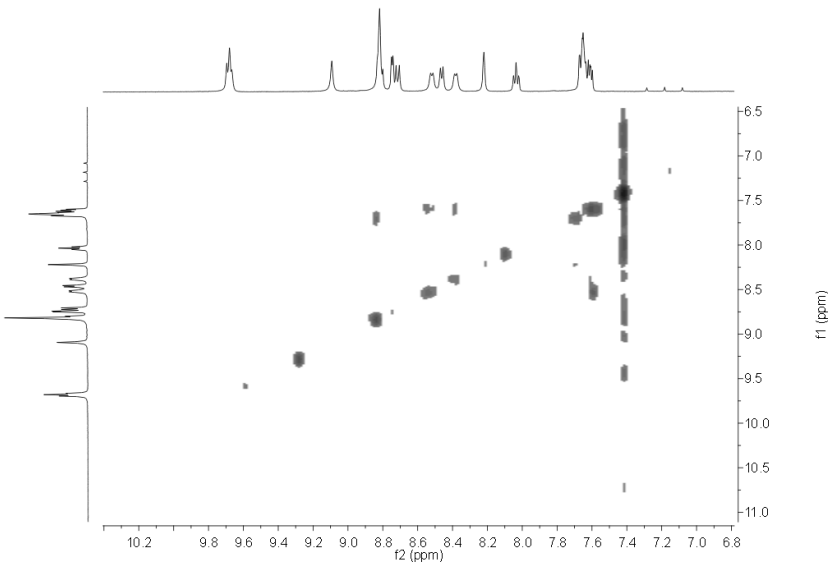


Fig. S10. H-H COSY of Tpy **4**.

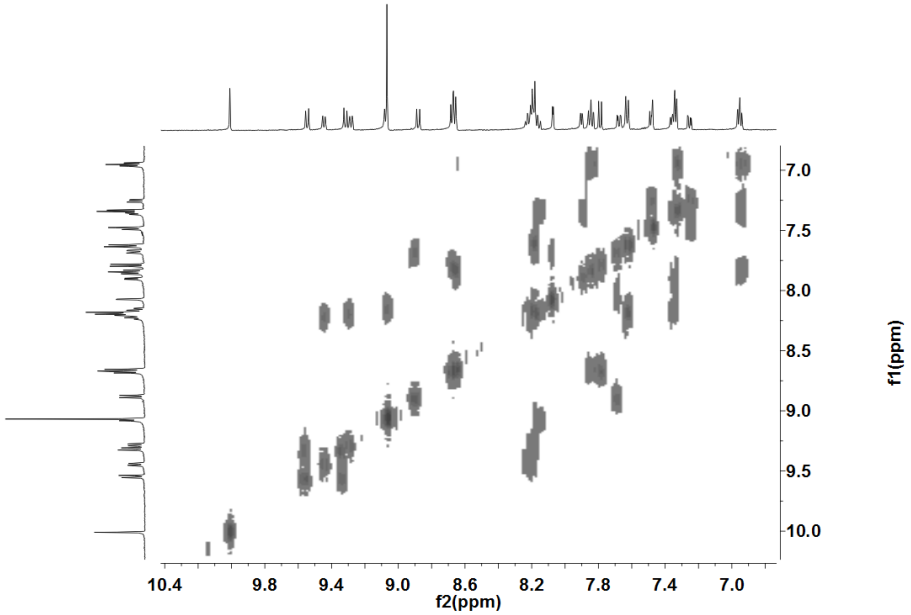


Fig. S11. H-H COSY of hetero Ru-Dimer **7**.

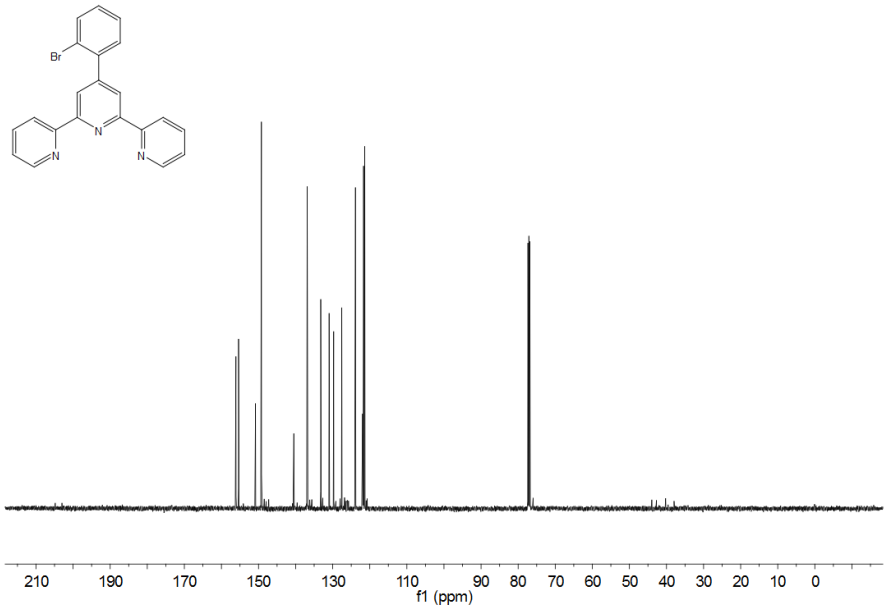


Fig. S12: ^{13}C NMR of Br-Tpy.

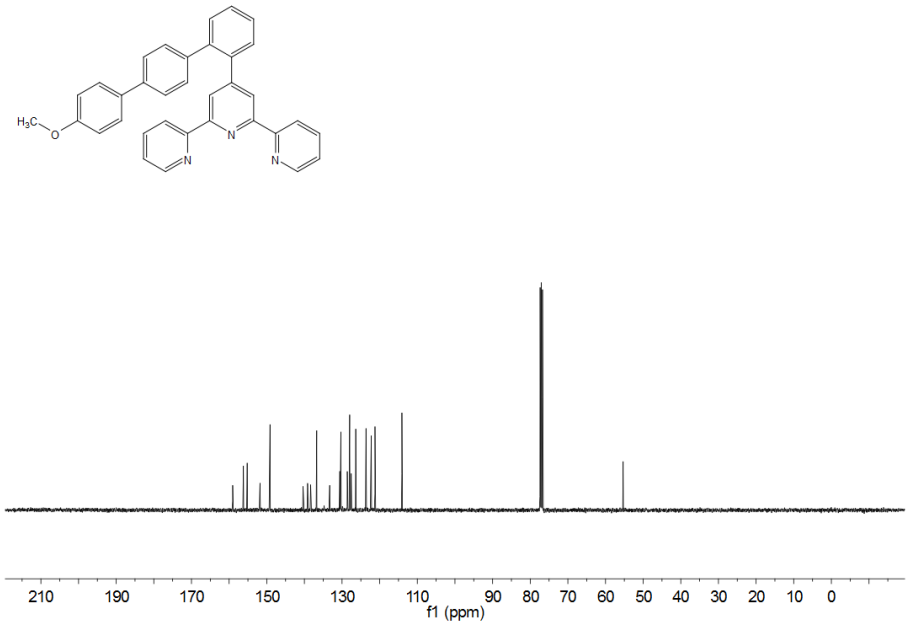


Fig. S13: ^{13}C NMR of Tpy **1**.

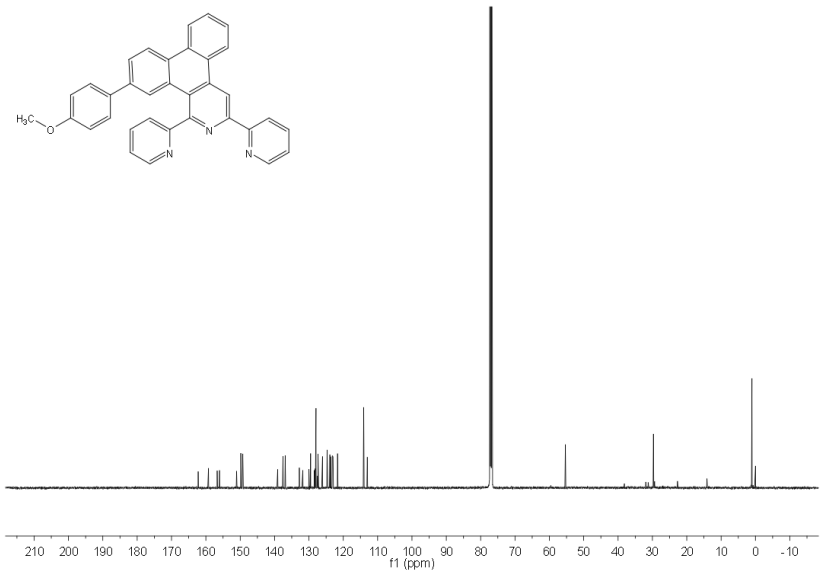


Fig.S14. ^{13}C NMR of Tpy **2**.

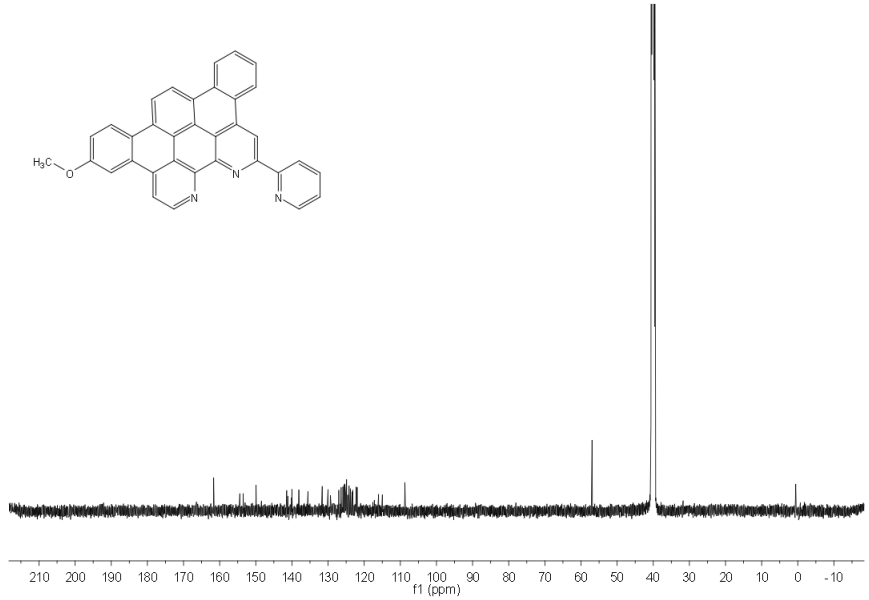


Fig.S15. ^{13}C NMR of Tpy **4**.

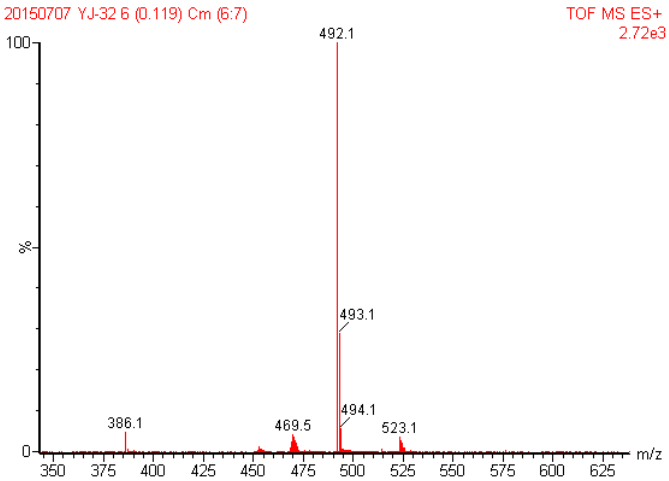


Fig. S16. MS of Tpy 1.

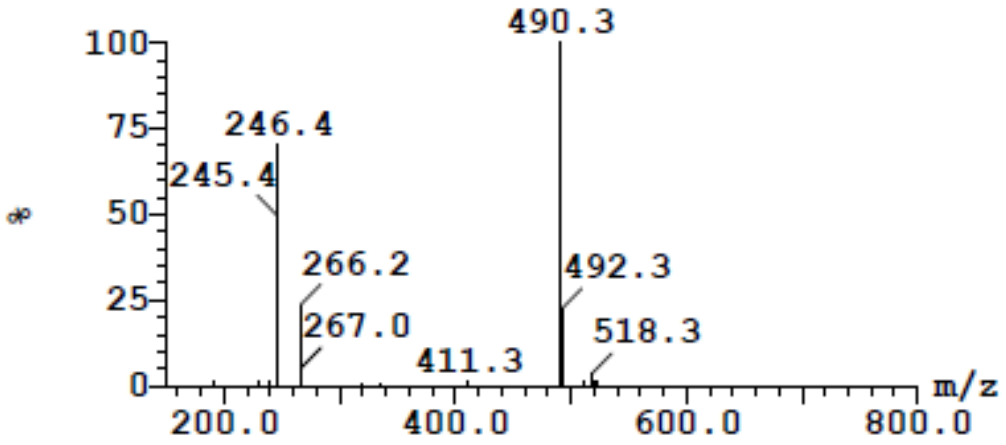


Fig. S17. MS of Tpy **2.**

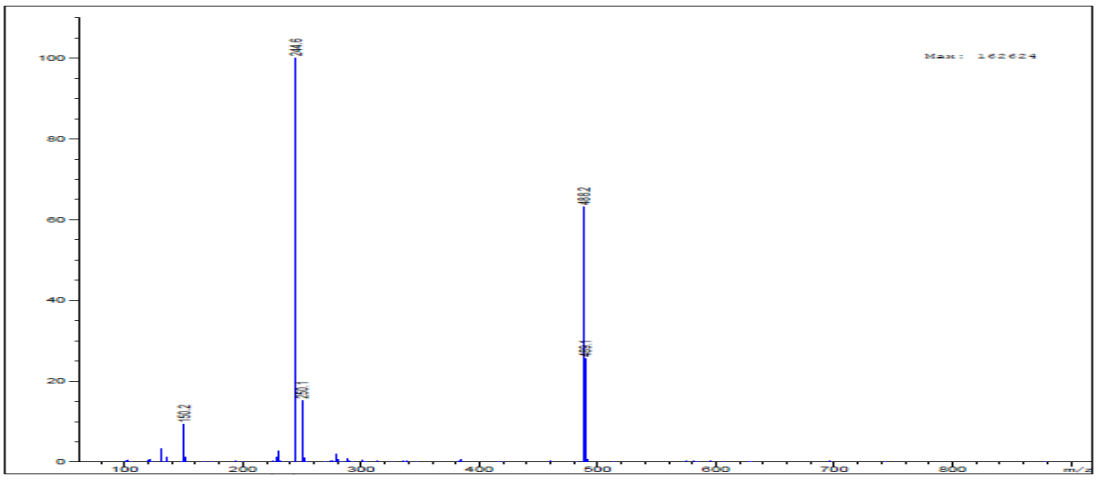


Fig. S18. MS of Tpy **3.**

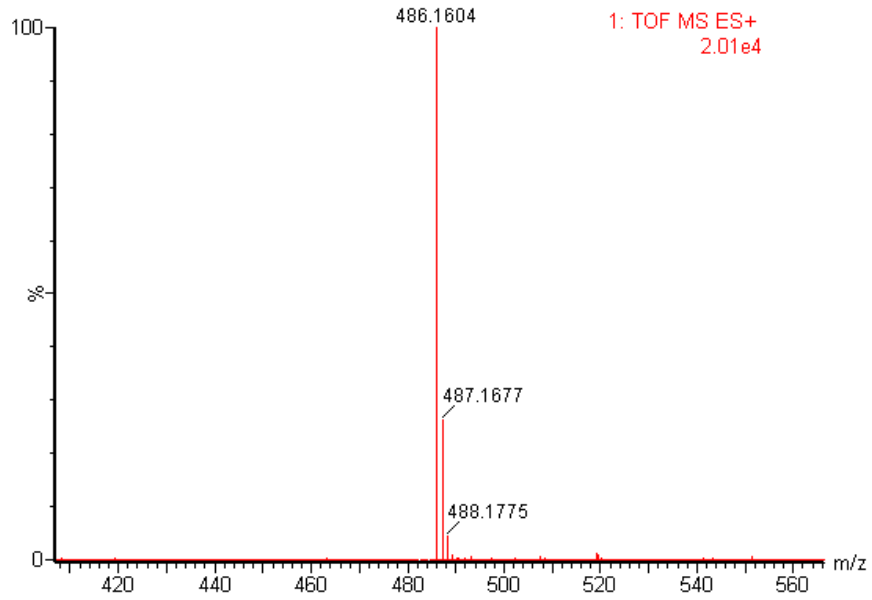


Fig. S19. high resolution MS of Tpy **4.**

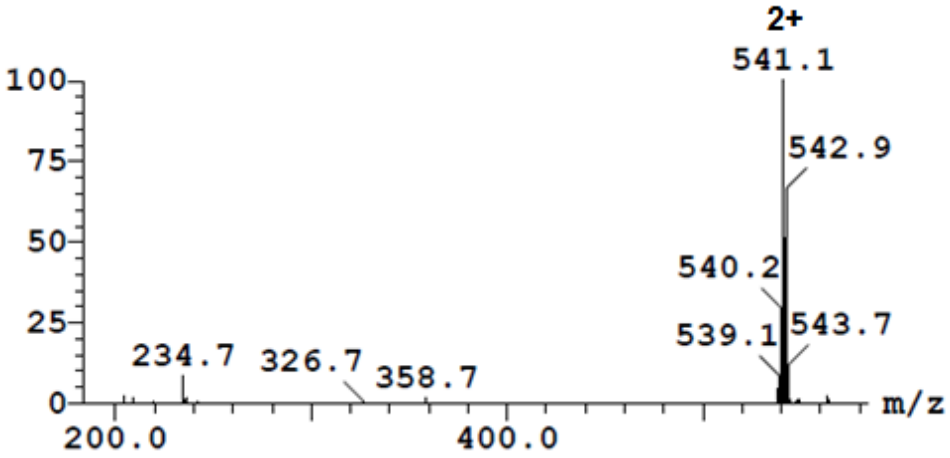


Fig. S20. MS of Ru-Dimer **5.**

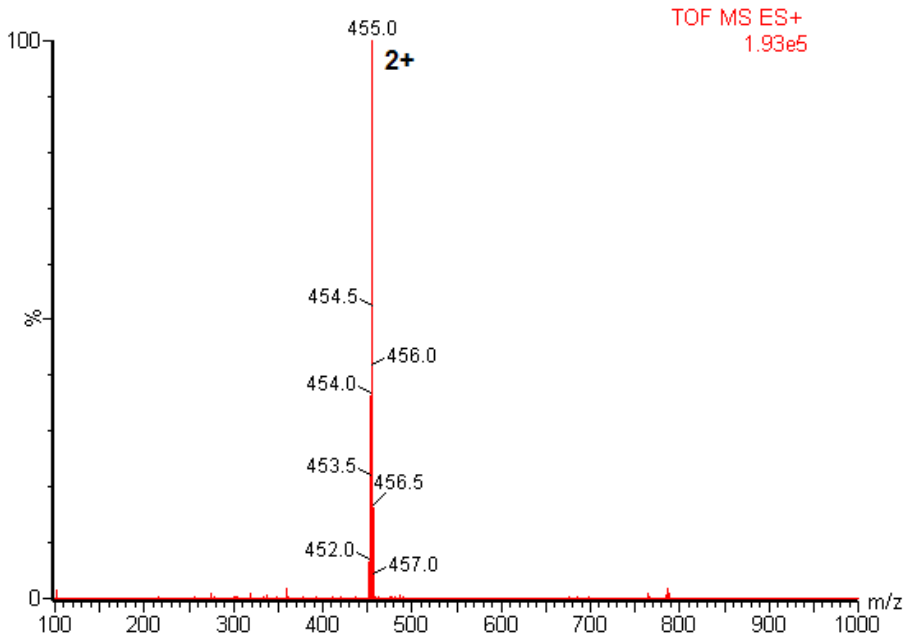


Fig. S21. MS of hetero Ru-Dimer **7.**

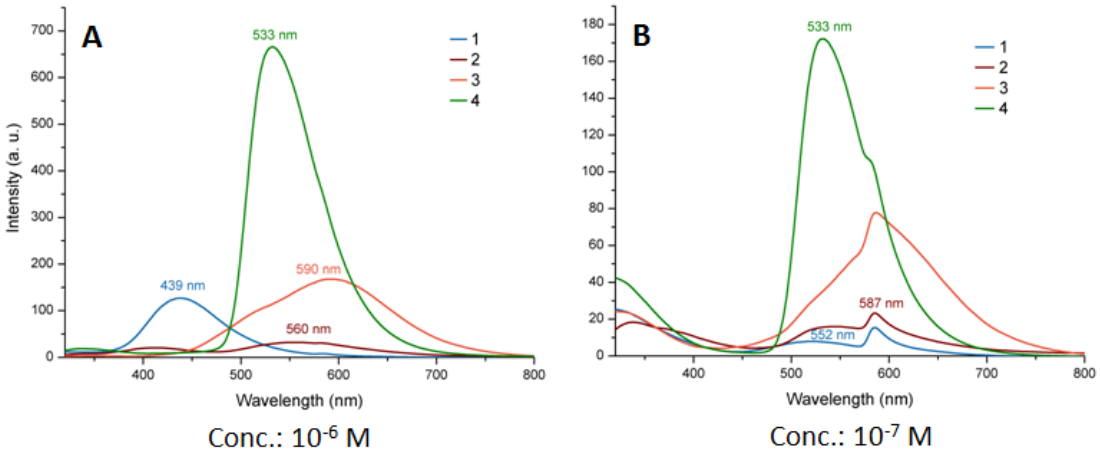


Fig. S22. Compared emission spectra of Tpy **1**-**4** measured at different concentrations. A-left, concentration at 10^{-6} M; and B-right, concentration at 10^{-7} M.

Reference:
S1. Liang, Y.-P.; He, Y.-J.; Lee, Y.-H.; Chan, Y.-T. *Dalton Trans.***2015**, *44*, 5139-5145.
S2. Kulhanek, J.; Bures F.; Ludwig, M. *Beilstein J of Org. Chem.***2009,** *5(11)*, doi:10.3762/bjoc.5.11.