Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synthesis and Characterization of a Modified "Picket Fence" Porphyrin Complex — Stronger π Bonding Interactions between Fe(II) and Axial Ligands

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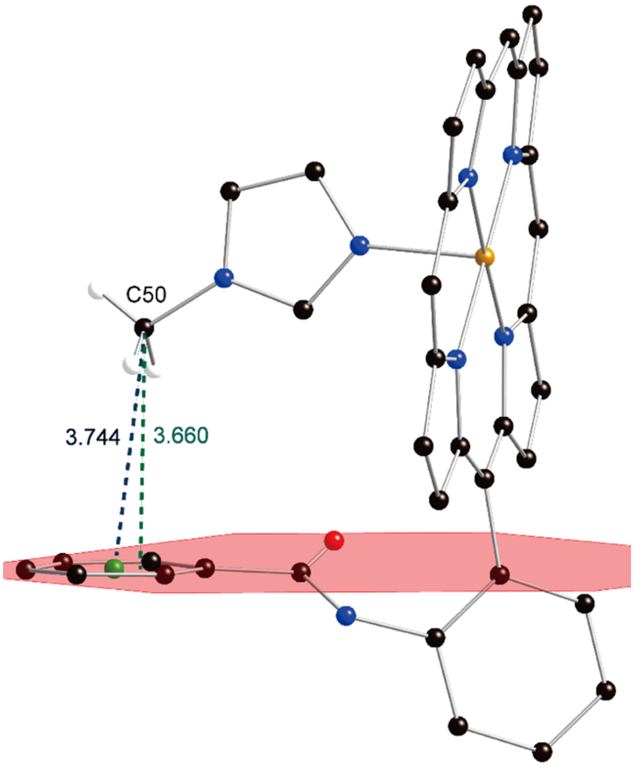

Figure S1. Distances between C50 and the benzene group on picket. The blue dotted line represents the distance between C50 and the center of benzene group (the green spot) and the distance is shown in figure as the blue number in Å. The green line represents the distance between C50 and the mean plane of benzene group (the pink plane) and the distance is shown in figure as the green number in Å. Three pickets and one 1-MeIm have been omitted for clarity.

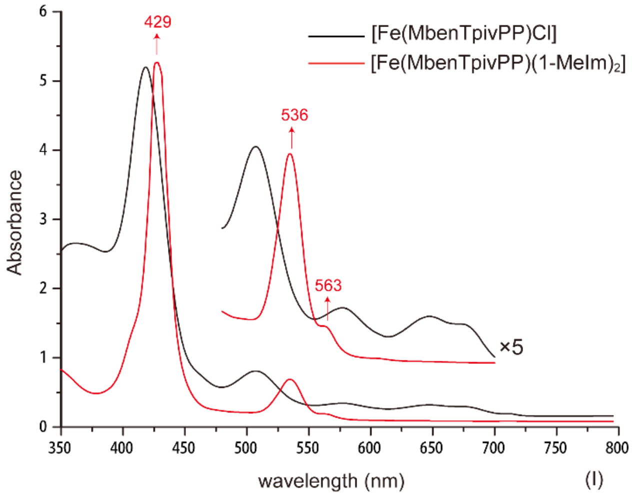

Figure S2 (I). The UV-vis spectra of [Fe(MbenTpivPP)Cl] (black) and [Fe(MbenTpivPP)(1-MeIm)$_2$] (red) were taken in benzene under argon atmosphere. The spectra from 480 to 700 nm are enlarged by 5 times.

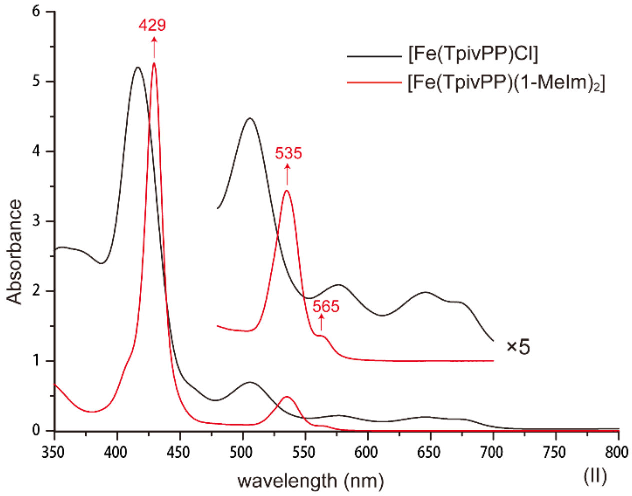

Figure S2 (II). The UV-vis spectra of [Fe(TpivPP)Cl] (black) and [Fe(TpivPP)(1-MeIm)$_2$] (red) were taken in benzene under argon atmosphere. The spectra from 480 to 700 nm are enlarged by 5 times.

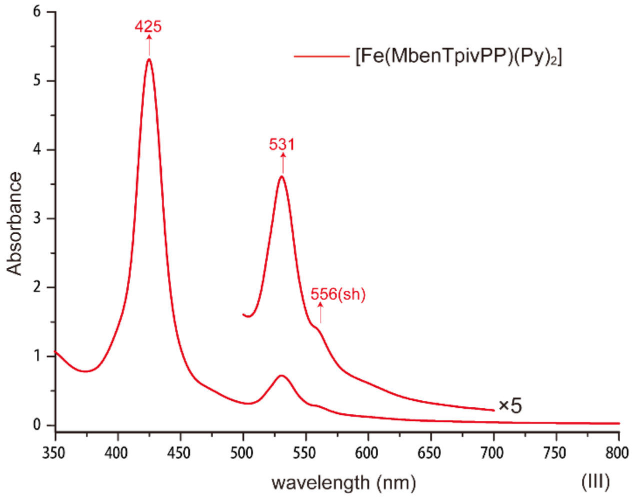

Figure S2 (III). The UV-vis spectrum of [Fe(MbenTpivPP)(Py)$_2$] was taken in benzene under argon atmosphere. The spectrum from 500 to 700 nm is enlarged by 5 times. The UV-vis data of [Fe(TpivPP)(Py)$_2$] was reported as: 425, 532 nm in THF.[1]

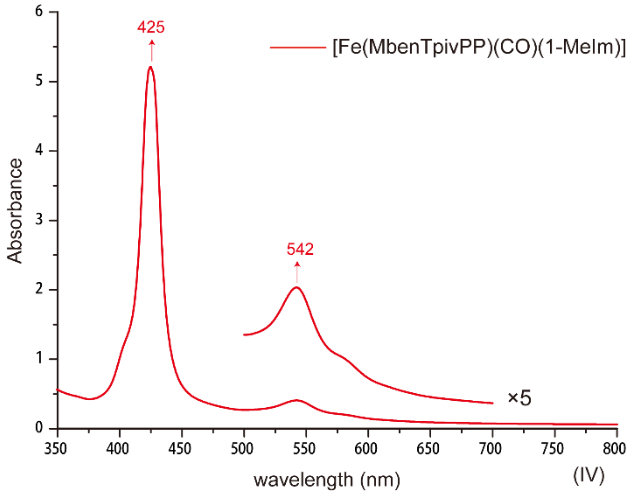

Figure S2 (IV). The UV-vis spectrum of [Fe(MbenTpivPP)(CO)(1-MeIm)] was taken in benzene under argon atmosphere. The spectrum from 500 to 700 nm is enlarged by 5 times. The UV-vis data of [Fe(TpivPP)(CO)(1-MeIm)] was reported as: 427, 542 nm in THF.[1]

1. J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang and W. T. Robinson, *J. Am. Chem. Soc.*, 1975, **97**, 1427.

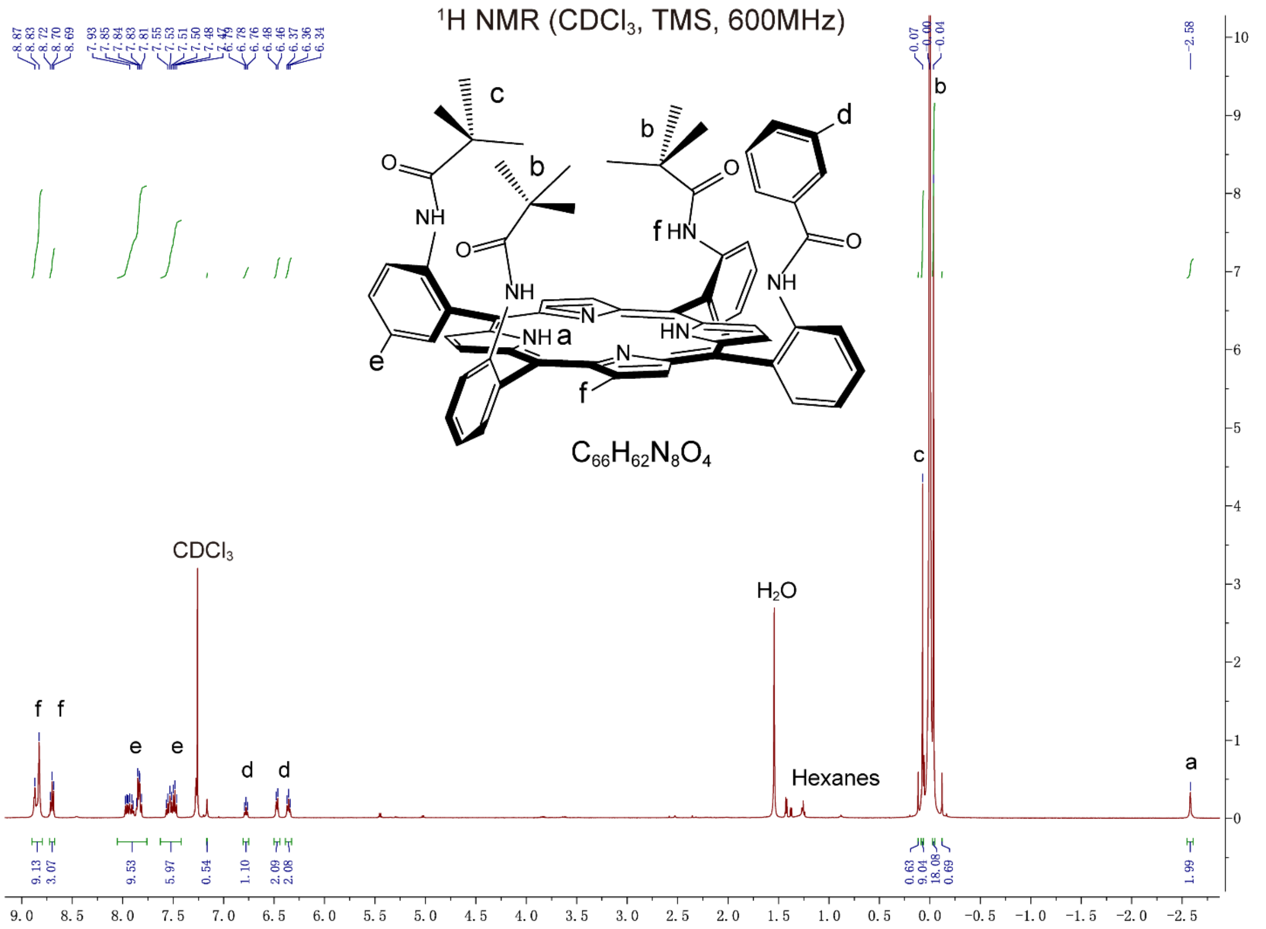

Figure S3. ^{1}H NMR (600MHz, CDCl$_3$, TMS) spectrum of H$_2$MbenTpivPP: δ -2.59 (s, 2H, NH$_{\text{pyrr}}$), -0.04 (s, 18H, CH$_3$), 0.07 (s, 9H, CH$_3$), 6.33–6.39 (t, J = 7.7 Hz, 2H, CH$_{\text{ben}}$), 6.44–6.50 (d, J = 7.6 Hz, 2H, CH$_{\text{ben}}$), 6.75–6.81 (t, J = 7.3 Hz, 1H, CH$_{\text{ben}}$), 7.42–7.63 (m, 6H, CH$_{\text{aryl}}$), 7.76–8.05 (m, 10H, CH$_{\text{aryl}}$), 8.67–8.72 (t, J = 7.6 Hz, 3H, NH$_{\text{piv}}$ and CH$_{\beta\text{pyrr}}$), 8.80–8.90 (d, J = 20.5 Hz, 9H, NH$_{\text{piv}}$ and CH$_{\beta\text{pyrr}}$)

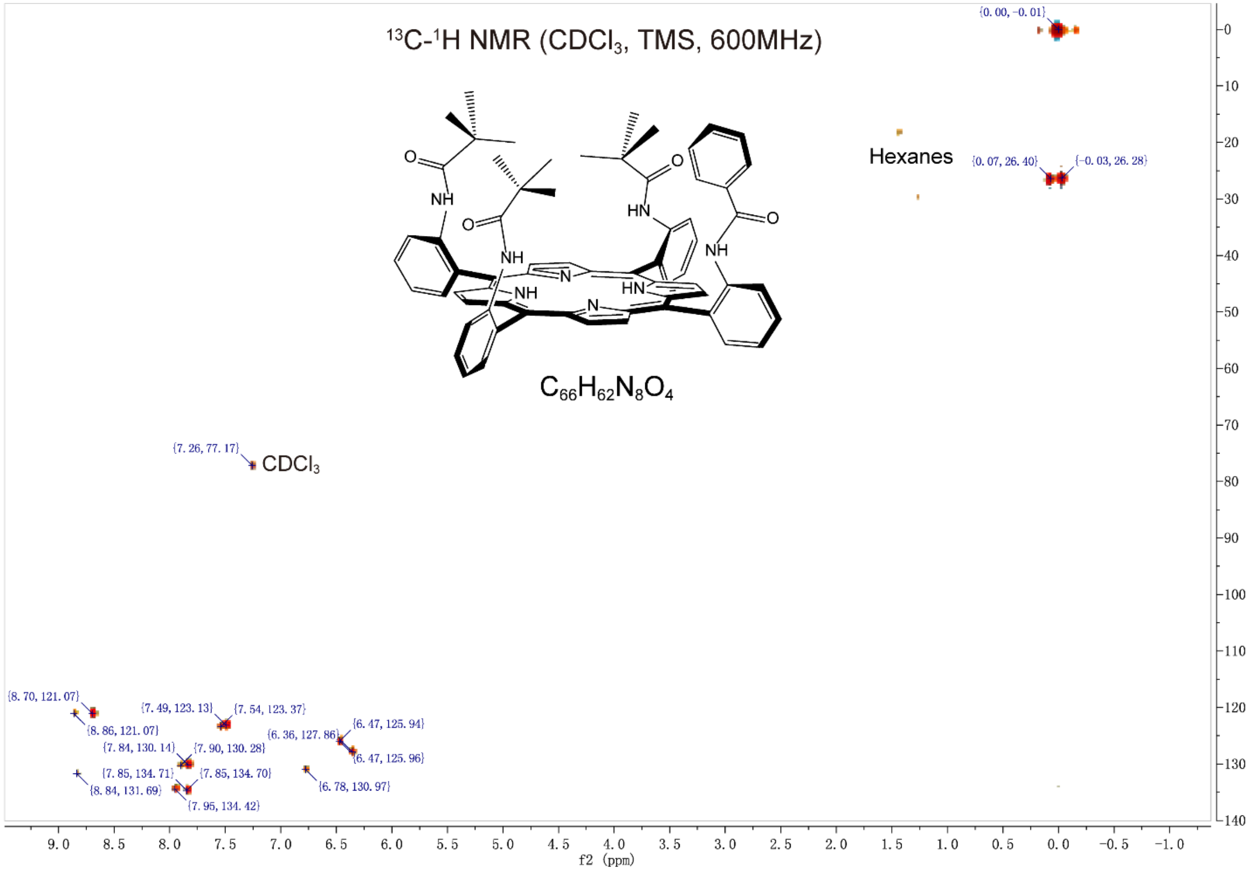

Figure S4. ^{13}C–^{1}H NMR (150MHz, CDCl$_3$, TMS) spectrum of H$_2$MbenTpivPP: ^{1}H NMR: δ_{H} -0.03, 0.07 (CH$_3$), 6.36, 6.47, 6.78 (H$_{\mathrm{ben}}$), 7.49, 7.54, 7.84, 7.85, 7.90, 7.95 (H$_{\mathrm{aryl}}$), 8.70, 8.84, 8.86 (H$_{\beta\mathrm{pyrr}}$); ^{13}C NMR: δ_{C} 26.28, 26.40 (CH$_3$), 125.94, 125.96, 127.86 (C$_{\mathrm{ben}}$), 123.13, 123.37, 130.14, 130.28, 134.42, 134.70, 134.71 (C$_{\mathrm{aryl}}$), 121.06, 121.07, 131.69 (C$_{\mathrm{pyrr}}$).

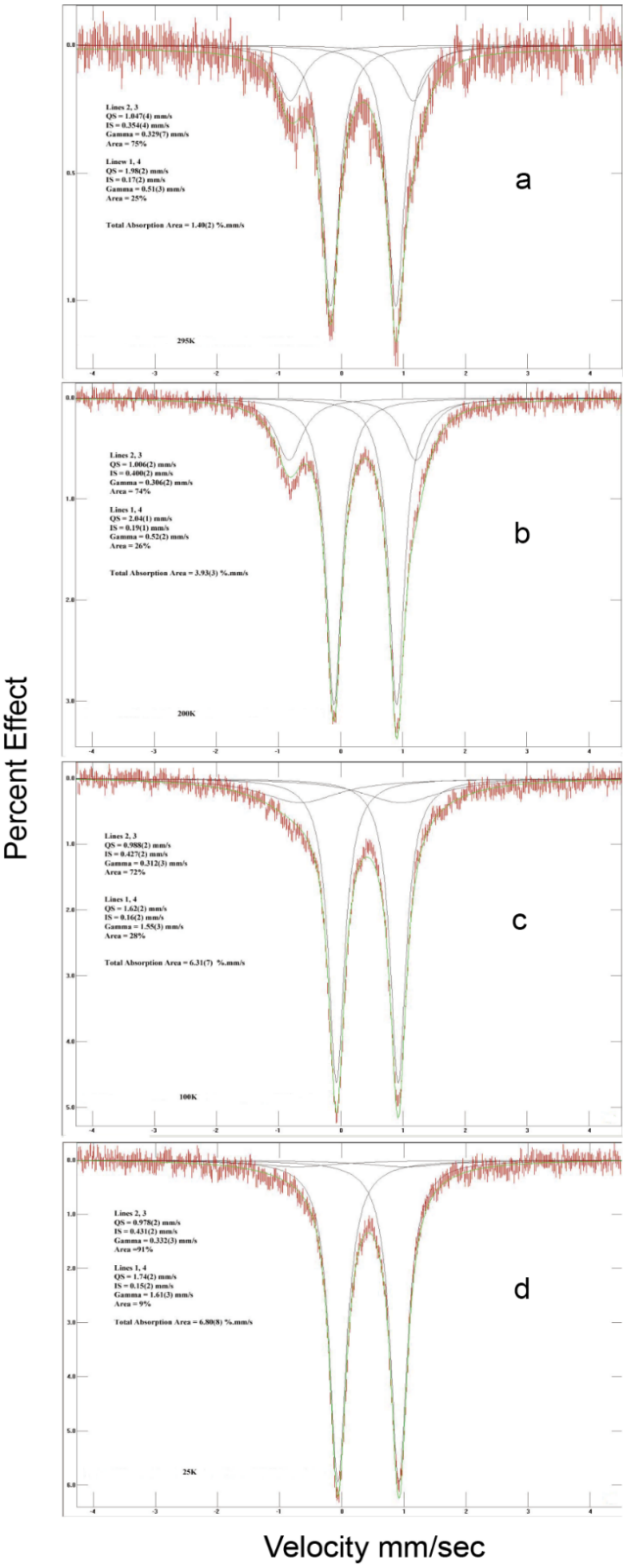

Figure S5. Figures showing experimental Mössbauer spectra for [Fe(MbenTpivPP)(1-MeIm)$_2$] over a range of temperatures: (a) 295 K, (b) 200 K, (c) 100 K, (d) 25 K.