

Supporting Information to accompany:

Hinged and wide: a new P[^]P ligand for emissive [Cu(P[^]P)(N[^]N)][PF₆] complexes

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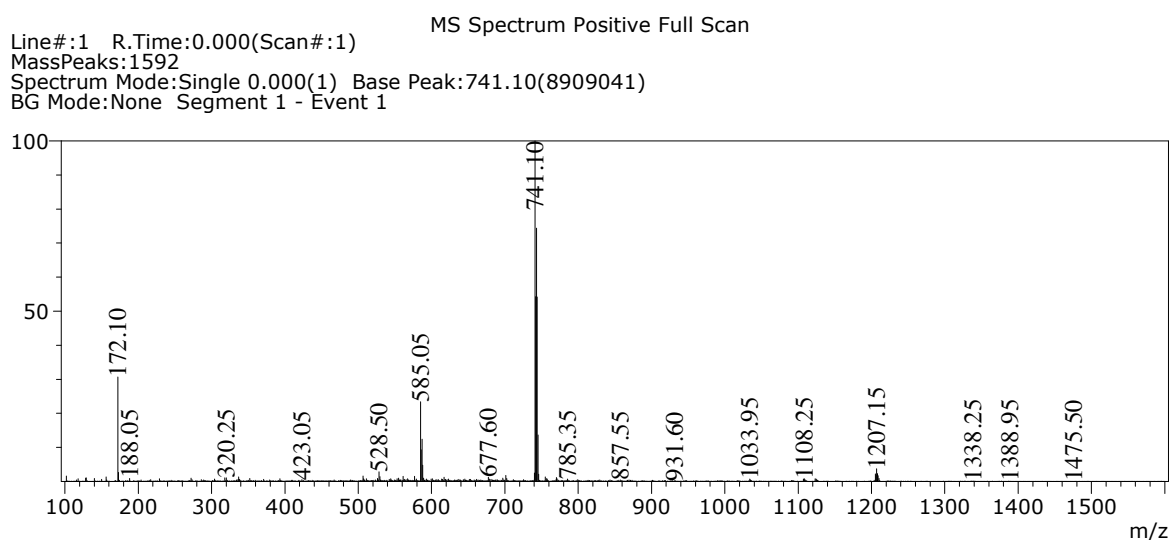


Figure S1. Electrospray mass spectrum (positive mode) of [Cu(BIPHEP)(bpy)][PF₆].

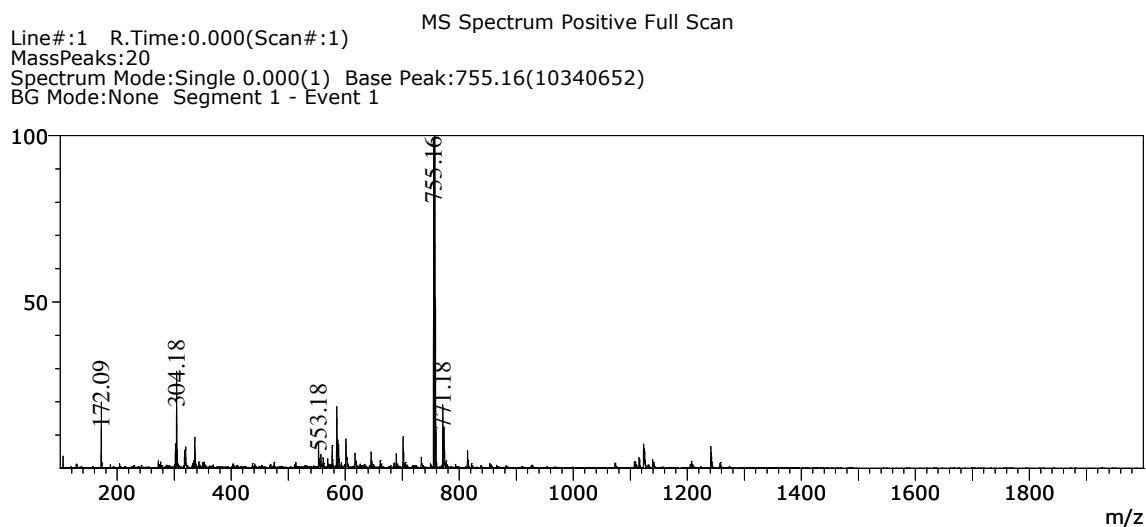


Figure S2. Electrospray mass spectrum (positive mode) of [Cu(BIPHEP)(6-Mebpy)][PF₆].

MS Spectrum Positive Full Scan
Line#:1 R.Time:0.000(Scan#:1)
MassPeaks:9
Spectrum Mode:Single 0.000(1) Base Peak:769.28(8365829)
BG Mode:None Segment 1 - Event 1

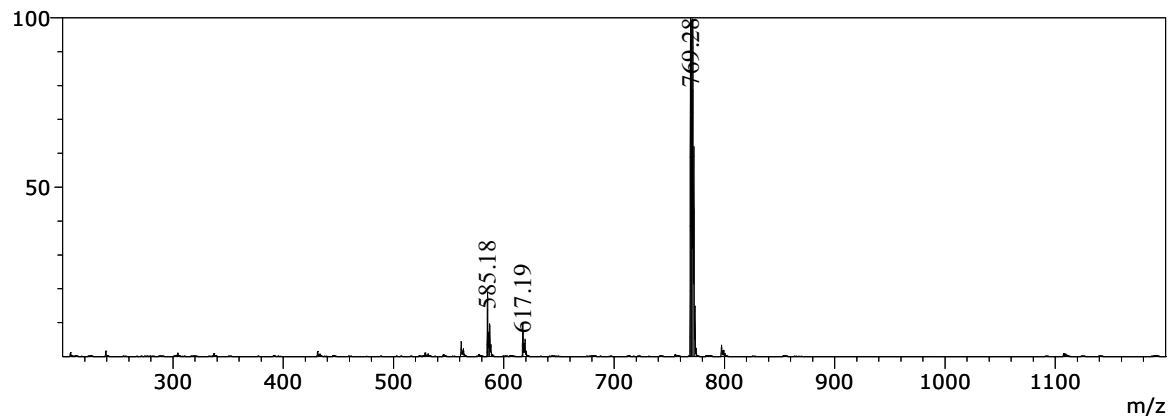


Figure S3. Electrospray mass spectrum (positive mode) of [Cu(BIPHEP)(6-Etbp)][PF₆].

MS Spectrum Positive Full Scan
Line#:1 R.Time:0.000(Scan#:1)
MassPeaks:6
Spectrum Mode:Single 0.000(1) Base Peak:769.28(8324878)
BG Mode:None Segment 1 - Event 1

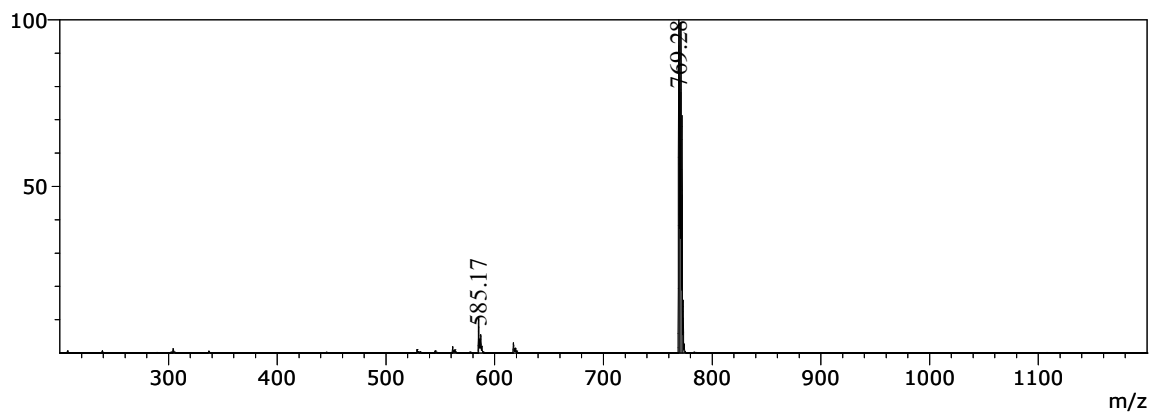


Figure S4. Electrospray mass spectrum (positive mode) of [Cu(BIPHEP)(5,5'-Me₂bp)][PF₆].

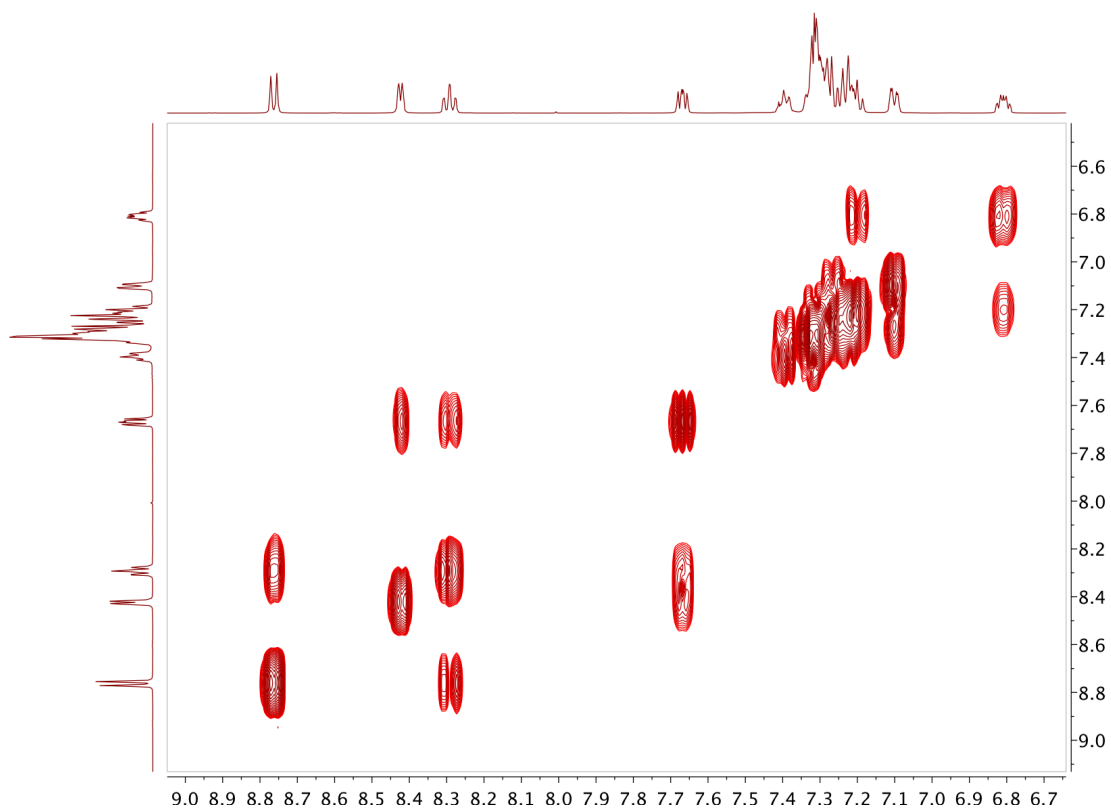


Figure S5. COSY spectrum of $[\text{Cu}(\text{BIPHEP})(\text{bpy})][\text{PF}_6]$ (500 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

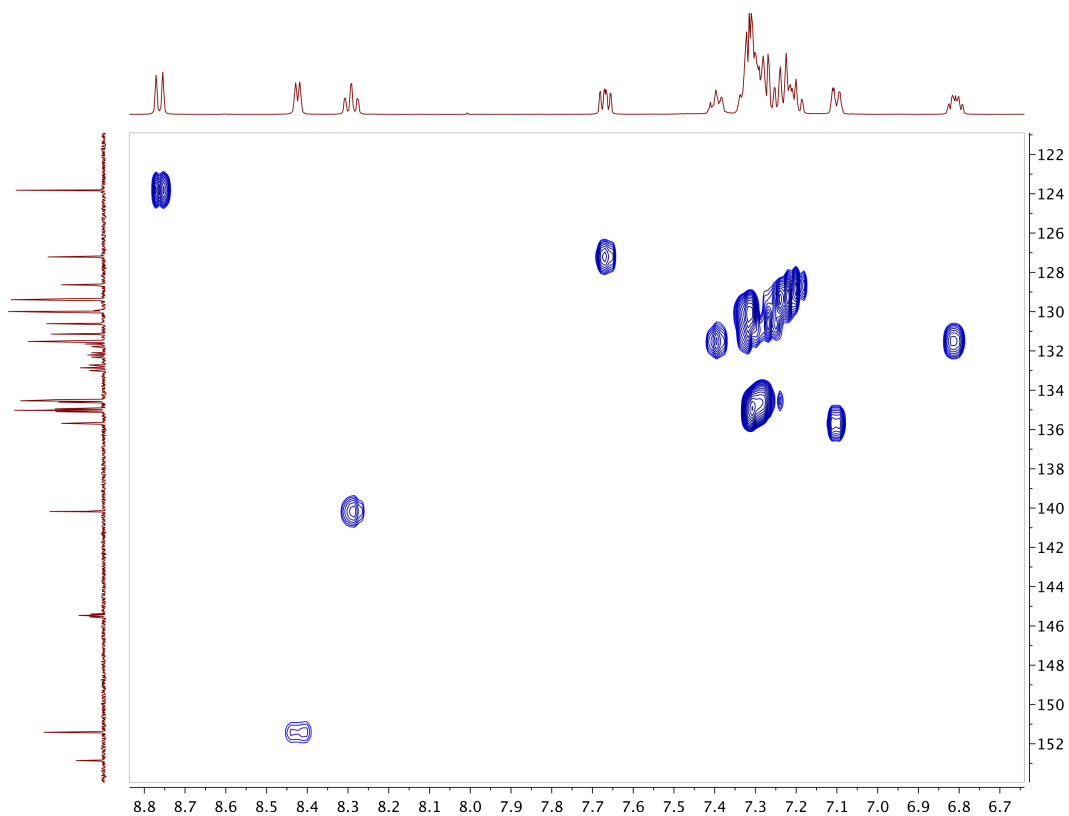


Figure S6. HMBC spectrum of $[\text{Cu}(\text{BIPHEP})(\text{bpy})][\text{PF}_6]$ (^1H 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ 126 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

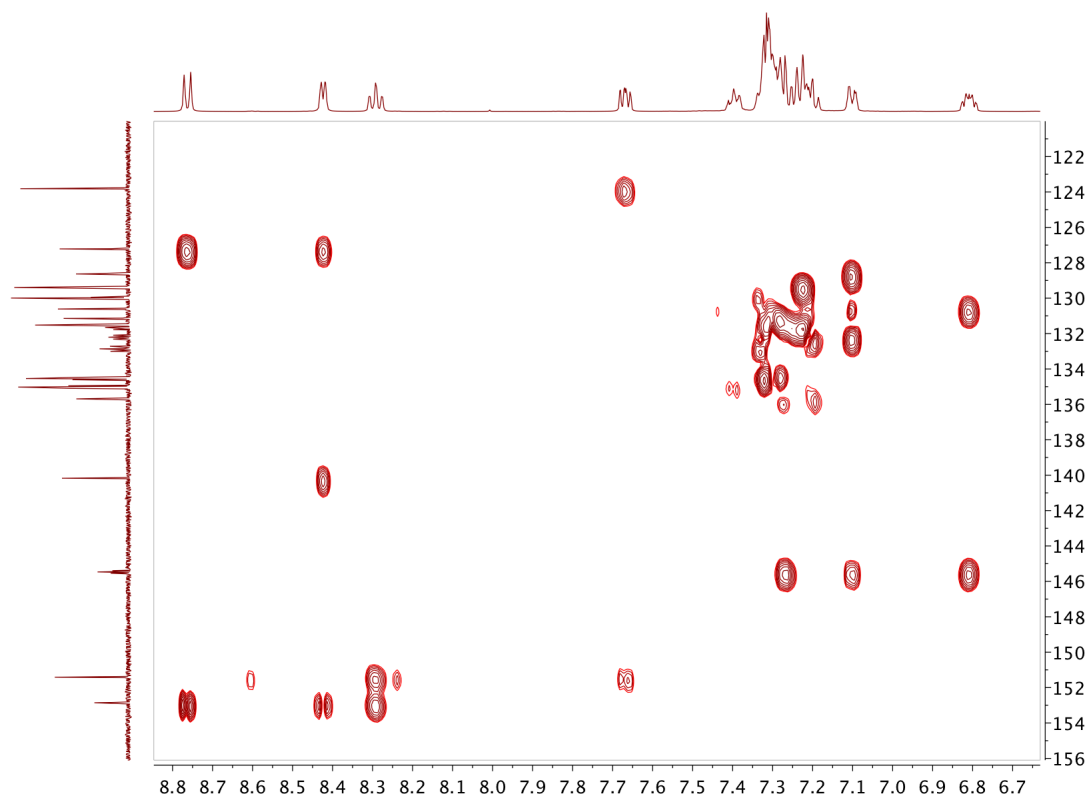


Figure S7. HMBC spectrum of [Cu(BIPHEP)(bpy)][PF₆] (¹H 500 MHz, ¹³C{¹H} 126 MHz, acetone-*d*₆, 298 K). Scales: δ / ppm.

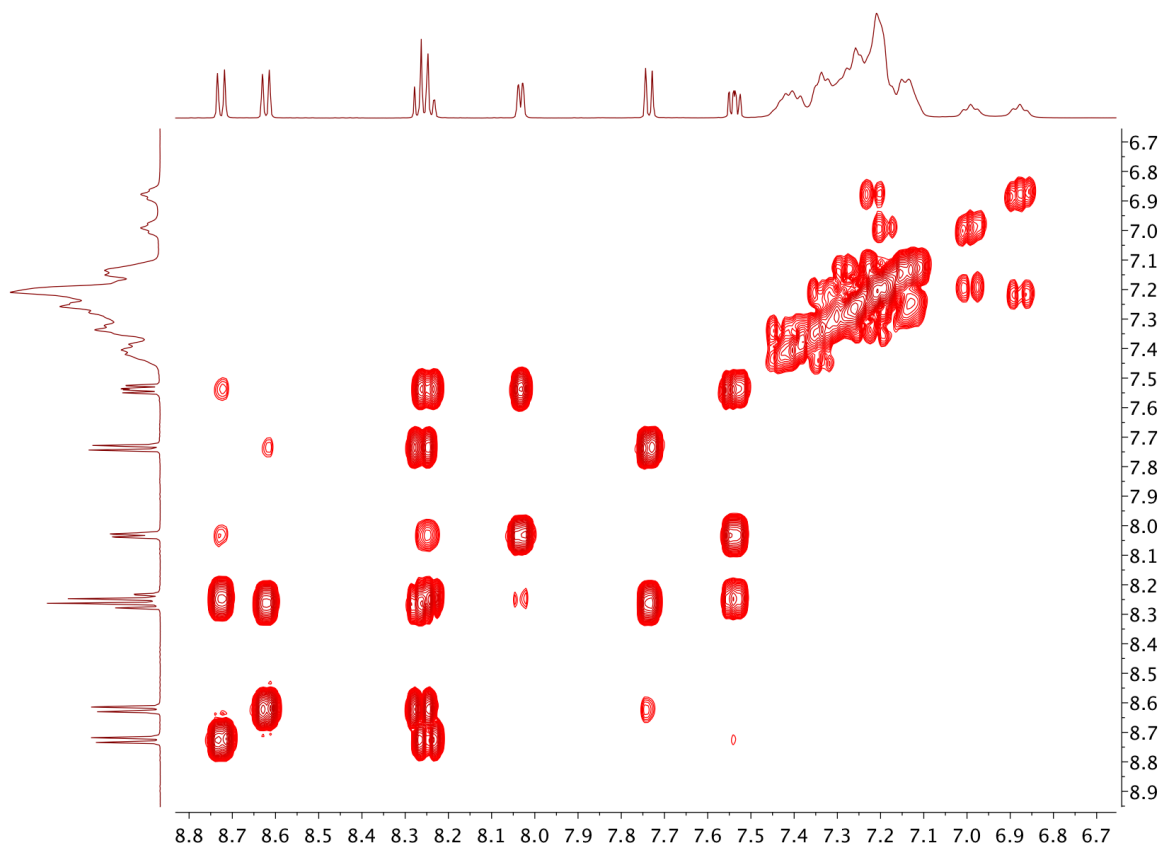


Figure S8. COSY spectrum of [Cu(BIPHEP)(6-Mebpy)][PF₆] (500 MHz, acetone-*d*₆, 298 K). Scales: δ / ppm.

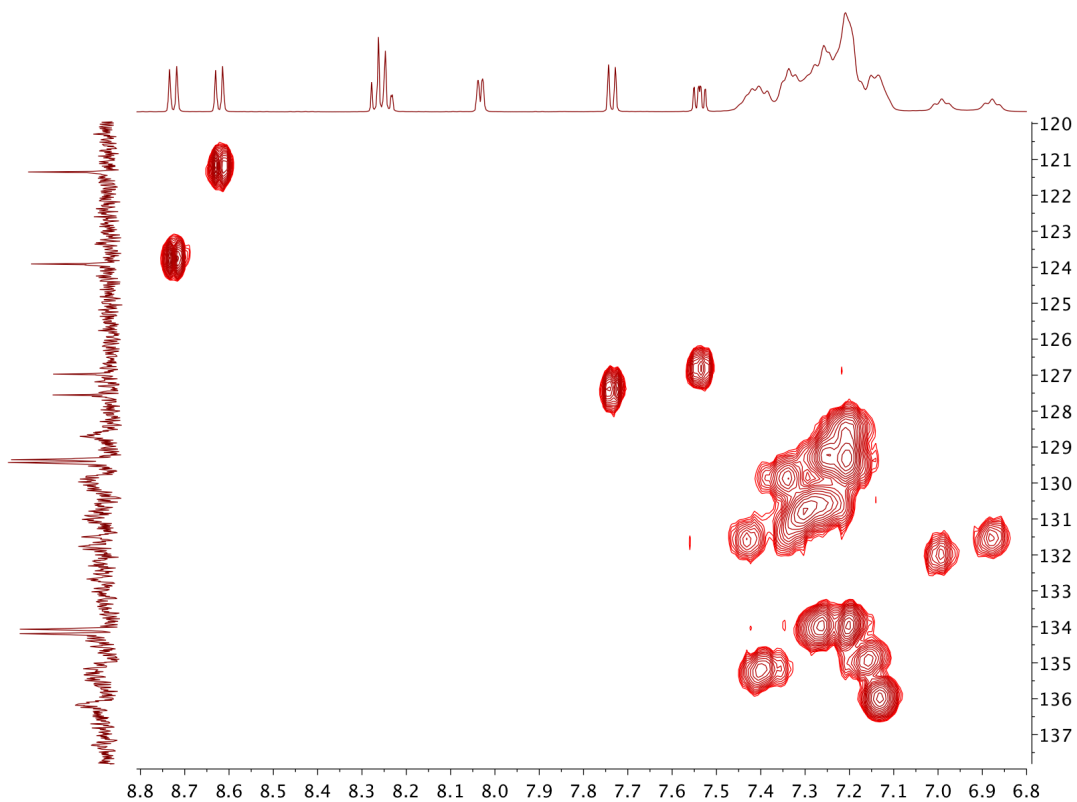


Figure S9. HMQC spectrum of $[\text{Cu}(\text{BIPHEP})(6\text{-Mebpy})][\text{PF}_6]$ (^1H 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ 126 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

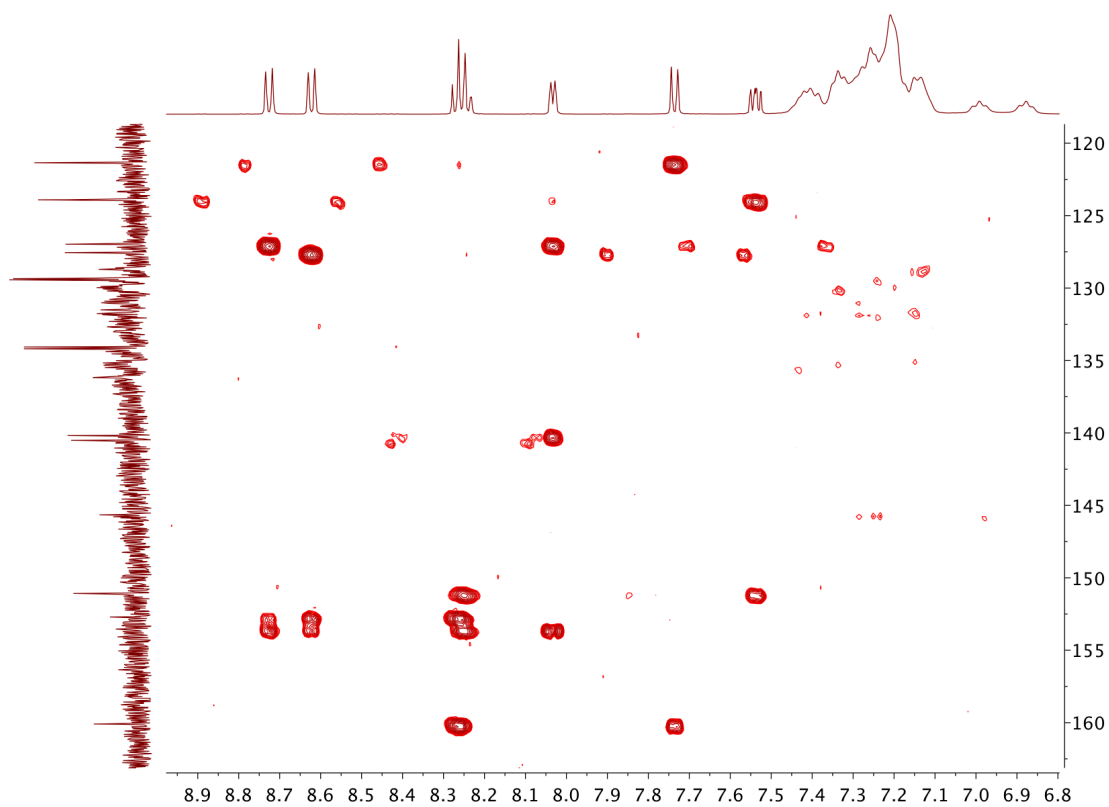


Figure S10. HMBC spectrum of $[\text{Cu}(\text{BIPHEP})(6\text{-Mebpy})][\text{PF}_6]$ (^1H 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ 126 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

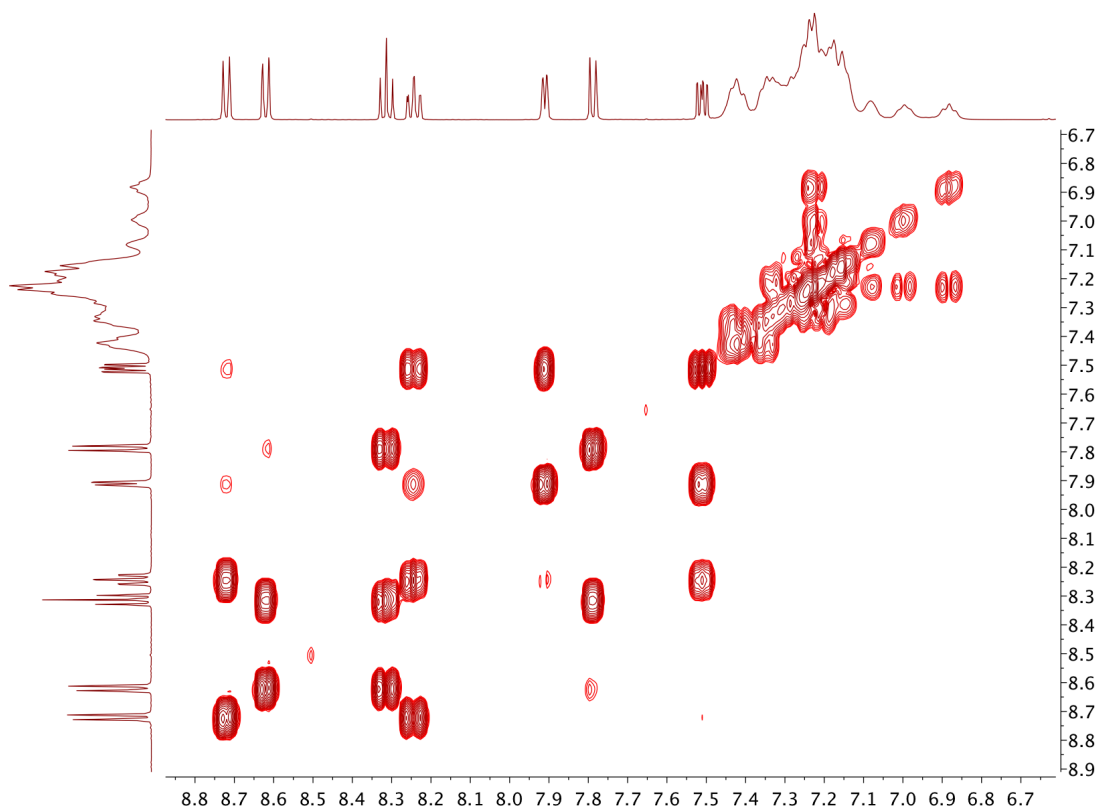


Figure S11. COSY spectrum of $[\text{Cu}(\text{BIPHEP})(6\text{-Etbp})][\text{PF}_6]$ (500 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

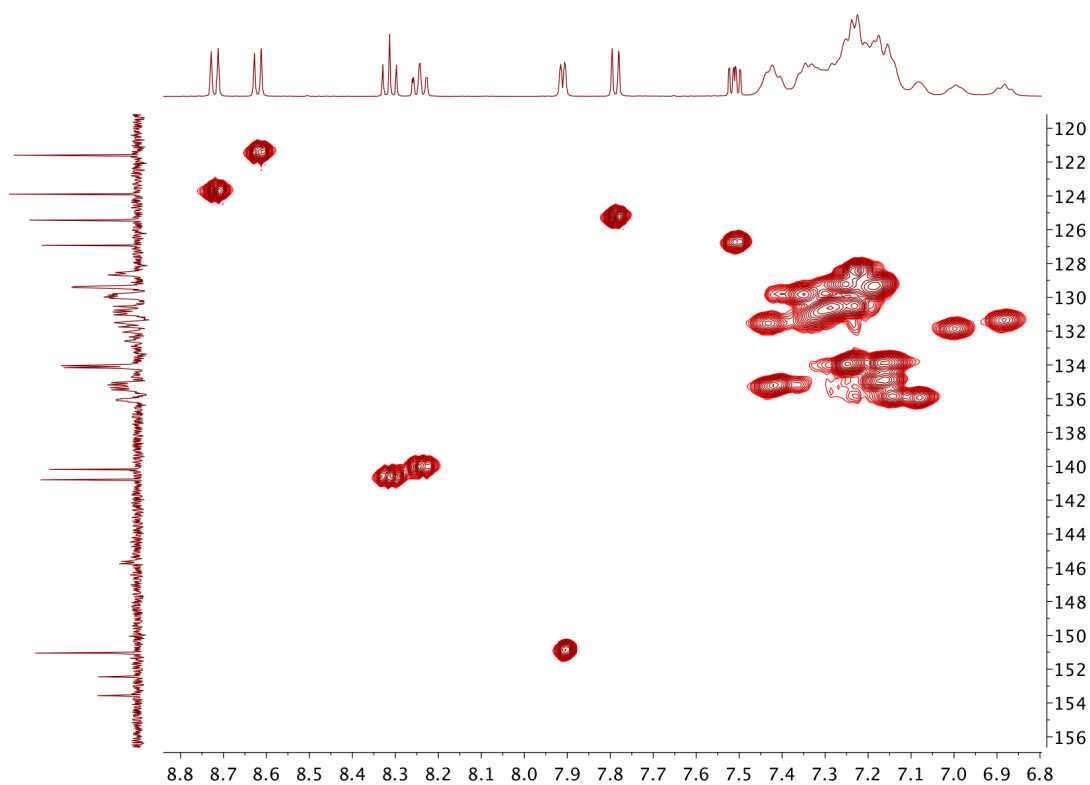


Figure S12. HMQC spectrum of $[\text{Cu}(\text{BIPHEP})(6\text{-Etbp})][\text{PF}_6]$ (^1H 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ 126 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

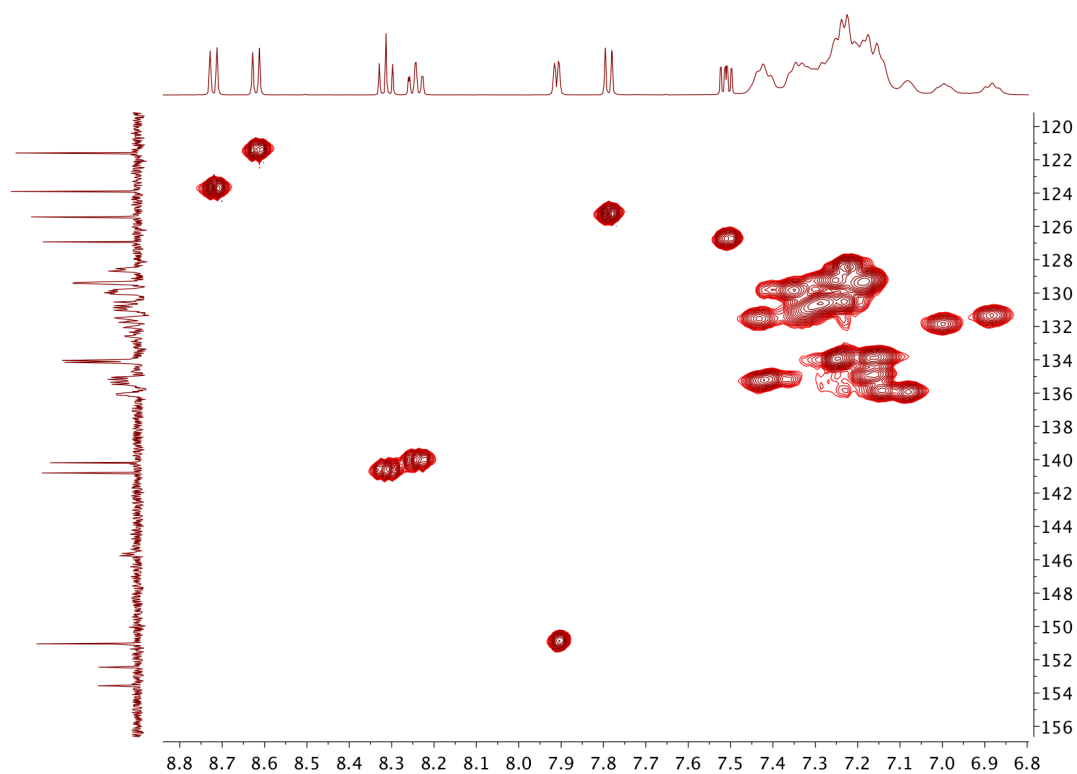


Figure S13. HMBC spectrum of $[\text{Cu}(\text{BIPHEP})(6\text{-Etbp})][\text{PF}_6]$ (^1H 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ 126 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

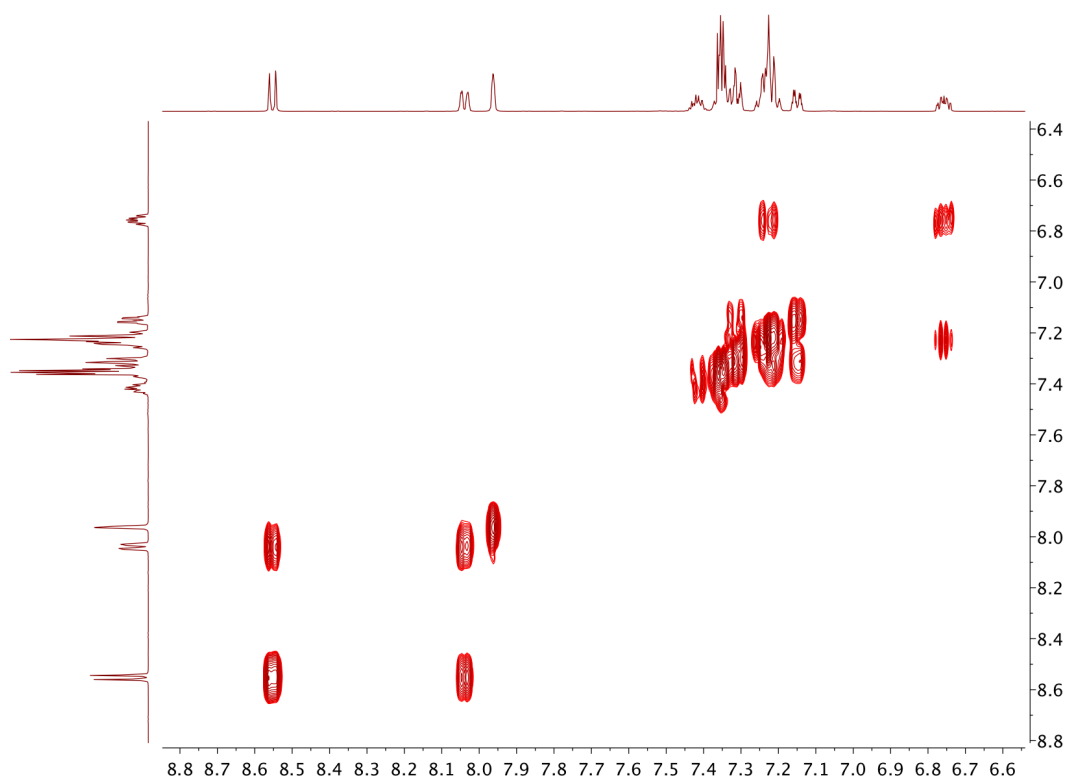


Figure S14. COSY spectrum of $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bp})][\text{PF}_6]$ (500 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

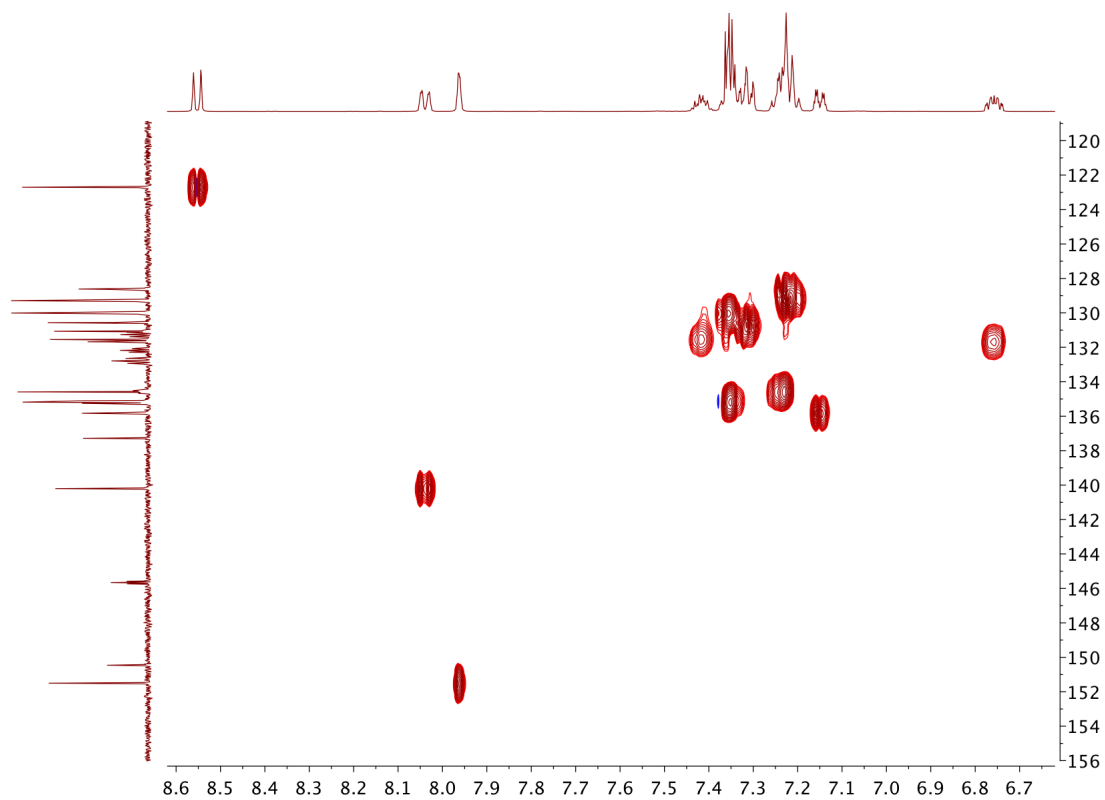


Figure S15. HMQC spectrum of $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bpy})][\text{PF}_6]$ (^1H 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ 126 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

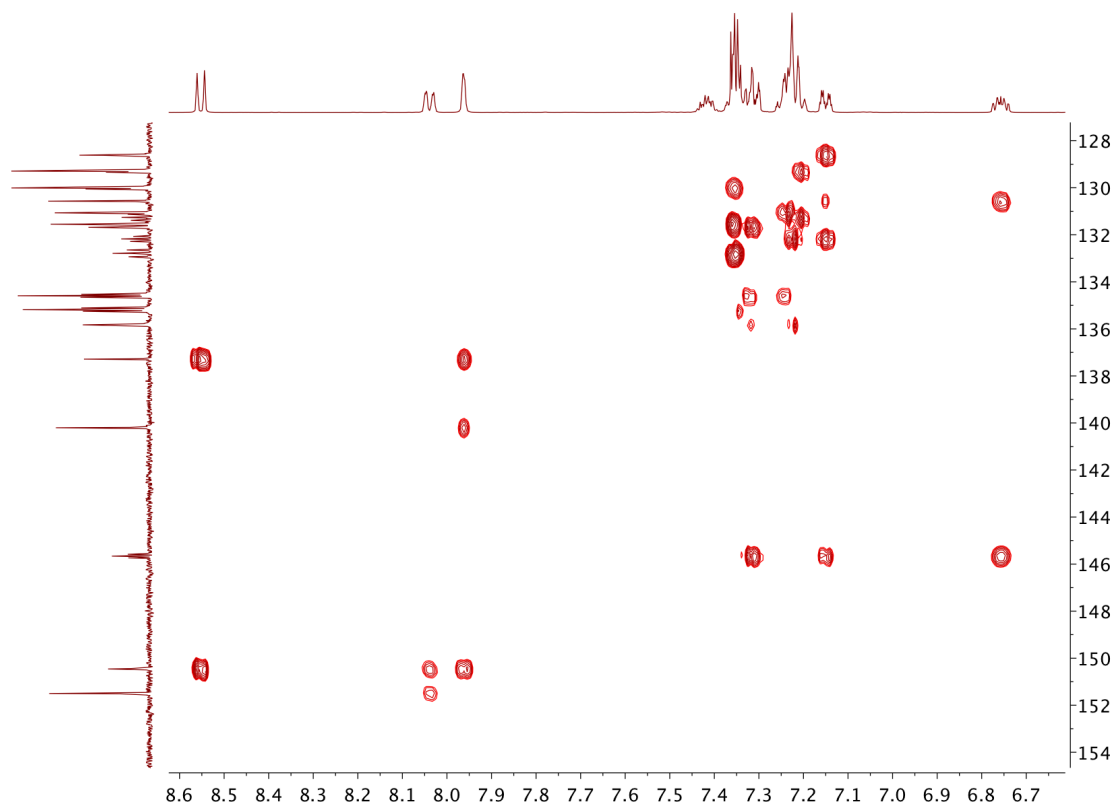


Figure S16. HMBC spectrum of $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bpy})][\text{PF}_6]$ (^1H 500 MHz, $^{13}\text{C}\{^1\text{H}\}$ 126 MHz, acetone- d_6 , 298 K). Scales: δ / ppm.

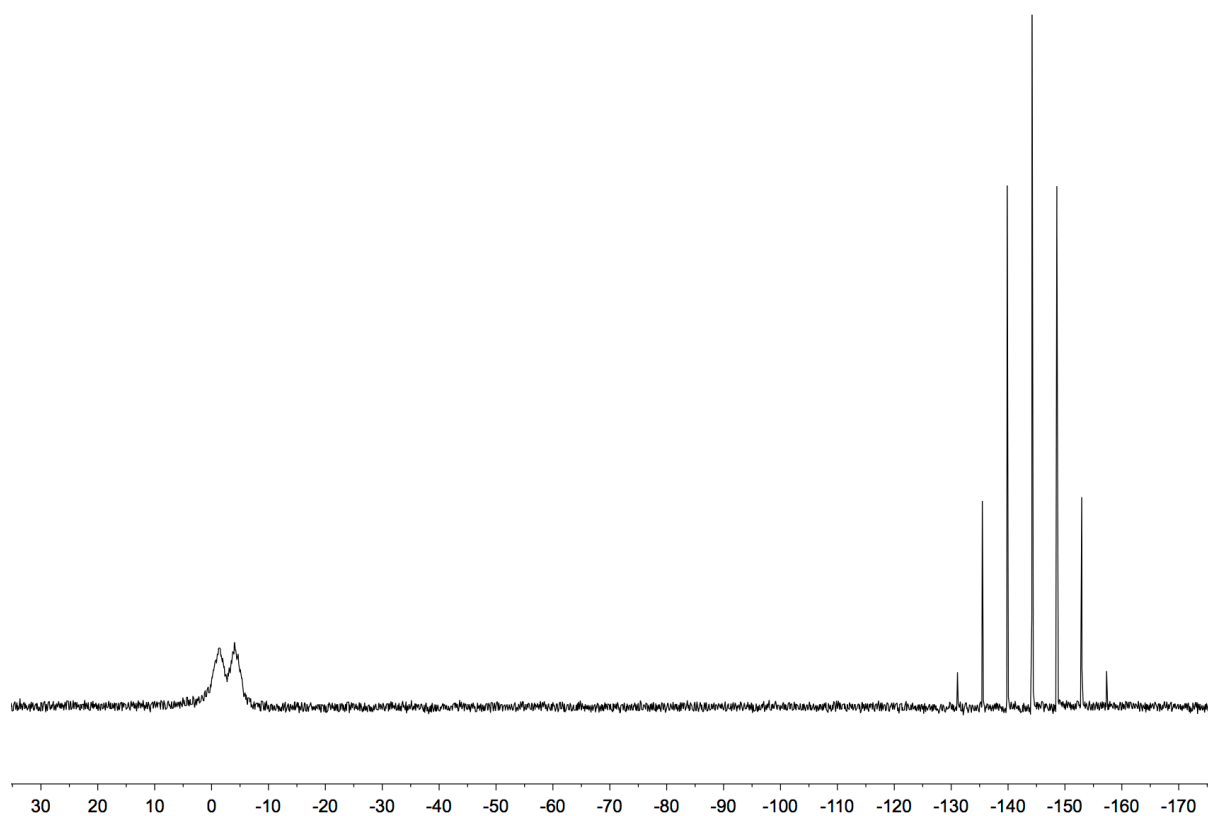


Figure S17. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz, acetone- d_6 , 298 K) of $[\text{Cu}(\text{BIPHEP})(6\text{-Etbpy})][\text{PF}_6]$. Scale: δ / ppm.

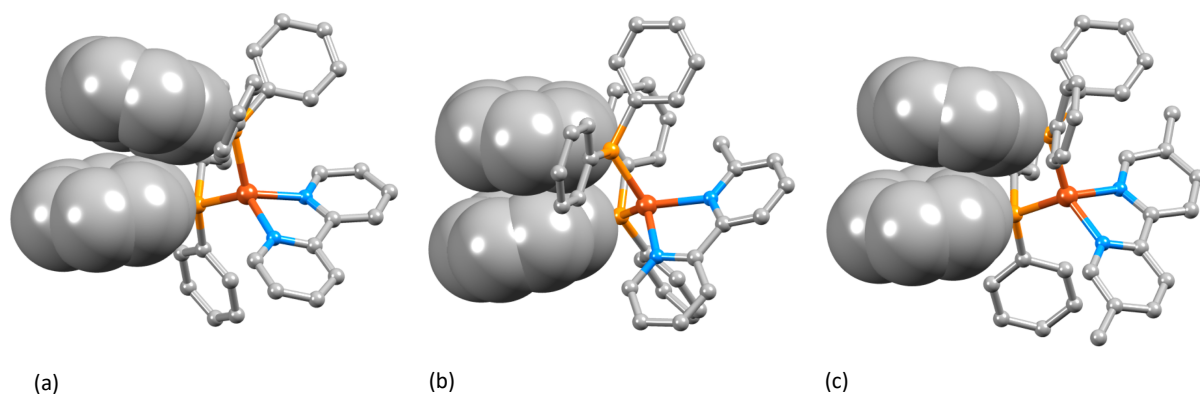


Figure S18. Space-filling representations of the π -stacking interactions between a phenyl ring of a PPh_2 group and one ring of the BIPHEP backbone in the complex cations in (a) $[\text{Cu}(\text{BIPHEP})(\text{bpy})][\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2$, (b) $[\text{Cu}(\text{BIPHEP})(6\text{-Me bpy})][\text{PF}_6] \cdot \text{Et}_2\text{O} \cdot 0.5\text{H}_2\text{O}$ and (c) $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bpy})][\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2$.

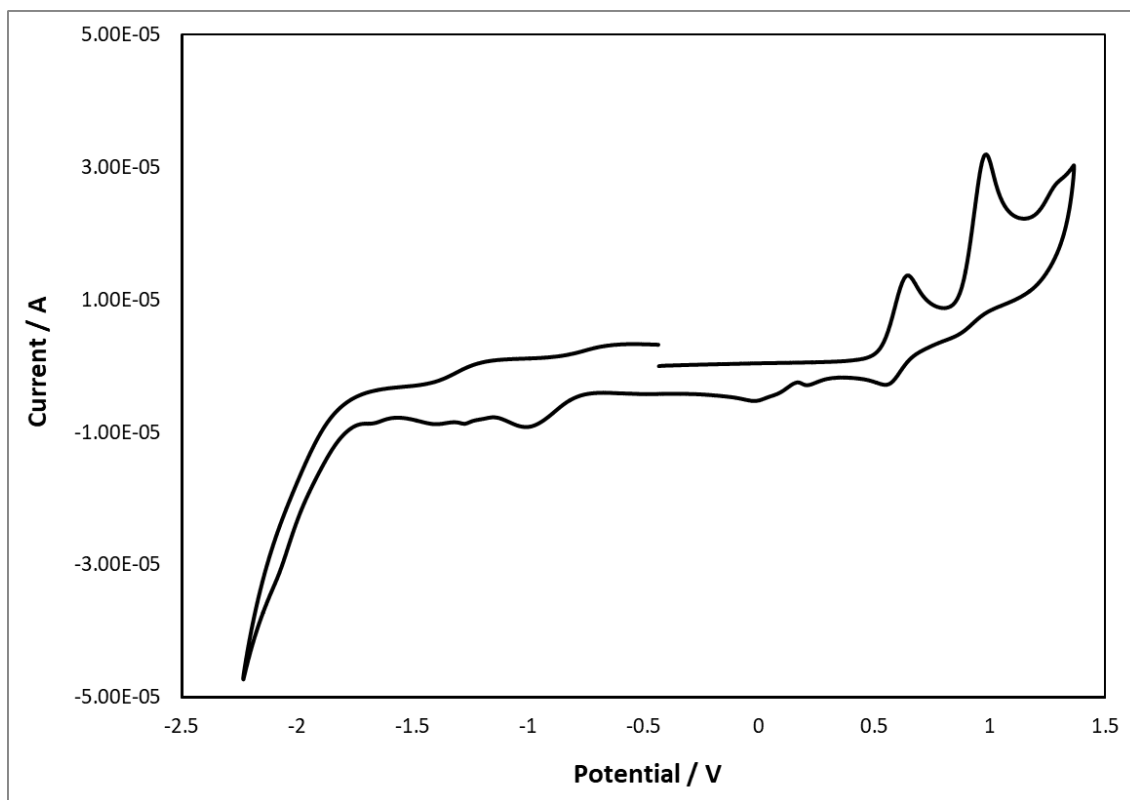


Figure S19. Cyclic voltammogram of a CH_2Cl_2 solution of $[\text{Cu}(\text{BIPHEP})(\text{bpy})][\text{PF}_6]$ (vs. Fc^+/Fc , $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte, scan rate = 0.1 V s^{-1}).

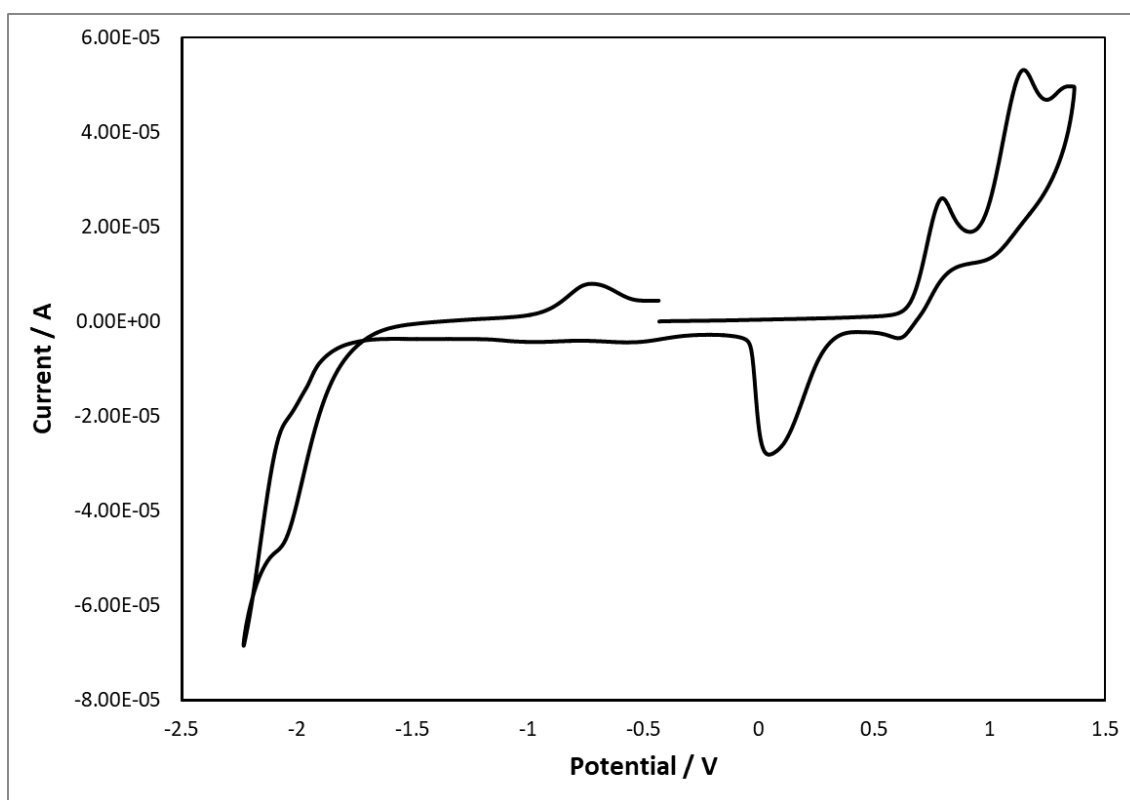


Figure S20. Cyclic voltammogram of a CH_2Cl_2 solution of $[\text{Cu}(\text{BIPHEP})(6\text{-Mebpy})][\text{PF}_6]$ (vs. Fc^+/Fc , $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte, scan rate = 0.1 V s^{-1}).

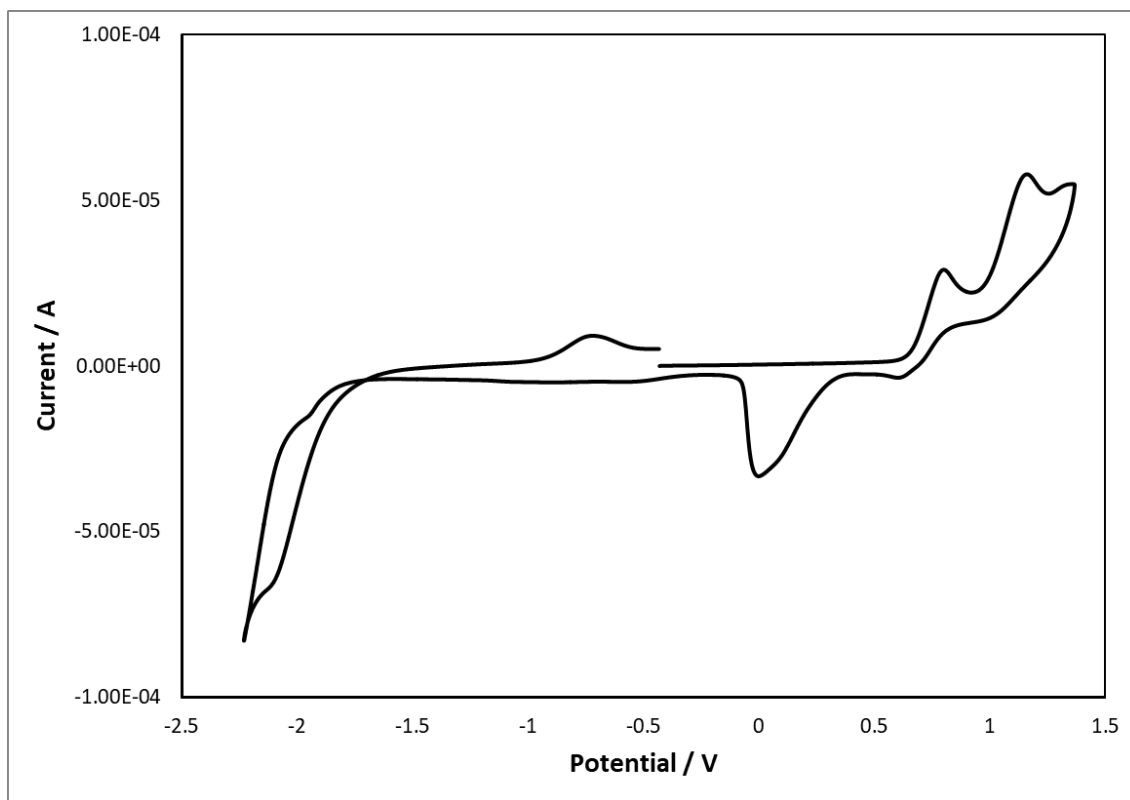


Figure S21. Cyclic voltammogram of a CH_2Cl_2 solution of $[\text{Cu}(\text{BIPHEP})(6\text{-Etbpy})][\text{PF}_6]$ (vs. Fc^+/Fc , $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte, scan rate = 0.1 V s^{-1}).

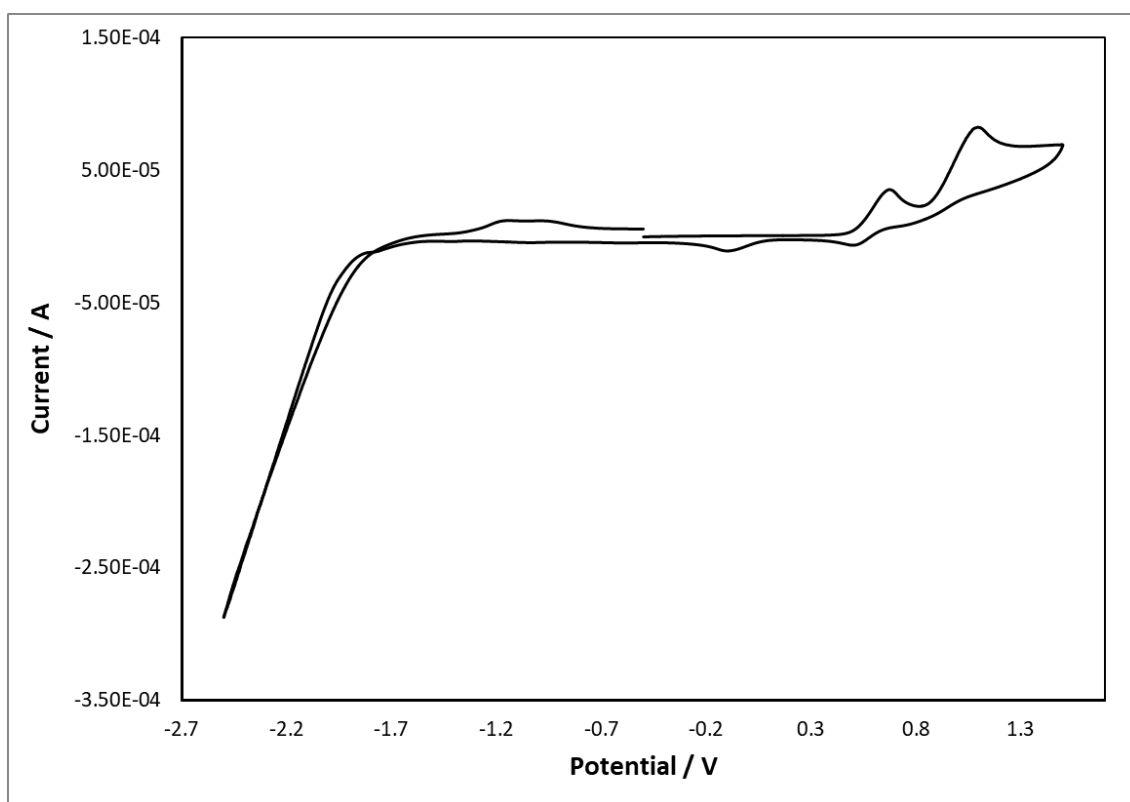


Figure S22. Cyclic voltammogram of a CH_2Cl_2 solution of $[\text{Cu}(\text{BIPHEP})(5,5'\text{-Me}_2\text{bpy})][\text{PF}_6]$ (vs. Fc^+/Fc , $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte, scan rate = 0.1 V s^{-1}).

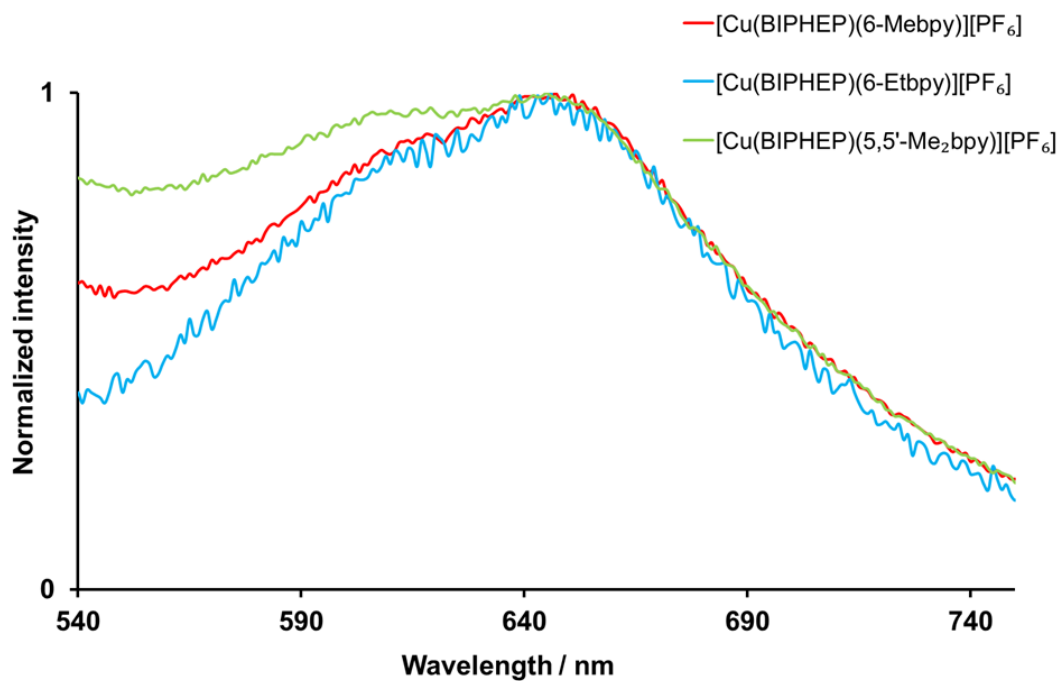


Figure 23. Normalized solution emission spectra of [Cu(BIPHEP)(N^N)]PF₆ with N^N = 6-Mebpy, 6-Etbpy and 5,5'-Me₂bpy (deaerated CH₂Cl₂, 5.0 × 10⁻⁵ mol dm⁻³). λ_{exc} = 390 nm.