# Electronic Supplementary Information for: Towards dipyrrins: oxidation and metalation of acyclic and macrocyclic Schiff-base dipyrromethanes

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## Contents



## 1 General Procedures

Syntheses of all organic compounds were carried out under a flow of $N_2$, having previously degassed the solvent by bubbling through $N_2$. The syntheses of compounds $Cu_2(\mathbf{L}^3)$ and $Cu_2(\mathbf{L}^4)$ were carried out in air. The syntheses of compounds $FeBr(\mathbf{L}^1)$ and $Cu_2(\mathbf{L}^5)$ were carried out under anaerobic conditions using standard Schlenk-line techniques.

Vacuum Atmospheres and MBraun glove boxes were used to manipulate and store air- and moisture-sensitive compounds under an atmosphere of dried and deoxygenated

dinitrogen. All gases were supplied by BOC gases UK. All glassware was dried in an oven at

160 $^{o}$C, cooled under $10^{-3}$ mbar vacuum and then purged with nitrogen. Prior to use, all Fisherbrand® 1.2 $\mu$m retention glass microfiber filters and cannulae were dried in an oven at 160 $^{o}$C overnight and all Celite® 545 filter aid was flame-dried under vacuum.

All solvents for use with air- and moisture-sensitive compounds were stored in ampoules containing pre-dried 4 Å molecular sieves. Solvents were collected from the Vac Atmospheres solvent tower drying system, where they had been passed over a column of molecular sieves for 24 hours prior to collection. They were then degassed prior to use and subsequent storage. The solvents benzene-$d_6$ and $d$-chloroform were used with moisture-stable compounds and were used as supplied. All solvents were purchased from Sigma-Aldrich or Fisher Scientific.

$^{1}$H-NMR spectra were recorded on a Bruker AVA400 spectrometer operating at 399.90 MHz, a Bruker AVA500 or Bruker PRO500 operating at 500.12 MHz or a Bruker AVA600 spectrometer operating at 599.81 MHz. $^{13}$C$\{^{1}$H$\}$-NMR spectra were recorded on a Bruker AVA500 or Bruker PRO500 operating at 125.76 MHz. $^{19}$F$\{^{1}$H$\}$-NMR spectra were recorded on a Bruker AVA500 spectrometer operating at 470.59 MHz. Chemical shifts are reported in parts per million (ppm). $^{1}$H- and $^{13}$C$\{^{1}$H$\}$-NMR spectra are referenced to residual solvent resonances calibrated against an external standard, $SiMe_4$ ($\delta = 0$ ppm). $^{19}$F$\{^{1}$H$\}$-NMR spectra are referenced to an external standard, $CCl_3F$ ($\delta = 0$ ppm). All spectra were recorded at 298 K.

Electrochemical measurements were made using an Autolab ECO Chemie PGSTAT potentiostat and the data processed using GPES Manager version 4.9. Experiments were undertaken under a flow of $N_2$ in a 10 mL cell. The solution employed was 3–5 mM of the compound in THF, with 0.2 M $[^{n}Bu_4][BF_4]$ as the supporting electrolyte. Cyclic

voltammograms were recorded for quiescent solutions at variable scan rates between 100 – 500 mV $s^{-1}$. The nature of an observed redox process (reduction or oxidation) was determined by linear sweep voltammetry measured for stirred solutions with scan rates between 10 – 20 mV $s^{-1}$. The working electrode used was either glassy carbon or platinum disc ($d$ = 1 mm), with a platinum gauze counter electrode. A $Ag/Ag^+$ pseudo-reference electrode was used with potentials calibrated against $[FeCp_2]^{0/+}$ ($Fc^+/Fc$ = 0 V).

Elemental analyses were performed by Mr Stephen Boyer at the London Metropolitan University, measured in duplicate. All FT-IR spectra were recorded using JASCO 410 or JASCO 460 plus spectrometers. All mass spectra were recorded by Dr Alan Taylor at the University of Edinburgh. All UV/vis absorption spectra were recorded on a Jasco V-670 spectrophotometer in a 10 mm quartz cuvette, fitted with a Young's tap for air-sensitive compounds. Extinction coefficients were determined from five independent $\mu$M solutions, taken from the slope of least-squares fitted plots of ABS against varying concentration.

X-ray crystallographic data were collected at 170 K on an Oxford Diffraction Excalibur diffractometer using graphite monochromated Mo-K$\alpha$ radiation equipped with an Eos CCD detector ($\lambda$ = 0.71073 Å), or at 120 K on a Supernova, Dual, Cu at Zero Atlas diffractometer using Cu-K$\alpha$ radiation ($\lambda$ = 1.5418 Å). Structures were solved using SIR-92 direct methods[1] and refined using a full-matrix least square refinement on $|F|^2$ using SHELX-2014.[2] All programs are used within the WinGX and ShelXle suites.[3] All non-hydrogen atoms refined with anisotropic displacement parameters and H-parameters were constrained to parent atoms and refined using a riding model unless otherwise stated. The PLATON SQUEEZE algorithm was used to remove solvent-accessible voids or solvent molecules that could not be adequately modelled.[4]

DFT calculations were performed using the Gaussian09 package on the Eddie server system at the University of Edinburgh.[9] Initial guess geometries were either generated

from X-ray crystal structures or from a drawn molecule using the Avogadro program (version 1.1.0). All structures discussed in the text were optimised and converged according to the criteria for maximum displacement and maximum force. Frequency calculations were conducted to confirm that the optimised structures represented minimum energy geometries, which were confirmed by having no imaginary frequencies. The "OPT=NoRaman" and "FREQ=NoRaman" options were used to improve computational efficiency. TD-DFT calculations were conducted on the first 30 excited states using the SCRF solvent model ("Solvent=Dichloromethane"). All optimisation, frequency and TD-DFT calculations were performed using the B3LYP functional and 6-311G(d,p) basis set. Data for plotting simulated absorption spectra were prepared using GaussSum software (version 3.0).[10]

The reagents $C_6F_5CHO$, *p*-toluenesulfonic acid (PTSA), propan-3-one, $POCl_3$, $InCl_3$, *ortho*-phenylene-diamine, $CF_3CO_2H$ (TFA), $NEt_3$, *t*-butylamine, *para-t*-butylaniline, 1,8-dinitroanthraquinone, $FeBr_2$ and $Cu(OAc)_2 \cdot H_2O$ were all used as supplied by Sigma-Aldrich, Fisher Scientific or VWR without further purification. Pyrrole (Sigma Aldrich) was freshly distilled prior to use.

5-pentafluorophenyl-dipyrromethane[5], 1,9-diformyl-5-pentafluorophenyl-dipyrromethane[6], 1,8-diaminoanthracene[7] and macrocycle $H_4\mathbf{L}$[5 8] were synthesised according to published procedures.

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## 2 Synthetic Procedures

### 2.1 Synthesis of 1,9-diformyl-5-pentafluorophenyl-dipyrromethane (1)[6]

Synthesised as a brown solid, according to published procedures.[6] Attempts to purify the compound by vacuum sublimation or column chromatography led to decomposition. Colourless, diffraction-quality crystals were grown from a hot aqueous ethanol solution (80 % ethanol v/v) on cooling to room temperature and the solid state structure was determined by X-ray crystallography (Figure 1). $^1$H-NMR ($CDCl_3$): $\delta_H$ / ppm: 10.51 (s, 2H, pyrrole N-H), 9.27 (s, 2H, imine), 6.90 (broad s, 2H, pyrrole $\beta$-H), 6.14 (broad s, 2H, pyrrole $\beta$-H), 6.03 (s, 1H, *meso*-H).

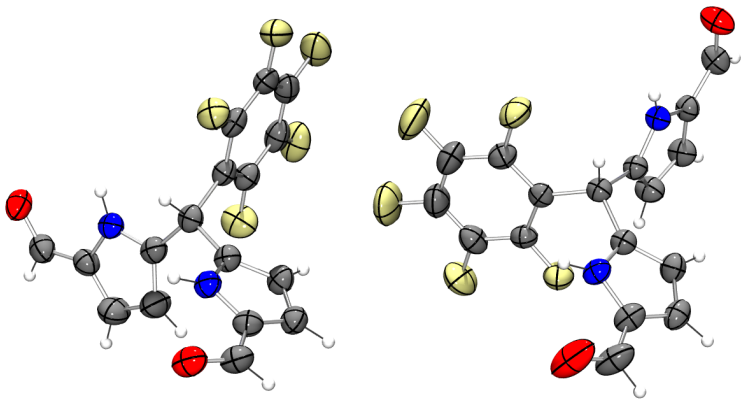


Figure 1: Solid-state structure of **1**, showing the asymmetric unit (displacement ellipsoids at 50 % probability). Grey = C, white = H, blue = N, red = O, khaki = F.

### 2.2 Synthesis of 2

To a brown solution of **1** (8.54 g, 23 mmol) in methanol (350 mL) was added *para-t*-butylaniline (6.22 g, 42 mmol, 1.8 eq). The solution was heated to 50 $^o$C and stirred for 30 minutes. TFA (3.5 mL, 46 mmol, 2 eq) was drop-wise added to the solution, turning

the solution dark green. The solution was stirred for 2 hours before $NEt_3$ (6.4 mL, 46 mmol, 2 eq) was slowly added, turning the solution dark blue and then dark pink. The mixture was allowed to stir for 30 minutes before methanol was evaporated from the mixture under vacuum. The dark pink residues were dissolved in toluene (200 mL) and washed with deionised water (3 × 50 mL). The yellow aqueous fractions were discarded and then toluene was evaporated from the organic fraction to yield a dark purple solid. The product was dried at 70 $^o$C overnight, under vacuum. Yield: 10.81 g, 74 %. $^1$H-NMR ($CDCl_3$): $\delta_H$ / ppm: 8.18 (s, 2H, imine), 7.36 (d, 4H, $^3J_{HH}$ = 10 Hz, Ph), 7.12 (d, 4H, $^3J_{HH}$ = 5 Hz, Ph), 6.56 (d, 2H, $^3J_{HH}$ = 5 Hz, pyrrole $\beta$-H), 6.02 (broad s, 2H, pyrrole $\beta$-H), 5.69 (s, 1H, *meso*-H), 1.32 (s, 18H, *t*Bu). $^{13}$C{$^1$H}-NMR ($CDCl_3$): $\delta_C$ / ppm: 149.0, 148.8, 148.1, 145.8, 144.1, 143.8, 141.6, 138.5, 136.9, 133.8, 131.5, 126.2, 120.6, 117.0, 115.1, 110.0, 34.6, 31.5. MS (EI): $m/z$: 630 ($M^+$). IR (ATR, solid-state): $\nu$ 1623 $cm^{-1}$ (imine). UV/vis ($CH_2Cl_2$): $\lambda_{max}$ 372 nm, $\epsilon = 41,000$ $dm^3$ $mol^{-1}$ $cm^{-1}$.

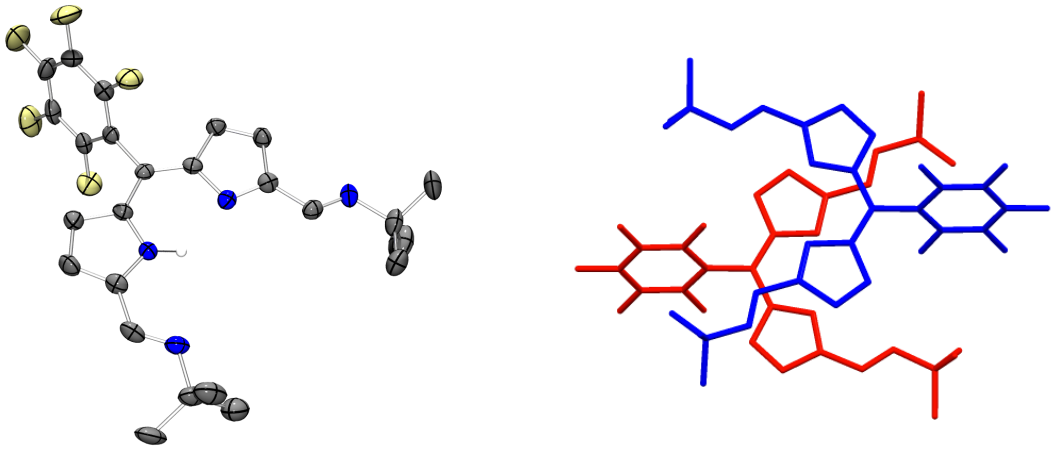
### 2.3 Synthesis of HL[1]

To a dark purple solution of **2** (6.03 g, 10 mmol) in $CH_2Cl_2$ (100 mL), DDQ (2.17 g, 10 mmol, 1 eq) was added and the mixture was stirred for 1 hour, turning the solution red/purple. Tan solids were removed from the mixture by suction filtration and $CH_2Cl_2$ was removed from the filtrate to yield a dark purple solid. The product was dried at 70 $^o$C overnight, under vacuum. Yield: 6.29 g, 100 %. $^1$H-NMR ($CDCl_3$): $\delta_H$ / ppm: 8.57 (s, 2H, imine), 7.45 (d, 4H, $^3J_{HH}$ = 10 Hz, Ph), 7.30 (d, 4H, $^3J_{HH}$ = 5 Hz, Ph) 7.02 (broad s, 2H, pyrrole $\beta$-H), 6.58 (broad s, 2H, pyrrole $\beta$-H), 1.37 (s, 18H, *t*Bu). $^{13}$C{$^1$H}-NMR ($C_6D_6$): $\delta_C$ / ppm: 155.68, 153.74, 151.33, 150.29, 149.47, 145.08 (d), 143.88, 141.9 (d), 137.7 (d), 134.14, 126.59, 126.50, 122.04, 121.53, 34.62, 31.46. $^{19}$F{$^1$H}-NMR ($CDCl_3$): $\delta_F$ / ppm: -137.9 (d, 2F, $^3J_{FF}$ = 20 Hz, $Ar^F$, *ortho*-F), -151.60 (broad s, 1F, $Ar^F$, *para*-F),

-160.47 (broad s, 2F, $Ar^F$, *meta*-F). MS (ESI): $m/z$: 628 ($M^+$). IR (ATR, solid-state): $\nu$ 1662 $cm^{-1}$ (imine). UV/vis ($CH_2Cl_2$): $\lambda_{max}$ 290 nm, $\epsilon = 19,000$ $dm^3$ $mol^{-1}$ $cm^{-1}$.

### 2.4 Synthesis of $HL^2$

To a brown solution of **1** (1.562 g, 4 mmol) in toluene (250 mL) was added $Na_2SO_4$ (3 g) and then *t*-butylamine (3 mL, 28 mmol, 7 eq). The solution was heated to the reflux temperature of the amine (45 $^o$C), turning the solution dark orange. The mixture was stirred for 48 hours and then allowed to cool to room temperature. $Na_2SO_4$ was removed from the mixture by filtration, washing with toluene. Removal of the solvent under vacuum afforded an orange oil. Dissolving the oil in hexanes allowed a brown solid to be removed by filtration. Removal of the solvent from the filtrate afforded the product as a red solid. Diffraction-quality crystals were grown from a hexanes solution cooled to -30 $^o$C (Figure 2). Yield: 0.975 g, 48 %. $^1$H-NMR ($CDCl_3$): $\delta_H$ / ppm: 7.71 (s, 2H, imine), 6.34 (broad s, 2H, pyrrole $\beta$-H), 5.76 (broad s, 2H, pyrrole $\beta$-H), 0.76 (s, 18H, *t*Bu). $^{13}$C{$^1$H}-NMR ($CDCl_3$): $\delta_C$ / ppm: 155.3 (pyrrole $\alpha$-C), 148.8 (imine), 144.0 (d, $^1J_{CF}$ = 251 Hz, $Ar^F$), 142.3 (pyrrole $\alpha$-C), 140.8 (d, $^1J_{CF}$ = 252 Hz, $Ar^F$), 136.6 ($^1J_{CF}$ = 252 Hz, $Ar^F$), 127.3 (pyrrole $\beta$-C), 123.0 (*meso*-C), 119.8 (pyrrole $\beta$-C), 58.2 ($\underline{C}Me_3$), 29.7 ($C\underline{Me}_3$). $^{19}$F{$^1$H}-NMR ($CDCl_3$): $\delta_F$ / ppm: -138.2 (dd, 2F, $^3J_{FF} = 4,24$ Hz, *ortho*-F), -152.2 (t, 1F, $^3J_{FF}$ = 24 Hz, *para*-F), -160.9 (m, 2F, $^3J_{FF}$ = 4 Hz, *meta*-F). MS (EI): $m/z$: 478 ($M^+$). IR (ATR, solid-state): $\nu$ 1582 $cm^{-1}$ (imine). UV/vis ($CH_2Cl_2$): $\lambda_{max}$ 486 nm, $\epsilon = 24,329 \pm 1262$ $dm^3$ $mol^{-1}$ $cm^{-1}$. Anal. Calcd. for $C_{25}H_{25}F_5N_4$ ($M_r$ = 476.48 g $mol^{-1}$): C, 63.02 %; H, 5.29 %; N, 11.76 %. Found: C, 62.88 %; H, 5.37 %; N, 11.63 %.



(a) (b)

Figure 2: Solid-state structure of H$\mathbf{L}^2$: (a) Ellipsoid plot, omitting most protons and a second molecule in the asymmetric unit for clarity (displacement ellipsoids at 50 % probability). Grey = C, white = H, blue = N, red = O, khaki = F. (b) Showing $\pi$-stacked, head-to-tail dimer.

### 2.5 Synthesis of $\mathbf{H_4L}^3$

To a brown solution of **1** (2.174 g, 6 mmol) in methanol (180 mL) was added 4,5-dimethyl-1,2-phenylenediamine (0.800 g, 6 mmol, 1 eq). TFA (0.9 mL, 12 mmol, 2 eq) diluted in methanol (20 mL) was added, forming a yellow/brown solution that was stirred for 3 hours at room temperature. $NEt_3$ (1.8 mL, 13 mmol, 2.1 eq) in methanol (20 mL) was added to the mixture and was stirred for 1 hour, precipitating a yellow solid. The product was isolated by vacuum filtration on a cintered funnel, washed with methanol until washings were colourless (5 × 30 mL) and then dried overnight at 70 $^o$C under vacuum. Diffraction-quality crystals were grown from a THF solution cooled to -30 $^o$C. Yield: 2.1341 g, 38 %. $^1$H-NMR ($CDCl_3$): $\delta_H$ / ppm: 8.09 (s, 4H, imine), 6.84 (s, 4H, Ar), 6.53 (s, 4H, pyrrole $\beta$-H), 6.12 (s, 4H, pyrrole $\beta$-H), 5.89 (s, 2H, *meso*-H), 2.26 (s, 12H, Ar-Me). $^{13}$C{$^1$H}-NMR ($CDCl_3$): $\delta_C$ / ppm: 149.42 (imine), 145.2 (d, $^1J_{CF}$ = 247 Hz, $Ar^F$), 142.49 ($Ar^F$, next to *meso*-C), 140.9 (d, $^1J_{CF}$ = 253 Hz, $Ar^F$), 138.1 (d, $^1J_{CF}$ = 246 Hz, $Ar^F$), 137.10 (Ar,

next to imine), 134.80 (Ar-Me), 133.43 (pyrrole $\alpha$-C), 131.57 (pyrrole $\alpha$-C), 120.61 (Ar C-H), 116.75 (pyrrole $\beta$-C), 114.34, 109.95 (pyrrole $\beta$-C), 33.90 (*meso*-C), 19.57 (Ar-Me). $^{19}$F{$^{1}$H}-NMR ($CDCl_3$): $\delta_F$ / ppm: -139.79 (d, 4F, $^3J_{FF}$ = 19 Hz, *ortho*-F), -154.83 (t, 2F, $^3J_{FF}$ = 24 Hz, *para*-F), -160.89 (t, 4F, $^3J_{FF}$ = 24 Hz, *meta*-F). MS (ESI): $m/z$: 937 ($M^+$), 959 ($M^+$+ Na), 977 ($M^+$+ Ca). IR (ATR, solid-state): $\nu$ 1620 $cm^{-1}$ (imine). UV/vis ($CH_2Cl_2$): $\lambda_{max}$ 320 nm, $\epsilon = 67,416 \pm 1588$ $dm^3$ $mol^{-1}$ $cm^{-1}$. Anal. Calcd. for $C_{50}H_{34}F_{10}N_8$ ($M_r$ = 937 g $mol^{-1}$): C, 64.10 %; H, 3.66 %; N, 11.96 %. Found: C, 63.70 %; H, 3.56 %; N, 11.82 %.

### 2.6 Synthesis of $H_4L^4$

Prepared as described for $H_4L^3$. To a brown solution of **1** (1.432 g, 4 mmol) in methanol (120 mL) was added 1,8-diaminoanthracene (0.809 g, 4 mmol, 1 eq). PTSA (1.38 g, 8 mmol, 2 eq) diluted in methanol (20 mL) was added. After 3 hours, $NEt_3$ (1.1 mL, 8.4 mmol, 2.1 eq) in methanol (20 mL) was added and stirred for 1 hour. Yield: 0.766 g, 42 %. $^1$H-NMR ($CDCl_3$): $\delta_H$ / ppm: 9.35 (broad s, pyrrole N-H), 9.20 (s, 2H, 9-anth), 8.43 (s, 2H, 10-anth), 8.40 (s, 4H, imine), 7.86 (d, 4H, $^3J_{HH}$ = 10 Hz, 2,7-anth), 7.44 (t, 4H, $^3J_{HH}$ = 10 Hz, 3,6-anth), 7.00 (d, 4H, $^3J_{HH}$ = 5 Hz, 4,5-anth), 6.65 (d, 4H, $^3J_{HH}$ = 0 Hz, pyrrole $\beta$-H), 6.20 (d, 4H, $^3J_{HH}$ = 5 Hz, pyrrole $\beta$-H), 5.97 (s, 2H, *meso*-H). $^{13}$C{$^{1}$H}-NMR ($CDCl_3$): $\delta_C$ / ppm: 150.2 (1,8-anth), 150.0 (imine), 145.4 (d, $^1J_{CF}$ = 253 Hz, $Ar^F$), 141.4 (d, $^1J_{CF}$ = 263 Hz, $Ar^F$), 138.2 (d, $^1J_{CF}$ = 253 Hz, $Ar^F$), 133.1 (pyrrole $\alpha$-C), 132.7 (pyrrole $\alpha$-C), 132.0 (anth), 131.5 ($Ar^F$, next to *meso*-C), 127.4 (anth), 126.5 (10-anth), 126.0 (3,6-anth), 125.8 (4,5-anth), 118.8 (9-anth), 117.0 (pyrrole $\beta$-C), 112.61 (2,7-anth), 110.4 (pyrrole $\beta$-C), 33.8 (*meso*-C). $^{19}$F{$^{1}$H}-NMR ($CDCl_3$): $\delta_F$ / ppm: -140.88 (d, 4F, $^3J_{FF}$ = 14 Hz, *ortho*-F), -153.98 (t, 2F, $^3J_{FF}$ = 23 Hz, *para*-F), -160.66 (t of d, 4F, $^3J_{FF} = 9,23$ Hz, *meta*-F). MS (ESI): $m/z$: 1080 ($M^+$). IR (ATR, solid-state): $\nu$ 1614

$cm^{-1}$ (imine). UV/vis ($CH_2Cl_2$): $\lambda_{max}$ 262 nm, $\epsilon = 56,262 \pm 3886$ $dm^3$ $mol^{-1}$ $cm^{-1}$. Anal. Calcd. for $C_{62}H_{34}F_{10}N_8$ ($M_r = 1080$ g $mol^{-1}$): C, 68.89 %; H, 3.17 %; N, 10.37 %. Found: C, 64.48 %; H, 2.68 %; N, 9.90 %.

### 2.7 Synthesis of FeBr($\mathbf{L}^1$)

To a purple solution of H$\mathbf{L}^1$ (180 mg, 0.3 mmol) in THF was added a solution of $LiN(SiMe_3)_2$ (48 mg, 0.3 mmol, 1 eq) in THF. The mixture was stirred for 4 hours, turning the solution blue, before it was added to a stirred suspension of $FeBr_2$ (61 mg, 0.3 mmol, 1 eq) in THF. The mixture was stirred for 16 hours before the solvent was removed under vacuum. The residues were washed with hexanes and the product was then extracted with toluene by filtration. Yield: 140 mg (64 %). MS (ESI): $m/z$: 762 ($M^+$, FeBr($\mathbf{L}^1$)), 683 (Fe($\mathbf{L}^1$)). UV/vis (THF): $\lambda_{max}$ 333 nm, $\epsilon = 26,000$ $dm^3$ $mol^{-1}$ $cm^{-1}$. Elemental analysis: no satisfactory analyses measured.

### 2.8 Synthesis of $Cu_2(\mathbf{L}^3)$

To a yellow solution of $H_4\mathbf{L}^3$ (0.2 g, 0.2 mmol) in THF (25 mL) was added $Cu(OAc)_2 \cdot H_2O$ (85.3 mg, 0.43 mmol, 2 eq), turning dark yellow after stirring for 10 minutes. After 30 minutes, $Et_3N$ (3 drops) was added, and the mixture was left to stir for 20 hours. THF was evaporated from the solution and the dark yellow residues were washed with hexanes. The crude product was purified by flash column chromatography (alumina) eluting an orange fraction with $CH_2Cl_2$, a light blue fraction with acetone, and an indigo fraction with methanol. The pure product was isolated from the $CH_2Cl_2$ fraction as a dark orange solid. Diffraction-quality crystals were grown from a pyridine solution on slow evaporation of the solvent. Yield: 1.248 g, 59 %. MS (ESI, methanol): $m/z$: 1058 ($M^+$, oxidised ligand), 529 ($M^{2+}$). IR (ATR, solid-state): $\nu$ 1552 $cm^{-1}$ (imine).

UV/vis (THF): $\lambda_{max}$ 220 nm, $\epsilon = 26,148 \pm 2326$ dm$^3$ mol$^{-1}$ cm$^{-1}$. Anal. Calcd. for $C_{70}H_{50}F_{10}N_{12}Cu_2$ ($M_r$ = 1374 g mol$^{-1}$): C, 61.12 %; H, 3.64 %; N, 12.22 %. Found: C, 60.86 %; H, 3.48 %; N, 11.88 %.

### 2.9 Synthesis of $Cu_2(L^4)$

Prepared as described for $Cu_2(\mathbf{L}^3)$. To a yellow solution of $H_4\mathbf{L}^4$ (0.726 g, 0.7 mmol) in THF (100 mL) was added $Cu(OAc)_2 \cdot H_2O$ (0.270 g, 1.3 mmol) and $Et_3N$ (3 drops). The product was purified by flash column chromatography (alumina), isolating the product from the orange $CH_2Cl_2$ fraction. Diffraction-quality crystals were grown by slow diffusion of hexane vapour into a THF solution at room temperature. Yield: 0.438 g, 52 %. MS (ESI): $m/z$: 1203 ($M^+$). IR (ATR, solid-state): $\nu$ 1574 cm$^{-1}$ (imine). UV/vis (THF): $\lambda_{max}$ 240 nm, $\epsilon = 102,218 \pm 1653$ dm$^3$ mol$^{-1}$ cm$^{-1}$. Anal. Calcd. for $C_{62}H_{30}F_{10}N_8Cu_2$ ($M_r$ = 1203 g mol$^{-1}$): C, 61.85 %; H, 2.51 %; N, 9.31 %. Found: C, 61.71 %; H, 2.60 %; N, 9.19 %.

### 2.10 Synthesis of $Cu_2(L^5)$

$H_4\mathbf{L}^5$ (0.095 g, 0.11 mmol) was combined with $LiN(SiMe_3)_2$ (0.073 g, 0.44 mmol, 4 eq) and THF (10 mL). The reaction was stirred for 4 hours and decanted onto a stirring suspension of $CuCl_2$ (0.030 g, 0.22 mmol, 2 eq) in THF (10 mL) at -80 $^o$C. The reaction mixture was warmed to room temperature and the resulting red solution was stirred for 16 hours. Cooling to -25 $^o$C resulted in the formation of red crystals that were isolated by cannula filtration and dried under vacuum for 16 hours to yield the product as a red solid. Diffraction-quality crystals were grown by diffusion of hexanes into a concentrated solution of $Cu_2(\mathbf{L}^5)$ in $CDCl_3$. Yield: 0.082 g, 57 %. MS (EI): $m/z$: 982.3 ($M^+$, 22 %), 953.3 ([M -2Et]$^+$, 100 %). IR (ATR, solid-state): $\nu$ 1570 cm$^{-1}$ (imine). UV/vis (THF):

$\lambda_{max}$ 240 nm, $\epsilon = 71,149 \pm 7018$ dm$^3$ mol$^{-1}$ cm$^{-1}$. Anal. Calcd. for $C_{58}H_{48}Cu_2N_8$ ($M_r$ = 984.15 g mol$^{-1}$): C, 70.78 %; H, 4.92 %; N, 10.39 %. Found: C, 70.66 %; H, 4.82 %; N, 10.25 %.

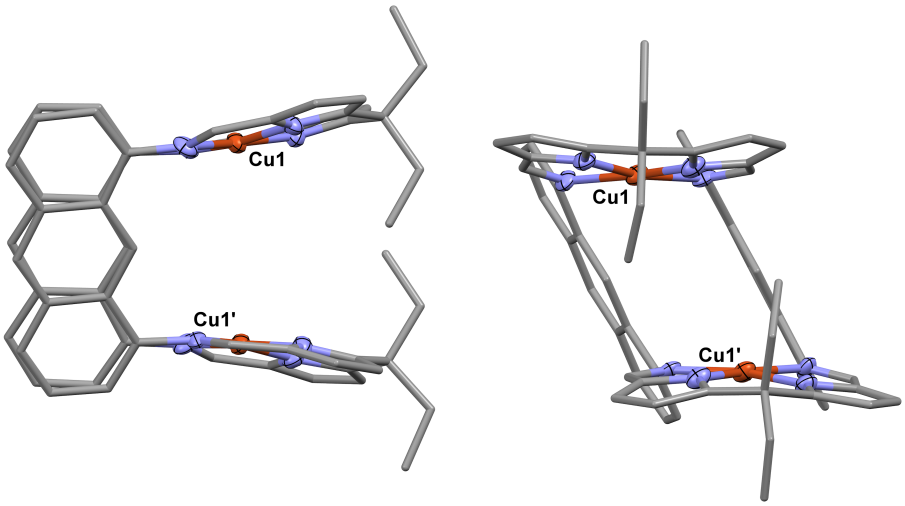



Figure 3: Solid-state structure of $Cu_2(\mathbf{L}^5)$. For clarity, protons and one symmetry-generated THF solvent molecule have been omitted (displacement ellipsoids at 50 %). Grey = C, blue = N, green = F, red = Cu. Cu···Cu, 5.345(1) Å; sum of planar angles, 359.9$^o$ around Cu1 and Cu1'; twisting angle, 30$^o$; bite angle, 14.83$^o$.

# 3 Electrochemical Data

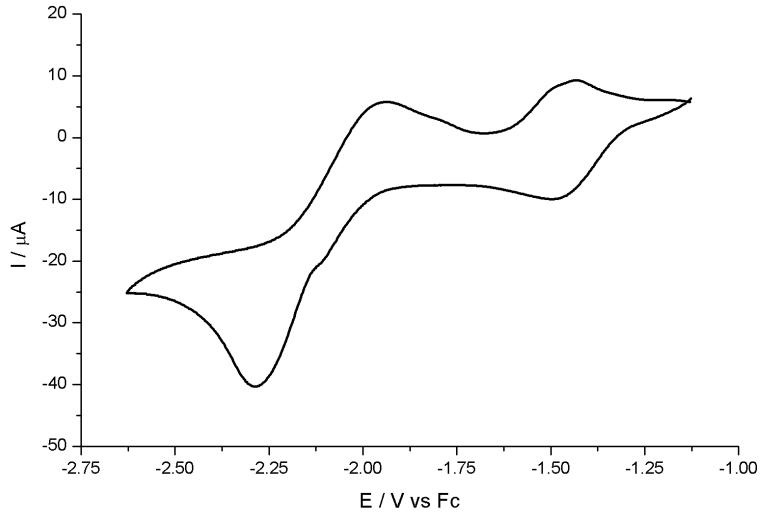



Figure 4: Cyclic voltammogram for $HL^2$, measured under $N_2$ at 100 mV $s^{-1}$ as a 6 mM THF solution, *versus* ferrocene. Electrolyte: 0.2 M $[^nBu_4N][BF_4]$. Pt disc working electrode, Pt gauze counter electrode, Ag wire pseudo-reference electrode.

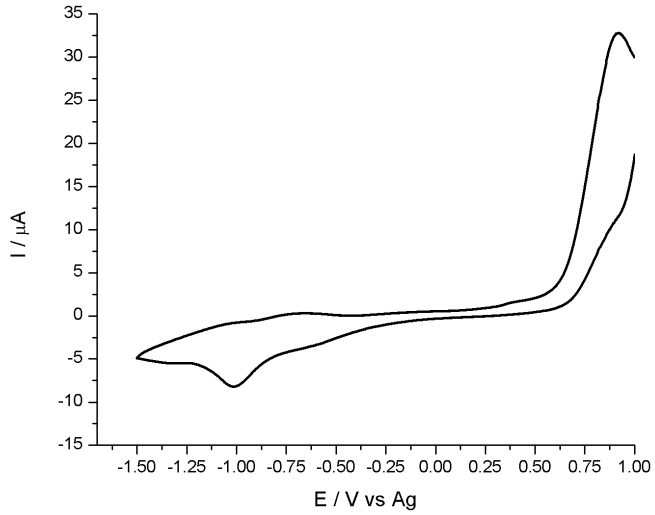



Figure 5: Cyclic voltammogram for $H_4L^3$, measured under $N_2$ at 100 mV $s^{-1}$ as a 5 mM THF solution, *versus* Ag. Electrolyte: 0.2 M $[^nBu_4N][BF_4]$. Pt disc working electrode, Pt gauze counter electrode, Ag wire pseudo-reference electrode.

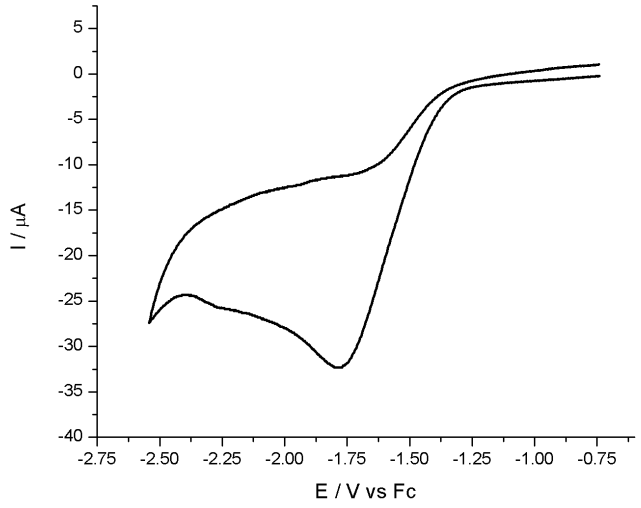



Figure 6: Cyclic voltammogram for $H_4L^4$, measured under $N_2$ at 100 mV $s^{-1}$ as a 4 mM THF solution, *versus* ferrocene. Electrolyte: 0.2 M $[^nBu_4N][BF_4]$. Pt disc working electrode, Pt gauze counter electrode, Ag wire pseudo-reference electrode.

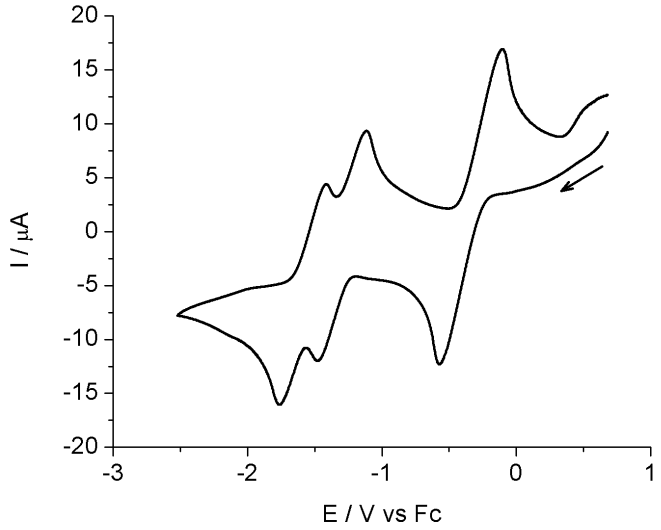



Figure 7: Cyclic voltammogram for $Cu_2L^3$, measured under $N_2$ at 100 mV $s^{-1}$ as a 3 mM THF solution, *versus* ferrocene. Electrolyte: 0.2 M $[^nBu_4N][BF_4]$. Pt disc working electrode, Pt gauze counter electrode, Ag wire pseudo-reference electrode.

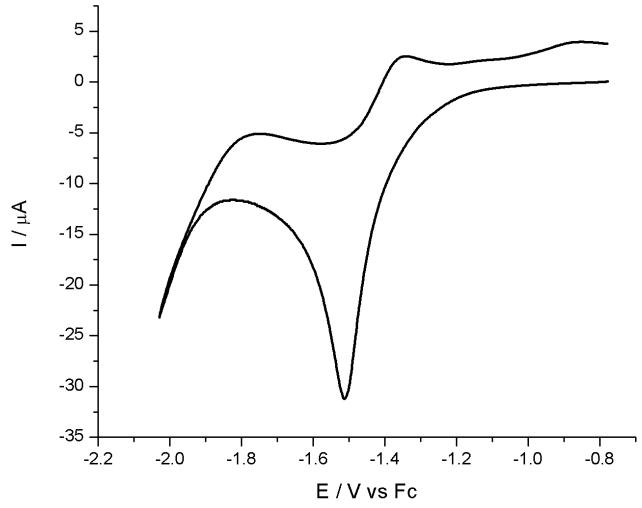



Figure 8: Cyclic voltammogram for $Cu_2L^4$, measured under $N_2$ at 100 mV $s^{-1}$ as a 3 mM $CH_2Cl_2$ solution, *versus* ferrocene. Electrolyte: 0.2 M $[^nBu_4N][BF_4]$. Pt disc working electrode, Pt gauze counter electrode, Ag wire pseudo-reference electrode.

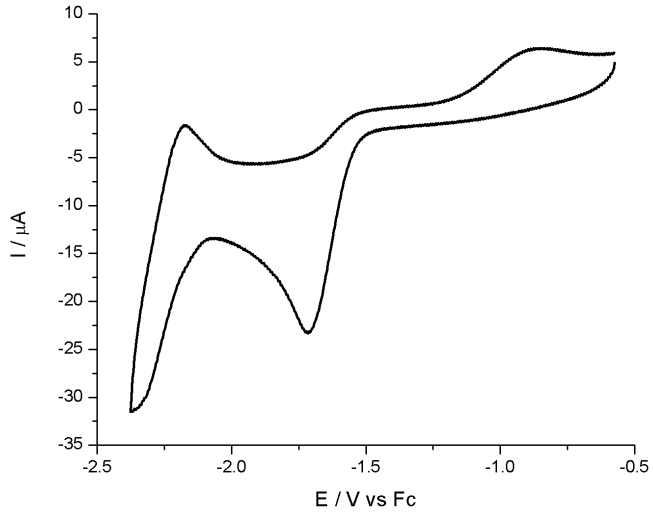



Figure 9: Cyclic voltammogram for $Cu_2L^5$, measured under $N_2$ at 500 mV $s^{-1}$ as a 5 mM THF solution, *versus* ferrocene. Electrolyte: 0.2 M $[^nBu_4N][BF_4]$. Glassy C working electrode, Pt gauze counter electrode, Ag wire pseudo-reference electrode.

| Compound | Redox Process | Description | $E_p^a$ / V | $E_p^c$ / V | $E_{1/2}$ / V | $\Delta E$ / V | $\frac{I_p^a}{I_p^c}$ | Assignment[†] |
|---|---|---|---|---|---|---|---|---|
| $HL^2$ | 1 | Reduction | -1.49 | -1.43 | -1.46 | 0.06 | 1.09 | R. |
| | 2 | Reduction | -2.28 | -1.95 | – | 0.33 | 7.45 | I. |
| $H_4L^3$ | 1 | Reduction | -1.41 | – | – | – | – | I. |
| $H_4L^4$ | 1 | Reduction | -1.78 | – | – | – | – | I. |
| $Cu_2L^3$ | 1 | Oxidation | -0.57 | -0.10 | – | 0.47 | 0.74 | Q.R.[a] |
| | 2 | Reduction | -1.47 | -1.12 | – | 0.36 | 1.32 | Q.R.[a] |
| | 3 | Reduction | -1.76 | -1.42 | – | 0.35 | 3.85 | Q.R.[a] |
| $Cu_2L^4$ [b] | 1 | Reduction | -1.51 | -1.35 | – | 0.07 | 12.14 | I. |
| $Cu_2L^5$ [c] | 1 | Reduction | -1.70 | – | – | – | – | I. |
| | 2 | Reduction | -2.30 | – | – | – | – | I. |

[†] R. = reversible, I. = irreversible, Q.R. = quasi-reversible.

[a] Assigned as quasi-reversible as, although $E_p^a$ and $E_p^c$ are scan-rate dependent, the peak separation is comparable to that of $Fc/Fc^+$ for the system.

[b] Measured as a $CH_2Cl_2$ solution due to poor solubility in THF.

[c] Measured using a glassy C working electrode at 500 mV $s^{-1}$.

Table 1: Summary of electrochemical data for $HL^2$, $H_4L^3$, $H_4L^4$, $Cu_2L^3$, $Cu_2L^4$ and $Cu_2L^5$. All potentials are reported *vs.* $Fc/Fc^+$. All measurements made as a THF solution at a Pt disc working electrode at 100 mV $s^{-1}$ unless stated otherwise.

# 4 Electronic Absorption Spectra

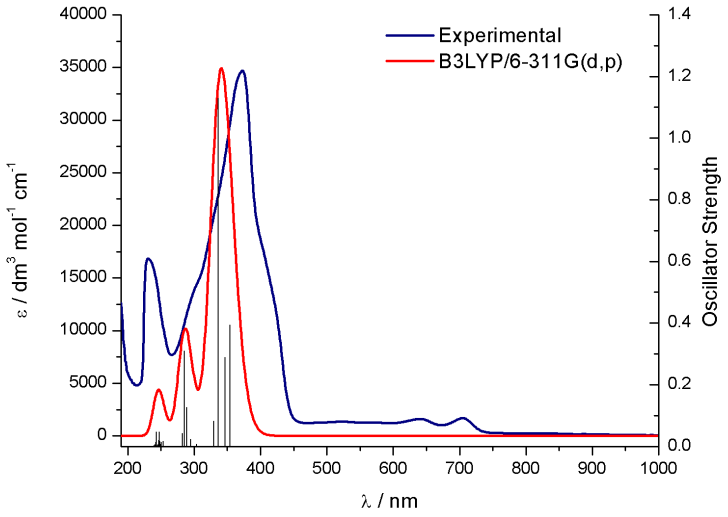



Figure 10: Experimental and simulated electronic absorption spectra of 2, measured as a $CH_2Cl_2$ solution.

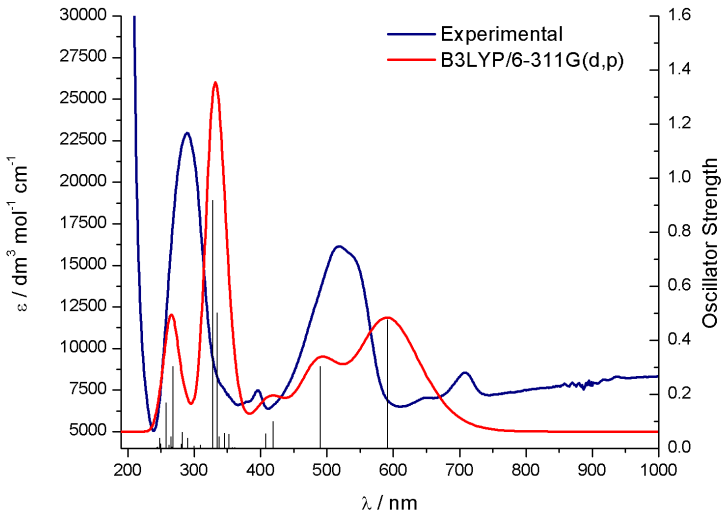



Figure 11: Experimental and simulated electronic absorption spectra of $HL^1$, measured as a $CH_2Cl_2$ solution.

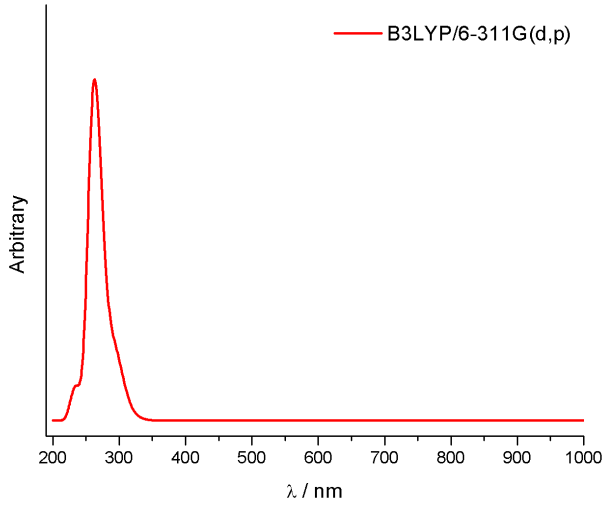



Figure 12: Simulated electronic absorption spectrum of $H_2L^2$.

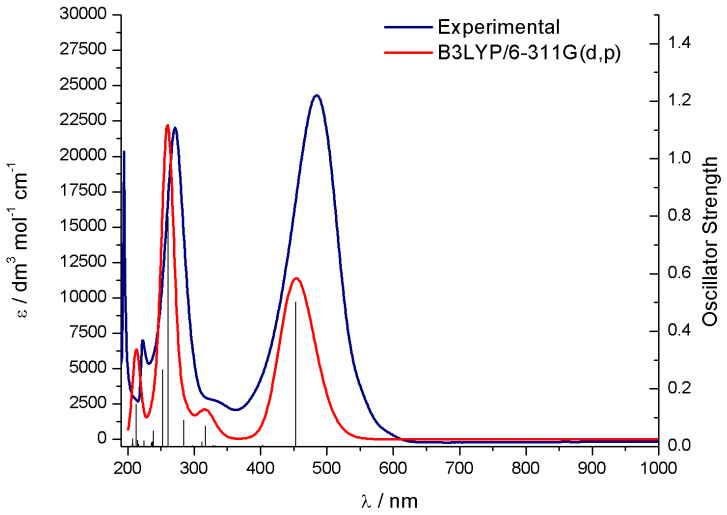



Figure 13: Experimental and simulated electronic absorption spectra of $HL^2$, measured as a $CH_2Cl_2$ solution.

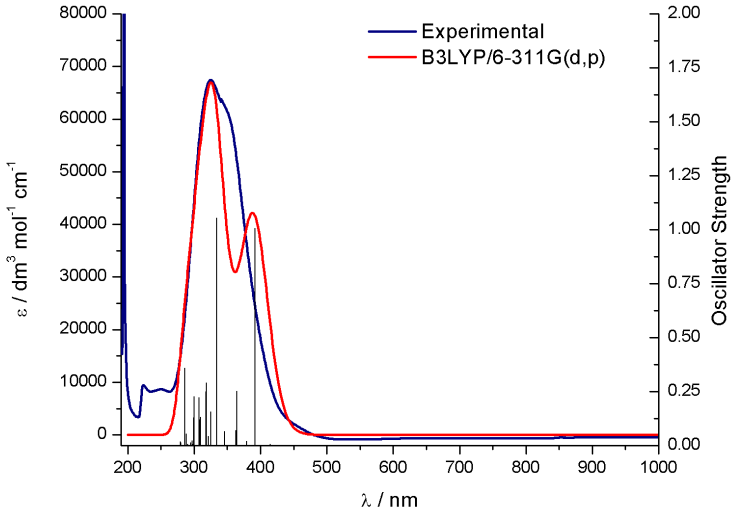



Figure 14: Experimental and simulated electronic absorption spectra of $H_4L^3$, measured as a $CH_2Cl_2$ solution.

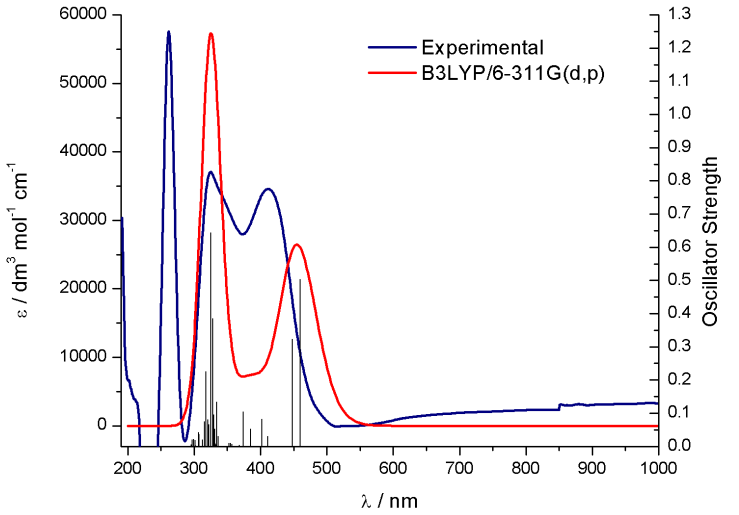



Figure 15: Experimental and simulated electronic absorption spectra of $H_4L^4$, measured as a $CH_2Cl_2$ solution.

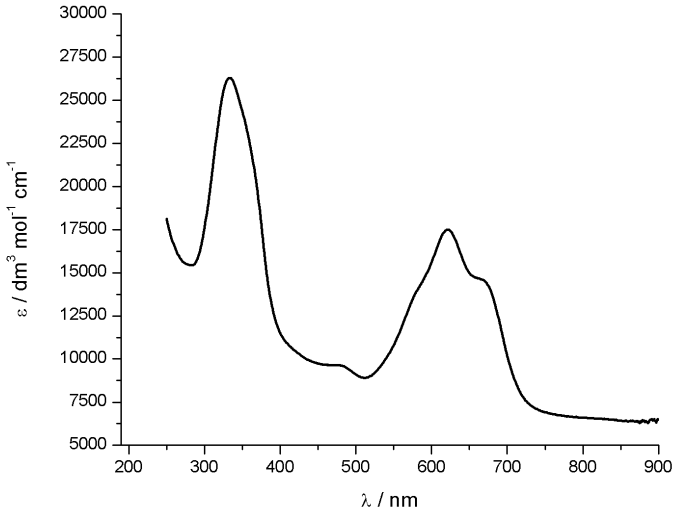



Figure 16: Electronic absorption spectrum of FeBr($L^1$), measured as a THF solution.

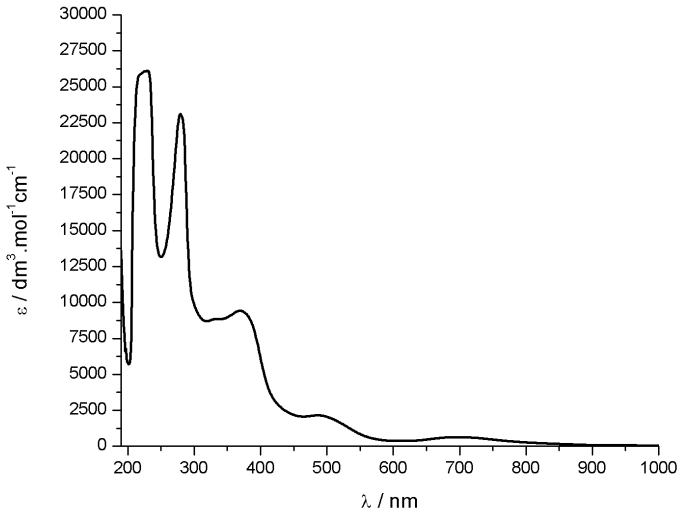



Figure 17: Electronic absorption spectrum of $Cu_2(L^3)$, measured as a THF solution.

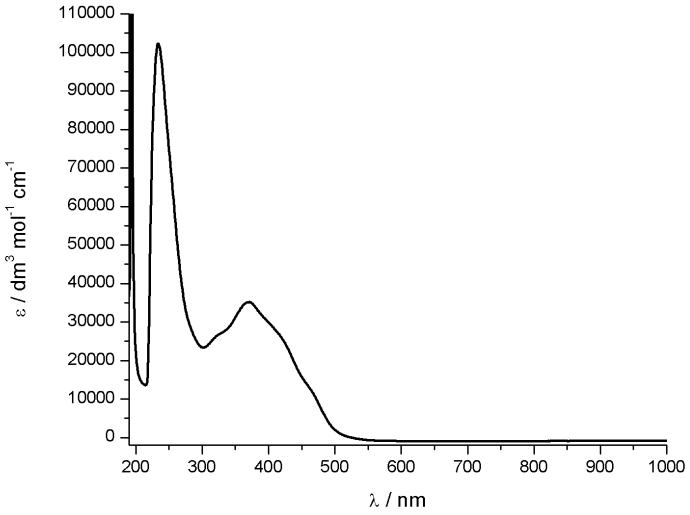



Figure 18: Electronic absorption spectrum of $Cu_2(L^4)$, measured as a THF solution.

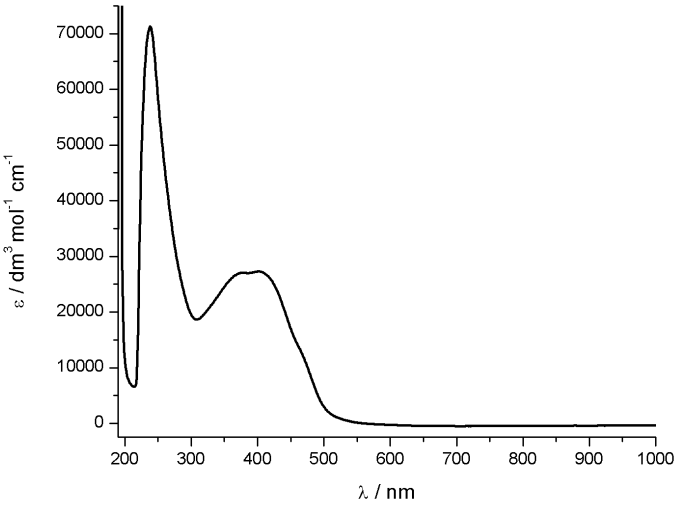



Figure 19: Electronic absorption spectrum of $Cu_2(L^5)$, measured as a THF solution.

# 5 Optimised DFT Geometries

## 5.1 Compound 2

Charge = 0 Multiplicity = 1

C 2.13244 -2.75679 0.78392

C 1.07109 -3.01778 -0.26445

C 1.13592 -3.6803 -1.48231

N -0.23202 -2.67684 -0.04952

C -0.17402 -3.72938 -2.00934

H 2.02888 -4.08323 -1.93304

C -1.01428 -3.0966 -1.10159

H -0.60705 -2.17111 0.74054

H -0.47925 -4.16832 -2.94689

C 1.86678 -1.53078 1.62464

C 1.51254 0.62914 2.13676

H 1.83622 0.01887 0.15397

C 1.46818 -0.09252 3.32341

H 1.72298 -2.28476 3.68201

H 1.29337 0.3215 4.30447

N 1.75161 -0.26466 1.11966

C 1.6889 -1.44974 2.99907

C 3.54217 -2.77227 0.19572

C 4.49761 -3.66325 0.6811

C 3.9539 -1.9115 -0.82015

C 5.79714 -3.70255 0.18968

C 5.24439 -1.92751 -1.33146

C 6.17188 -2.82911 -0.82243

F 3.09008 -1.02214 -1.3445

F 5.59948 -1.08547 -2.30517

F 7.41514 -2.85336 -1.30366

F 6.68251 -4.57311 0.68192

F 4.17558 -4.52902 1.65728

C -2.43108 -2.84789 -1.12822

C 1.35072 2.03761 1.87806

H -2.967 -3.21988 -2.00921

H 1.15765 2.66665 2.75477

N -3.00968 -2.21184 -0.17559

N 1.44869 2.50652 0.68877

C 1.23094 3.87029 0.43613

C 0.28408 4.65148 1.11827

C 1.96481 4.47605 -0.58848

C 0.11355 5.9915 0.79869

H -0.34479 4.19765 1.87613

C 1.79613 5.82398 -0.88883

H 2.67927 3.87291 -1.13644

C 0.86814 6.6187 -0.20496

H -0.63646 6.5566 1.34065

H 2.39918 6.24989 -1.67978

C -4.40099 -2.02714 -0.18001

C -5.31647 -2.97899 -0.65765

C -4.91182 -0.84668 0.36938

C -6.68163 -2.73125 -0.61054

H -4.958 -3.9302 -1.03512

C -6.28136 -0.60367 0.39808

H -4.21282 -0.11688 0.76102

C -7.20377 -1.5367 -0.09114

H -7.35442 -3.4968 -0.98054

1 -6.62488 0.3319 0.81966

C -8.72487 -1.30824 -0.06387

C -9.40077 -2.41628 0.77731

C -9.09955 0.05344 0.5491

C -9.27804 -1.3536 -1.50744

H -9.21728 -3.41018 0.36264

H -9.02613 -2.4088 1.80444

H -10.48401 -2.26282 0.80822

H -8.67438 0.8852 -0.01913

H -10.18647 0.17218 0.54439

H -8.76317 0.13937 1.58592

H -10.3612 -1.19648 -1.50499

H -8.8222 -0.57392 -2.12367

H -9.08191 -2.31535 -1.98731

C 0.64133 8.10675 -0.52282

C 1.56872 8.6135 -1.64241

C -0.82166 8.32023 -0.97723

C 0.91144 8.95148 0.74417

H 2.62376 8.51261 -1.37354

H 1.40193 8.07953 -2.5818

H 1.37497 9.67354 -1.82697

H -1.53381 8.02447 -0.20347

H -0.99835 9.3755 -1.20774

H -1.04031 7.73448 -1.87415

H 0.75166 10.01373 0.53472

H 0.25026 8.67136 1.56737

H 1.94236 8.82317 1.08508

H 2.10119 -3.58868 1.49279

### 5.2 $HL^1$

Charge = 0 Multiplicity = 1

6 5.24289 -0.05163 -0.00165

6 5.97046 0.21515 1.158

6 7.3596 0.19043 1.17337

6 8.0527 -0.1049 0.00539

6 7.35469 -0.37277 -1.1659

6 5.96512 -0.34316 -1.1585

9 5.33121 0.49935 2.29868

9 8.03133 0.44442 2.30009

9 9.38603 -0.13133 0.00906

9 8.02174 -0.65354 -2.289

9 5.32329 -0.60132 -2.30343

6 3.74954 -0.02542 -0.00388

6 3.05816 -1.22481 -0.0309

6 3.60461 -2.57223 -0.04622

7 1.67245 -1.27319 -0.0361

6 2.53239 -3.40752 -0.06428

1 4.65037 -2.83909 -0.03981

6 1.35102 -2.55387 -0.0558

1 2.53559 -4.48809 -0.07952

6 3.1271 1.25537 0.01972

6 3.71791 2.53928 0.03602

7 1.7656 1.4395 0.02459

6 2.68845 3.47549 0.05467

1 4.77714 2.74039 0.03095

6 1.47405 2.76433 0.04551

1 1.11131 0.6531 0.00923

1 2.78314 4.55018 0.0706

6 -0.01721 -3.05393 -0.06353

1 -0.11446 -4.14699 -0.10472

6 0.12229 3.26981 0.05153

1 0.02383 4.36055 0.09591

7 -1.0354 -2.27954 -0.04277

7 -0.87748 2.46893 0.02565

6 -2.33219 -2.80574 0.00024

6 -2.68633 -3.9931 0.66417

6 -3.34986 -2.07034 -0.61913

6 -4.00302 -4.42966 0.67051

1 -1.93439 -4.55336 1.20825

6 -4.66244 -2.53064 -0.62405

1 -3.08442 -1.14073 -1.10822

6 -5.02553 -3.72051 0.01907

1 -4.23827 -5.34259 1.20593

1 -5.40978 -1.93662 -1.13312

6 -2.19506 2.94034 -0.01274

6 -2.58988 4.16542 -0.5779

6 -3.18938 2.10685 0.51228

6 -3.92456 4.54148 -0.57732

1 -1.85598 4.80853 -1.05039

6 -4.52265 2.50423 0.52279

1 -2.89075 1.14895 0.92101

6 -4.9266 3.73059 -0.01808

1 -4.19195 5.48775 -1.03389

1 -5.2519 1.83214 0.95511

6 -6.46913 -4.25047 0.04988

6 -6.95366 -4.34682 1.51576

6 -7.44341 -3.33778 -0.71714

6 -6.51494 -5.65447 -0.59732

1 -6.33014 -5.02172 2.10644

1 -6.93369 -3.36587 1.99819

1 -7.98053 -4.72351 1.55214

1 -7.17117 -3.24796 -1.77221

1 -8.45196 -3.75717 -0.67084

1 -7.48403 -2.33347 -0.28682

1 -7.53646 -6.04711 -0.58107

1 -6.18189 -5.61455 -1.63789

1 -5.87613 -6.36613 -0.06941

6 -6.39112 4.19956 -0.03573

6 -6.85219 4.39863 -1.49878

6 -7.33817 3.18596 0.63211

6 -6.50947 5.54124 0.72487

1 -6.24672 5.14524 -2.01764

1 -6.7818 3.46291 -2.05984

1 -7.89314 4.73521 -1.52612

1 -7.07839 3.01667 1.68052

1 -8.36239 3.56731 0.60316

1 -7.33133 2.22144 0.11725

1 -7.54622 5.8918 0.7169

1 -6.19639 5.42807 1.76628

1 -5.89109 6.32024 0.27313

### 5.3 $\mathbf{H_2L^2}$

Charge = 0 Multiplicity = 1

6 -1.05866 -1.25432 0.90948

6 -0.49089 -0.01732 1.56314

6 -0.28242 0.22893 2.91196

7 -0.08015 1.09352 0.87576

6 0.26379 1.52901 3.03154

1 -0.50857 -0.45797 3.71323

6 0.37953 2.04746 1.75002

1 -0.10025 1.2396 -0.12336

1 0.54508 2.03412 3.94284

6 -0.11593 -1.91343 -0.07575

6 1.87297 -2.58881 -0.87965

1 1.74303 -1.31199 0.78077

6 0.88729 -3.15887 -1.67153

1 -1.33822 -2.99752 -1.54672

1 1.0571 -3.80221 -2.52147

6 -2.44308 -1.01449 0.30911

6 -2.65604 -0.23649 -0.82755

6 -3.57547 -1.56416 0.90704

6 -3.92324 -0.00985 -1.3471

9 -1.61459 0.32948 -1.46543

6 -4.85656 -1.35499 0.41016

9 -3.45231 -2.33042 2.00454

6 -5.03059 -0.57282 -0.72349

9 -4.08542 0.74351 -2.43838

9 -5.91628 -1.90078 1.01387

9 -6.2538 -0.36061 -1.21148

6 -0.36436 -2.73402 -1.16526

7 1.23825 -1.83986 0.08303

6 3.31776 -2.66501 -0.94096

6 0.87393 3.32537 1.27439

1 3.71459 -3.28089 -1.75511

1 1.2081 4.01452 2.05714

7 4.04041 -2.04662 -0.09213

7 0.89953 3.58799 0.02826

6 5.51028 -2.09868 -0.12434

6 6.11885 -2.93016 -1.26606

6 5.98668 -0.63708 -0.23471

6 5.94919 -2.68139 1.2336

1 5.81376 -3.97923 -1.21198

1 5.83564 -2.53906 -2.24764

1 7.2093 -2.90147 -1.20201

1 5.55076 -0.03801 0.56736

1 7.07676 -0.57734 -0.16578

1 5.67669 -0.20288 -1.18892

1 7.03848 -2.65925 1.33084

1 5.51259 -2.1034 2.05072

1 5.61466 -3.71737 1.33463

6 1.392 4.87123 -0.49646

6 2.57759 4.52933 -1.41995

6 0.23917 5.46009 -1.33313

6 1.83677 5.89274 0.5636

1 3.40406 4.1048 -0.84373

1 2.27375 3.79445 -2.16803

1 2.93872 5.42507 -1.9332

1 -0.61529 5.70165 -0.69521

1 0.55824 6.37375 -1.8427

1 -0.09108 4.73754 -2.08209

1 2.17368 6.8088 0.07247

1 1.01704 6.16198 1.23615

1 2.66907 5.51813 1.16646

1 -1.21379 -1.95518 1.73418

### 5.4 $HL^2$

Charge = 0 Multiplicity = 1

C 2.97175 -0.02696 -0.0007

C 3.6936 0.31924 1.14103

C 5.08291 0.31547 1.1584

C 5.78155 -0.03898 0.01032

C 5.08884 -0.38633 -1.14309

C 3.69894 -0.37647 -1.13777

F 3.04858 0.66209 2.26212

F 5.74962 0.6465 2.26816

F 7.11531 -0.04598 0.01602

F 5.76122 -0.72462 -2.2472

F 3.06194 -0.71199 -2.26524

C 1.47727 -0.02044 -0.00488

C 0.80715 -1.2268 0.06287

C 1.3836 -2.55738 0.16141

N -0.58152 -1.30702 0.05461

C 0.33022 -3.41443 0.20973

H 2.4351 -2.79833 0.19541

C -0.87007 -2.59022 0.14015

H 0.35673 -4.49223 0.28538

C 0.8451 1.25424 -0.08151

C 1.43215 2.53312 -0.1799

N -0.51863 1.43602 -0.07544

C 0.39878 3.46709 -0.23118

H 2.49077 2.73458 -0.21354

C -0.8105 2.75746 -0.16486

H -1.17345 0.65297 -0.02498

H 0.49077 4.53947 -0.30729

C -2.22872 -3.14474 0.16585

H -2.26026 -4.23868 0.23933

C -2.16852 3.27559 -0.18286

H -2.23924 4.36604 -0.25794

N -3.27041 -2.42042 0.10807

N -3.16916 2.49432 -0.114

C -4.61978 -3.00545 0.13562

C -5.32946 -2.36121 1.34317

C -5.30148 -2.54662 -1.16886

C -4.69211 -4.53807 0.24779

H -4.85583 -2.67063 2.27857

H -5.27002 -1.27348 1.27744

H -6.3817 -2.65788 1.37388

H -4.80714 -2.98838 -2.0381

H -6.35282 -2.84805 -1.17892

H -5.24371 -1.4608 -1.26231

H -5.73787 -4.85459 0.26007

H -4.20941 -5.03209 -0.60036

H -4.2274 -4.90135 1.16895

C -4.55362 2.98894 -0.12737

C -5.23394 2.29904 -1.32626

C -5.19004 2.49029 1.18515

C -4.71443 4.51379 -0.2403

H -4.79907 2.64451 -2.26792

H -5.09409 1.21839 -1.26497

H -6.30514 2.51885 -1.33914

H -4.71891 2.9681 2.04826

H -6.25921 2.71916 1.20454

H -5.05704 1.41125 1.28067

H -5.77615 4.77181 -0.24176

H -4.25137 5.03523 0.60255

H -4.28069 4.90094 -1.16697

### 5.5 $H_4L^3$

Charge = 0 Multiplicity = 1

C 1.53006 5.06507 0.74826

H 1.58932 6.15832 0.69926

C 2.69604 4.36542 0.28408

C 3.90456 4.85404 -0.19814

H 4.15465 5.89679 -0.32033

C 4.7276 3.74473 -0.48995

H 5.73635 3.7732 -0.86922

C 4.00794 2.59827 -0.18633

C 4.41752 1.14331 -0.18805

H 4.65778 0.88435 0.84887

C 5.70303 0.89975 -0.97615

C 5.81699 1.16709 -2.34049

C 6.98273 0.90456 -3.04834

C 8.07818 0.3542 -2.39305

C 7.99779 0.0738 -1.03578

C 6.8198 0.34845 -0.35163

C 3.31797 0.19588 -0.61257

C 2.4144 0.23144 -1.66694

H 2.33415 1.02517 -2.39139

C 1.65483 -0.95853 -1.61613

H 0.85945 -1.24883 -2.28441

C 2.10512 -1.69969 -0.53028

C 1.68468 -2.97044 0.00596

H 0.87293 -3.47632 -0.51652

C 1.89631 -4.6342 1.67152

C 2.92257 -5.33178 2.32894

H 3.91866 -4.909 2.25893

C 2.71608 -6.50613 3.04014

C 1.39973 -7.00496 3.14733

C 0.37047 -6.31241 2.52053

H -0.64731 -6.66236 2.65573

C 0.57549 -5.14929 1.75664

C 3.87322 -7.20651 3.70875

H 3.73367 -7.27345 4.79309

H 4.80933 -6.67678 3.52526

H 3.99131 -8.23157 3.34149

C -1.53025 -5.06513 0.74846

H -1.58949 -6.15838 0.69944

C -2.69627 -4.3655 0.28436

C -3.90486 -4.8541 -0.19772

H -4.155 -5.89684 -0.31979

C -4.7279 -3.74478 -0.48946

H -5.7367 -3.77326 -0.86863

C -4.00815 -2.59833 -0.18601

C -4.41767 -1.14334 -0.18783

H -4.65803 -0.88436 0.84905

C -5.70306 -0.89972 -0.9761

C -6.81985 -0.34823 -0.35181

C -7.99772 -0.07352 -1.03615

C -8.07797 -0.3541 -2.39338

C -6.98247 -0.90465 -3.04846

C -5.81686 -1.1672 -2.34043

C -3.31803 -0.19598 -0.61228

C -2.41437 -0.2316 -1.66658

H -2.33409 -1.02534 -2.39101

C -1.65474 0.95832 -1.61572

H -0.85931 1.24859 -2.28396

C -2.10507 1.69952 -0.52992

C -1.68465 2.97027 0.00637

H -0.87288 3.47617 -0.51608

C -1.89637 4.63415 1.67172

C -2.92259 5.33178 2.32915

H -3.91868 4.90899 2.25926

C -2.71604 6.50621 3.04021

C -1.39968 7.00506 3.14724

C -0.37046 6.31248 2.5204

H 0.64732 6.66246 2.65543

C -0.57556 5.14927 1.75666

C -3.87311 7.2066 3.70894

H -4.80933 6.67723 3.52503

H -3.99083 8.23187 3.34216

H -3.73372 7.27298 4.79334

C -1.10126 8.24844 3.9484

H -1.40062 8.13557 4.99585

H -1.64115 9.11772 3.55799

H -0.03542 8.48242 3.9297

N 0.49101 4.44696 1.18566

N 2.78666 2.99018 0.28373

H 2.02549 2.38673 0.55909

N 3.11266 -0.97692 0.06213

H 3.60235 -1.31948 0.87667

N 2.2763 -3.44987 1.04035

N -0.49115 -4.44701 1.18572

N -2.78685 -2.99025 0.28394

H -2.02563 -2.38682 0.55922

N -3.11275 0.97685 0.06237

H -3.60254 1.3195 0.87681

N -2.27634 3.44974 1.04069

F 4.7871 1.69623 -3.01404

F 7.05818 1.17717 -4.3541

F 9.20057 0.09698 -3.0659

F 9.04641 -0.45499 -0.39857

F 6.7803 0.05724 0.96214

F -6.78053 -0.05689 0.96195

F -9.04636 0.45547 -0.39914

F -9.20023 -0.09686 -3.06644

F -7.05779 -1.17739 -4.35421

F -4.78693 -1.69651 -3.01376

C 1.10137 -8.24829 3.94859

H 1.40103 -8.13547 4.99596

H 1.64106 -9.11764 3.55803

H 0.03551 -8.48216 3.93016

### 5.6 $\mathbf{H_4L^4}$

Charge = 0 Multiplicity = 1

6 -2.89582 2.09941 -3.5036

1 -2.94114 2.40985 -4.55353

6 -1.72956 2.5089 -2.76769

6 -0.63987 3.28949 -3.1315

1 -0.44601 3.67676 -4.11988

6 0.14344 3.49654 -1.97274

1 1.04289 4.08533 -1.89941

6 -0.47503 2.82894 -0.92419

6 -0.16084 2.71267 0.55191

1 -0.28995 1.65901 0.82006

6 1.25394 3.09083 0.92298

6 1.73952 3.77209 2.02931

1 1.14264 4.18246 2.8274

6 3.14481 3.82757 1.91501

1 3.83272 4.29885 2.60001

6 3.49686 3.16752 0.74557

6 4.78183 2.99972 0.12114

1 5.61158 3.5446 0.58684

6 6.18149 2.31019 -1.59307

6 6.72497 3.50284 -2.02121

1 6.19634 4.42665 -1.81639

6 7.92628 3.53552 -2.77626

1 8.31375 4.49347 -3.10516

6 8.58285 2.38108 -3.09471

1 9.498 2.40451 -3.67616

6 8.07282 1.11786 -2.66643

6 8.73268 -0.07902 -2.95821

1 9.64924 -0.04539 -3.5391

6 8.25687 -1.31695 -2.51616

6 8.93984 -2.53491 -2.8133

1 9.84118 -2.49397 -3.41506

6 8.45854 -3.72901 -2.35526

1 8.97152 -4.65345 -2.59642

6 7.28384 -3.78135 -1.56226

1 6.90308 -4.74256 -1.23688

6 6.58995 -2.63436 -1.23661

6 7.04782 -1.35779 -1.73302

6 6.37245 -0.16527 -1.45556

1 5.46037 -0.20001 -0.87647

6 6.85041 1.06932 -1.90346

6 5.33872 -3.39831 0.56769

1 6.20034 -3.95137 0.95864

6 4.1089 -3.52898 1.30202

6 3.79897 -4.21741 2.46917

1 4.49047 -4.80371 3.05456

6 2.42998 -4.00058 2.74064

1 1.86437 -4.40262 3.56557

6 1.92922 -3.18458 1.73603

6 0.54152 -2.65712 1.46553

1 0.67233 -1.72696 0.90141

6 -0.26024 -3.59508 0.59

6 0.08147 -4.82791 0.05844

1 1.00572 -5.35002 0.24418

6 -0.99708 -5.25906 -0.74262

1 -1.0632 -6.17993 -1.30143

6 -1.98055 -4.27991 -0.68761

6 -3.27709 -4.24245 -1.30326

1 -3.54423 -5.13266 -1.88449

6 -5.36975 -3.35963 -1.71919

6 -6.13556 -4.48923 -1.51274

1 -5.73783 -5.29425 -0.906

6 -7.44671 -4.5998 -2.04088

1 -8.01616 -5.50274 -1.85034

6 -7.98777 -3.58634 -2.77957

1 -8.98714 -3.67104 -3.19215

6 -7.25004 -2.38605 -3.00885

6 -7.7795 -1.33489 -3.76164

1 -8.77036 -1.44376 -4.19165

6 -7.0765 -0.14674 -3.97561

6 -7.62926 0.91952 -4.74688

1 -8.61543 0.79301 -5.18002

6 -6.9338 2.08272 -4.91853

1 -7.36323 2.89818 -5.48982

6 -5.65392 2.25205 -4.33369

1 -5.1535 3.20888 -4.42564

6 -5.06212 1.24849 -3.59233

6 -5.76724 0.00313 -3.39058

6 -5.22275 -1.05539 -2.65677

1 -4.23667 -0.94775 -2.22744

6 -5.92641 -2.24713 -2.45343

6 -1.19263 3.47829 1.37884

6 -1.29191 4.87037 1.35318

6 -2.24375 5.55252 2.1002

6 -3.141 4.84261 2.89067

6 -3.08237 3.45596 2.92259

6 -2.12055 2.79997 2.16464

6 -0.16747 -2.24635 2.75555

6 -0.15074 -0.91266 3.16055

6 -0.76521 -0.47427 4.32491

6 -1.42044 -1.39393 5.13385

6 -1.44672 -2.73467 4.76899

6 -0.82181 -3.1451 3.59701

7 -3.84152 1.44135 -2.93583

7 -1.59881 2.23158 -1.42623

1 -2.30087 1.71334 -0.91785

7 2.32925 2.71493 0.16743

1 2.30655 2.23916 -0.72245

7 4.94965 2.27482 -0.92443

7 5.41158 -2.66301 -0.48186

7 2.95632 -2.90911 0.87957

1 2.92366 -2.35471 0.03624

7 -1.50711 -3.27262 0.12636

1 -2.05231 -2.45165 0.34269

7 -4.07588 -3.24228 -1.19134

9 -0.45652 5.59154 0.59726

9 -2.3055 6.88596 2.06204

9 -4.05766 5.49139 3.60862

9 -3.94975 2.76444 3.66556

9 -2.12461 1.4508 2.18824

9 0.48199 0.00338 2.40117

9 -0.72987 0.81564 4.67049

9 -2.01501 -0.99435 6.25746

9 -2.06327 -3.62336 5.55177

9 -0.84882 -4.45195 3.30274

# 6 X-ray Crystallographic Data

| | **1** | **HL**$^2$ | **H$_4$L**$^3$ | **H$_4$L**$^4$ |
|---|---|---|---|---|
| CCDC Registry | 1032820 | 1032821 | 1032823 | 1032824 |
| Formula | $C_{17}H_9F_5N_2O_2$ | $C_{25}H_{25}F_5N_4$ | $C_{50}H_{34}F_{10}N_8 \cdot 4\,(C_4H_8O)$ | $C_{62}H_{34}F_{10}N_8,\ 4\,(CH_3OH),\ H_2O$ |
| $M_r$ / g mol$^{-1}$ | 736.52 | 476.49 | 1225.26 | 1227.15 |
| Colour, habit | Colourless block | Red plate | Yellow plate | Pale brown needle |
| Crystal size / mm$^3$ | 0.51 × 0.26 × 0.07 | 0.43 × 0.20 × 0.07 | 0.60 × 0.34 × 0.18 | 0.3512 × 0.0378 × 0.0262 |
| Crystal system | Triclinic | Triclinic | Orthorhombic | Triclinic |
| Space group | P -1 (no. 2) | P -1 (no. 2) | Pnn2 (no. 34) | P-1 (no. 2) |
| a / Å | 10.0877(8) | 12.0938(6) | 29.8511(18) | 13.5433(7) |
| b / Å | 11.7180(8) | 14.2191(11) | 27.674(2) | 14.8529(9) |
| c / Å | 13.6686(9) | 14.6822(11) | 7.7730(8) | 17.1922(7) |
| $\alpha$ / deg | 95.540(6) | 104.393(7) | 90 | 107.163(5) |
| $\beta$ / deg | 93.267(6) | 90.013(5) | 90 | 98.360(4) |
| $\gamma$ / deg | 95.334(6) | 95.477(5) | 90 | 108.596(5) |
| V / Å$^3$ | 1597.7(2) | 2433.6(3) | 6421.3(9) | 3020.3(3) |
| Z | 2 | 4 | 4 | 2 |
| T / K | 170(2) | 173(2) | 170(2) | 120(2) |
| F(000) | 744 | 992 | 2560 | 1268 |
| Radiation type | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ | Cu K$\alpha$ |
| $\mu$ / mm$^{-1}$ | 0.141 | 0.11 | 0.100 | 0.917 |
| Absorption correction | Multi-scan | Multi-scan | Multi-scan | Gaussian |
| Transmission factors | 0.51189 – 1.0 | 0.909 – 1.0 | 0.61005 – 1.0 | 0.929 – 0.991 |
| $2\theta_{max}$ / deg | 54.968 | 53.764 | 52.1 | 102.5 |
| Total no. of reflns | 15,419 | 14,436 | 31,363 | 31,215 |
| No. of unique reflns | 7326 | 14,436 | 9433 | 6323 |
| No. of reflns with I $\geq 2\sigma$(I) | 3678 | 9136 | 5814 | 3782 |
| $R_{int}$ | 0.052 | 0.00 | 0.047 | 0.089 |
| $(\sin\theta)/\lambda$ / Å$^{-1}$ | 0.649 | 0.662 | 0.618 | 0.230 |
| No. of parameters | 469 | 634 | 797 | 837 |
| H-atom treatment | Constrained | Mixed | Constrained | Mixed |
| R (F$^2$, all data) | 0.1438 | 0.1404 | 0.1145 | 0.1361 |
| $R_w$ (F$^2$, all data) | 0.1939 | 0.1692 | 0.2004 | 0.2337 |
| R (F, I $>2\theta$(I)) | 0.0626 | 0.0831 | 0.0651 | 0.0781 |
| $R_w$ (F, I $>2\theta$(I)) | 0.1379 | 0.1487 | 0.1737 | 0.1949 |
| G.O.F. | 0.865 | 1.125 | 0.961 | 1.024 |

Table 2: Summary of X-Ray crystallographic data for compounds **1**, **HL**$^2$, **H$_4$L**$^3$ and **H$_4$L**$^4$.

| | $\{FeBr(L^1)\}_2(\mu\text{-}O)$ | $Cu_2L^3$ | $Cu_2L^4$ | $Cu_2L^5$ |
|---|---|---|---|---|
| CCDC Registry | 1032822 | 1032825 | 1032826 | 1032827 |
| Formula | $C_{37}H_{32}BrF_5FeN_4O_{0.5}$ | $C_{70}H_{50}Cu_2F_{10}N_{12} \cdot 3\,(C_5H_5N)$ | $C_{62}H_{30}Cu_2F_{10}N_8$ | $C_{58}H_{48}Cu_2N_8$ |
| $M_r$ / g mol$^{-1}$ | 1542.85 | 1613.60 | 1204.02 | 984.12 |
| Colour, habit | Green needle | Red block | Dark brown block | Dark brown block |
| Crystal size / mm$^3$ | 0.59 × 0.23 × 0.17 | 0.29 × 0.22 × 0.11 | 0.5629 × 0.2172 × 0.0353 | 0.1258 × 0.0689 × 0.0366 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic |
| Space group | C2/c (no. 15) | P -1 (no. 2) | P -1 (no. 2) | C 1 2/c 1 (no. 15) |
| a / Å | 23.483(5) | 12.1160(3) | 8.0044(2) | 12.3900(7) |
| b / Å | 19.497(5) | 14.6689(4) | 16.3501(4) | 24.4018(14) |
| c / Å | 20.550(5) | 21.0498(5) | 20.0568(4) | 19.8715(10) |
| $\alpha$ / deg | 90.00 | 89.765(2) | 97.223(2) | 90.00 |
| $\beta$ / deg | 107.498(5) | 86.422(2) | 98.673(2) | 103.654(5) |
| $\gamma$ / deg | 90.00 | 85.304(2) | 92.044(2) | 90.00 |
| V / Å$^3$ | 8973(4) | 3721.32(16) | 2570.28(10) | 5838.1(6) |
| Z | 4 | 2 | 2 | 4 |
| T / K | 173 | 170(2) | 170(2) | 170(2) |
| F(000) | 3136 | 1656 | 1212 | 2040 |
| Radiation type | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ |
| $\mu$ / mm$^{-1}$ | 1.27 | 0.655 | 0.915 | 0.768 |
| Absorption correction | Multi-scan | Multi-scan | Multi-scan | Multi-scan |
| Transmission factors | 0.695 – 0.809 | 0.94412 – 1.0 | 0.82365 – 1.0 | 0.89271 – 1.0 |
| $2\theta_{max}$ / deg | 50.12 | 58.4 | 58.772 | 41.5284 |
| Total no. of reflns | 22,615 | 42,650 | 13,677 | 16,353 |
| No. of unique reflns | 7939 | 17,034 | 13,677 | 3057 |
| No. of reflns with I $\geq 2\sigma$(I) | 3732 | 12,537 | 10,767 | 2022 |
| $R_{int}$ | 0.077 | 0.033 | 0.04 | 0.111 |
| $(\sin\theta/\lambda)$ / Å$^{-1}$ | 0.596 | 0.649 | 0.707 | 0.500 |
| No. of parameters | 443 | 990 | 740 | 309 |
| H-atom treatment | Mixed | Mixed | Mixed | Mixed |
| R ($F^2$, all data) | 0.1389 | 0.0872 | 0.0556 | 0.1042 |
| $R_w$ ($F^2$, all data) | 0.2018 | 0.1779 | 0.1182 | 0.1603 |
| R (F, I >2$\theta$(I)) | 0.0703 | 0.0607 | 0.0405 | 0.0614 |
| $R_w$ (F, I >2$\theta$(I)) | 0.1661 | 0.1605 | 0.1109 | 0.1443 |
| G.O.F. | 0.907 | 1.024 | 1.026 | 0.991 |

Table 3: Summary of X-Ray crystallographic data for compounds $\{FeBr(L^1)\}_2(\mu\text{-}O)$, $Cu_2L^3$, $Cu_2L^4$ and $Cu_2L^5$.