Electronic Supplementary Information (ESI)

Boronic acid-substituted metal complexes: versatile building blocks for the synthesis of multimetallic assemblies

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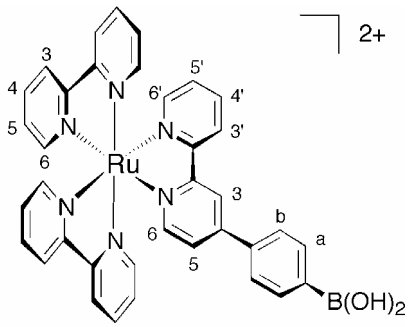
1. Selected synthetic and analytical details

The ligand bpy-ϕ-Br (ϕ = 1,4-C_6H_4-) was prepared as described by Schmehl,[(a)] and converted to bpy-ϕ-Bneo using the procedure we reported previously for tpy-ϕ-Bneo {Bneo represents the neopentylglycolate ester of the boronic acid).[(b)] The bis-cyclometalated iridium complexes $[Ir(ppy)_2(bpy\text{-}\phi\text{-}Br)](PF_6)$ and $[Ir(F_2\text{-}ppy)_2\{bpy\text{-}\phi\text{-}B(OH)_2\}](PF_6)$ were prepared by reaction of $[Ir(ppy)_2\mu\text{-}Cl]_2$ with tpy-ϕ-Br and tpy-ϕ-B*neo*, respectively, using the conditions of Neve *et al.* (CH_2Cl_2 / MeOH at gentle reflux).[(c)] ^{1}H NMR resonances are referenced relative to residual protio-solvent resonances, and coupling constants are in Hertz. Spectra were assigned using a combination of ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY NMR spectroscopy. However, the tetramer was too large to obtain a NOESY spectrum, and ROESY was therefore employed in this case. Although the products comprise mixtures of diastereoisomers, in each of which no two ligands are strictly equivalent, the inequivalence of protons in the pairs of bpy and ppy ligands led only to additional fine structure in some resonances, at the field strength employed (500 MHz). In the spectral assignments below, such ligands are therefore treated as being equivalent. We note that the presence of isomeric species is not expected to have a significant effect on the photophysical properties.[(d)]

Ru-B $[Ru(bpy)_2\{bpy\text{-}\phi\text{-}B(OH)_2\}](PF_6)_2$

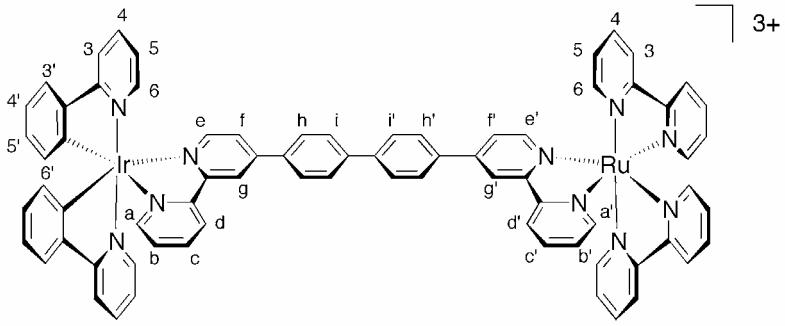
A solution of $Ru(bpy)_2Cl_2.2H_2O$ (156 mg, 0.3 mmol) and $AgBF_4$ (140 mg, 0.7 mmol) in acetone (25 mL, pre-distilled from K_2CO_3) was stirred at room temperature for 18 h under a nitrogen atmosphere. The resulting fine precipitate of AgCl was removed by filtration through celite, and the filtrate concentrated to 15 mL under reduced pressure. A solution of bpy-ϕ-$B(OH)_2$ (0.3 mmol) in acetone (10 mL) was added, and the mixture stirred under



Ru–B

nitrogen at room temperature for 96 h. The solvent was then removed under reduced pressure, and the residue subject to ion-exchange with aqueous KPF_6. Purification of the hexafluorophosphate salt was achieved via column chromatography on silica, gradient elution from 100% CH_3CN to 80% CH_3CN / 19.7% H_2O / 0.3% KNO_3, followed by a second ion exchange with KPF_6 (aq) to yield the desired complex, in which the boronate ester had hydrolysed to the acid (144 mg, 49%). R_f (tlc) = 0.4 in 80% CH_3CN / 18% H_2O / 2% KNO_3. ^{1}H NMR (400 MHz, CD_3CN): δ 8.76 (1H, d, *J 1.6*, bpy-ϕ-H^3), 8.69 (1H, d, *J 8.2*, bpy-ϕ-$H^{3'}$), 8.52 (4H, dd, *J 8.0, 4.8*, bpy-H^3), 8.11 – 8.03 (5H, m, bpy-H^4 and bpy-ϕ-$H^{4'}$), 7.96 (2H, d, *J 7.9*, H^a), 7.87 (2H, d, *J 7.9*, H^b), 7.83 – 7.73 (6H, m, bpy-H^6, bpy-ϕ-H^6 and bpy-ϕ-$H^{6'}$), 7.67 (1H, dd, *J 6.1, 2.0*, bpy-ϕ-H^5), 7.46 – 7.37 (5H, m, bpy-H^5 and bpy-ϕ-$H^{5'}$), 6.19 (2H, s, OH). MS (ES+): m/z = 345.1, $[Ru(bpy)_2\{bpy\text{-}\phi\text{-}B(OH)_2\}]^{2+}$ and 352.1, $[Ru(bpy)_2\{bpy\text{-}\phi\text{-}B(OH)(OMe)\}]^{2+}$.

Ir–Ru $[Ir(ppy)_2\mu\text{-}(bpy\text{-}\phi\text{-}\phi\text{-}bpy)Ru(bpy)_2](PF_6)_3$



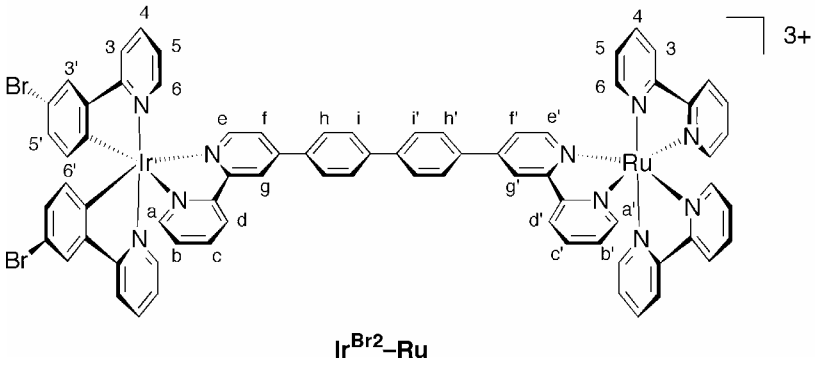
Ir–Ru

A Schlenk tube was charged with **Ru-B** (84 mg, 0.086 mmol), $[Ir(ppy)_2(bpy\text{-}\phi\text{-}Br)](PF_6)$ (72 mg, 0.075 mmol), DMSO (8 mL) and Na_2CO_3 (26 mg in 100 μL water, 0.25 mmol). The solution was thoroughly degassed by three freeze-pump-thaw cycles, and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol) was then added under a positive pressure of nitrogen gas. The solution was stirred at 80°C for 96 h, after which, it was diluted with acetonitrile (5 mL) and filtered into a saturated aqueous solution of KPF_6. Purification of the hexafluorophosphate salt which precipitated was achieved via column chromatography on silica, gradient elution from 100% CH_3CN to 86% CH_3CN / 13.7% H_2O / 0.3% KNO_3. A further ion exchange of appropriate fractions led to the desired complex (90 mg, 66%). R_f (tlc) = 0.5 in 80% CH_3CN / 18% H_2O / 2% KNO_3. ^{1}H NMR (500 MHz, CD_3CN): δ 8.82 – 8.78 (2H, m, H^g and $H^{g'}$), 8.76 – 8.69 (2H, m, H^d and $H^{d'}$), 8.52 (4H, t, *J 7.8*, bpy-H^3), 8.17 (1H, td, *J 8.0, 1.4*, H^c), 8.12 – 7.95 (17H, m, ppy-H^3, H^a, H^e, H^h, $H^{h'}$, H^i, $H^{i'}$, $H^{c'}$ and bpy-H^4), 7.90 – 7.65 (11H, m, ppy-$H^{3'}$, ppy-H^4, H^f, $H^{a'}$, $H^{e'}$ and bpy-H^6), 7.71 (1H, dd, *J 6.0, 1.9*, $H^{f'}$), 7.68 and 7.67 (2H, two overlapping d, ppy-H^6), 7.54 (1H, t, *J 6.5*, H^b), 7.45 – 7.38 (5H, m, $H^{b'}$ and bpy-H^5), 7.10 – 7.03 (4H, m, ppy-H^5 and ppy-

$H^{4'}$), 6.95 and 6.94 (2H, two overlapping t, *J 7.4*, ppy-$H^{5'}$), 6.32 and 6.31 (2H, two overlapping d, ppy-$H^{6'}$). MS (ES^+): m/z = 459.1, M^{3+}. HRMS (ES^+): m/z = 459.1060; calc. for $C_{74}H_{54}N_{10}IrRu$, M^{3+}: 459.1063.

Ir^{Br2}-Ru [Ir(4'-Brppy)$_2$μ-(bpy-ϕ-ϕ-bpy)Ru(bpy)$_2$](PF$_6$)$_3$

A solution of **Ir–Ru** (18 mg, 0.010 mmol) and N-bromosuccinimide (4 mg, 0.022 mmol) in CH_3CN (4 mL) was stirred at room temperature for 18h. Having concentrated the solution to a volume of 0.5 mL under reduced pressure, it was added dropwise to a saturated aqueous solution of KPF_6. The resulting precipitate was collected, washed with water and dried under vacuum, to give the dibrominated complex in quantitative yield (20 mg). ^{1}H NMR (400 MHz, CD_3CN): δ 8.81 and 8.80 (2H, two overlapping d, H^g and $H^{g'}$), 8.75 and 8.72 (2H, two overlapping d, H^d and $H^{d'}$), 8.52 (4H, t, *J 6.8*, bpy-H^3), 8.19 (1H, td, *J 7.9, 1.5*, H^c), 8.15 – 7.95 (19H, m, ppy-H^3, ppy-$H^{3'}$, H^a, H^e, H^h, $H^{h'}$, H^i, $H^{i'}$, $H^{c'}$ and bpy-H^4), 7.90 and 7.85 (2H, two overlapping td, *J 7.9, 1.4*, ppy-H^4), 7.85 – 7.74 (7H, m, H^f, $H^{a'}$, $H^{e'}$, and bpy-H^6), 7.71 (1H, dd, *J 6.0, 1.*8, $H^{f'}$), 7.68 and 7.66 (2H, two overlapping d, *J 6.7*, ppy-H^6), 7.55 (1H, ddd, *J 7.6, 5.4, 1.0*, H^b), 7.46 – 7.39 (5H, m, $H^{b'}$ and bpy-H^5), 7.15 – 7.02 (4H, m, ppy-H^5 and ppy-$H^{5'}$), 6.22 - 6.17 (2H, two overlapping d, ppy-$H^{6'}$). MS (ES^+): m/z = 511.8, M^{3+}. HRMS (ES^+): m/z = 511.0464; calc. for $C_{74}H_{52}N_{10}Br_2IrRu$, M^{3+}: 511.0472.

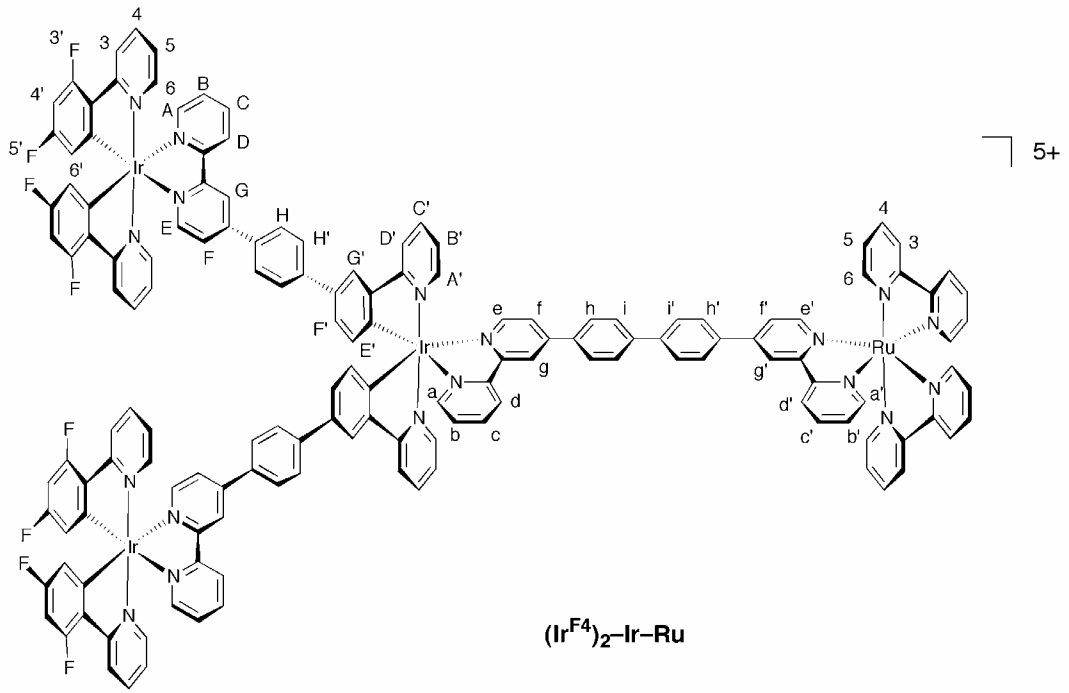


Ir^{Br2}–Ru

$(Ir^{F4})_2$–Ir–Ru [{Ir(F_2ppy)$_2$μ-(bpy-ϕ-ppy)}$_2$Ir-μ-(bpy-ϕ-ϕ-bpy)Ru(bpy)$_2$](PF$_6$)$_5$

A Schlenk tube was charged with **Ir^{Br2}-Ru** (17 mg, 0.0086 mmol), [Ir(F_2-ppy)$_2${bpy-ϕ-B(OH)$_2$}](PF$_6$), (**Ir^{F4}–B**, 25 mg, 0.025 mmol), Na_2CO_3 (5 mg in 100 μL water, 0.050 mmol) and DMSO (5 mL). The solution was degassed via three freeze-pump-thaw cycles before adding $Pd(PPh_3)_4$ (2 mg, 0.0017 mmol) under a positive pressure of nitrogen. The solution was stirred at 80°C for 72 h. After this time, the DMSO solution was diluted with acetonitrile (3 mL) and filtered into a saturated aqueous solution of KPF_6. Purification of the precipitated hexafluorophosphate salt

was achieved by column chromatography on silica gel, gradient elution from 100% acetonitrile to 88% CH_3CN / 11.8% H_2O / 0.2% KNO_3. After further ion exchange of the selected fractions using KPF_6 (aq), the desired product was obtained (13 mg, 41%). R_f (tlc) = 0.7 in 80% CH_3CN / 18% H_2O / 2% KNO_3. ^{1}H NMR (500 MHz, CD_3CN): δ 8.87 – 8.69 (8H, m, H^D, H^G, H^d, H^g, $H^{d'}$and $H^{g'}$), 8.52 (4H, t, *J = 7.4*, bpy-H^3), 8.37 – 8.30 (4H, m, F_2ppy-H^3), 8.25 – 8.17 (4H, m, H^C and $H^{D'}$), 8.15 – 7.89 (36H, m, F_2ppy-H^4, H^A, H^E, H^H, $H^{C'}$, $H^{G'}$, $H^{H'}$, H^a, H^c, H^e, H^h, H^i, $H^{c'}$, $H^{h'}$, $H^{i'}$ and bpy-H^4), 7.87 – 7.64 (15H, m, F_2ppy-H^6, $H^{a'}$, $H^{A'}$, $H^{e'}$, H^f, H^F and bpy-H^6), 7.60 – 7.54 (3H, m, H^b and H^B), 7.45 – 7.34 (7H, m, $H^{b'}$, $H^{F'}$ and bpy-H^5), 7.19 – 7.06 (7H, m, F_2ppy-H^5, $H^{B'}$ and $H^{f'}$), 6.77 – 6.68 (4H, m, F_2ppy-$H^{4'}$), 6.50 and 6.49 (2H, two overlapping d, $H^{E'}$), 5.76 (4H, d, *J = 8.5*, F_2ppy-$H^{6'}$). ^{19}F NMR (200 MHz, CD_3CN): δ -73.28 (30F, d, *J 707*, PF_6), -108.64 (4F, m, F_2ppy-$F^{5'}$), -110.51 (4F, t, *J 11.3*, F_2ppy-$F^{3'}$). MS (ES^+): m/z = 596.2, M^{5+}; 745.3, $[M^{5+}\text{-}H^+]^{4+}$; 781.7 $[M^{5+}+PF_6^-]^{4+}$; 1091.0, $[M^{5+}+PF_6^-]^{4+}$. HRMS (ES^+): m/z = 782.1417; calc. for $C_{150}H_{98}N_{18}F_8Ir_3RuPF_6$, M^{4+}: 782.1411. Found: C, 48.67%; H, 2.91%; N, 6.74%. Calc. for $C_{150}H_{98}N_{18}F_8Ir_3RuP_5F_{30}$: C, 48.60%; H, 2.66%; N, 6.80%.



(a) M. Montali, S. Wadhwa, W.Y. Kim, R.A. Kipp and R.H. Schmehl, *Inorg. Chem.*, 2000, **39**, 76.

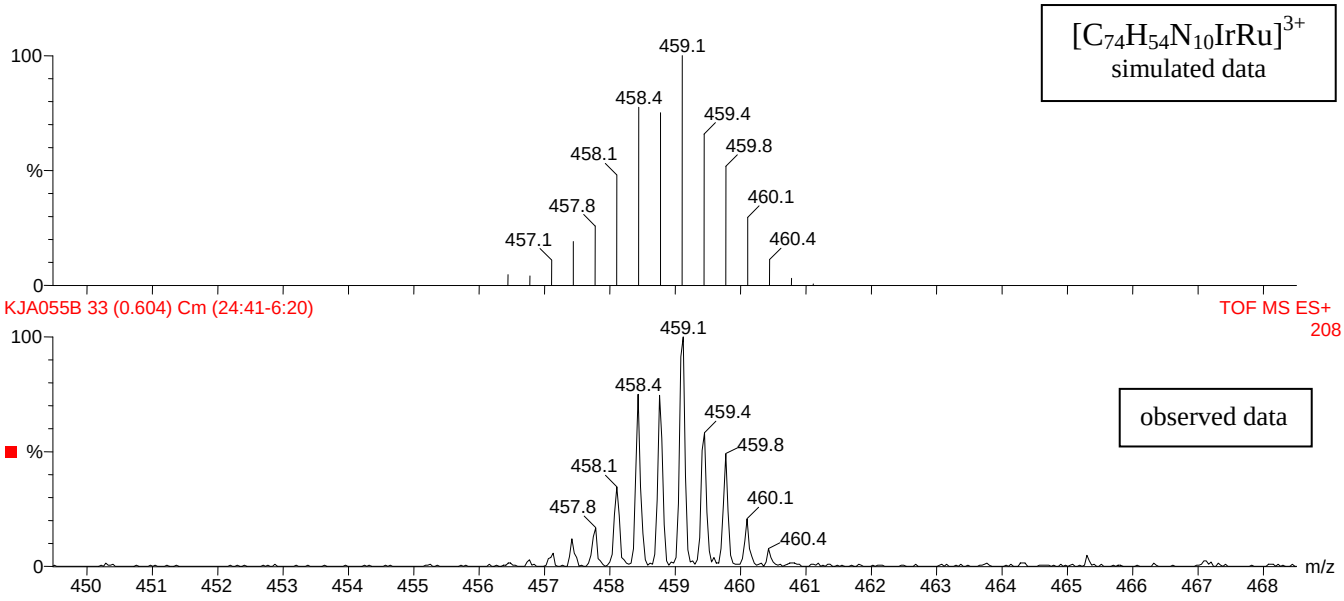
(b) C.J. Aspley and J.A.G. Williams, *New J. Chem.*, 2001, **25**, 1136.

(c) F. Neve, A. Crispini, S. Campagna and S. Serroni, *Inorg. Chem.*, 1999, **38**, 2250.

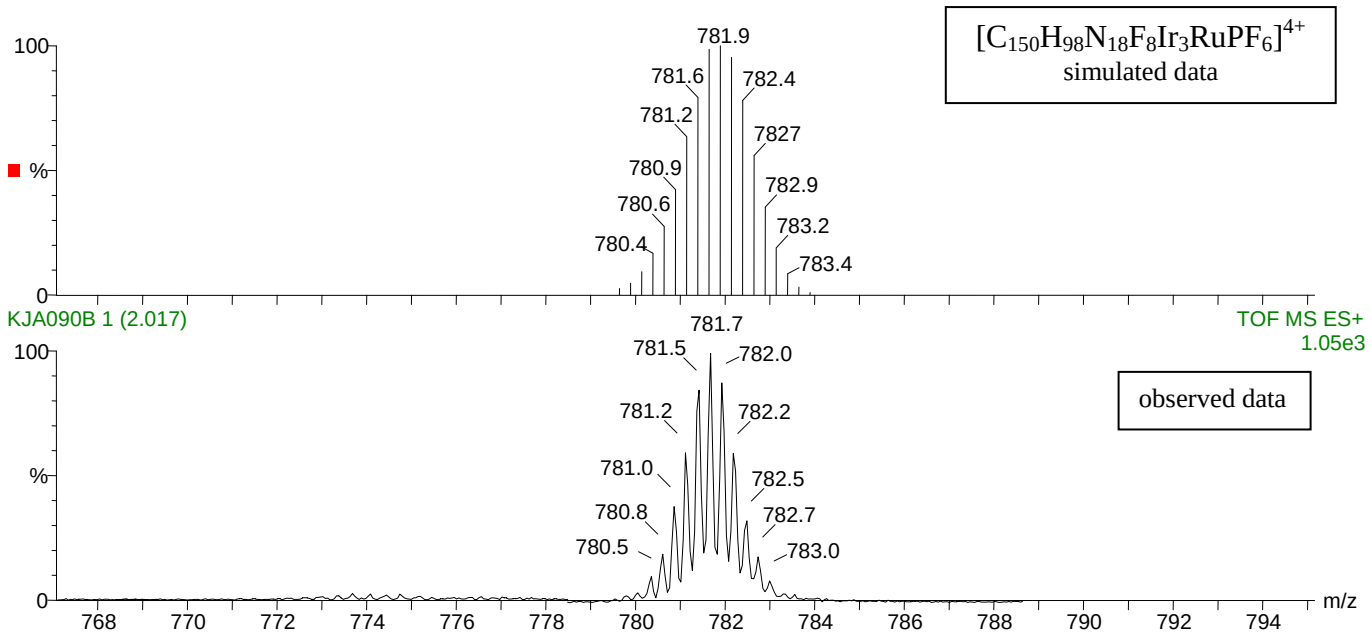
(d) See, for example, S. Campagna, S. Serroni, S. Bodige and F.M. MacDonnell, *Inorg. Chem.*, 1999, **38**, 692.

2. Selected mass spectral data for the dimer and tetramer: experimental and simulated isotope patterns.

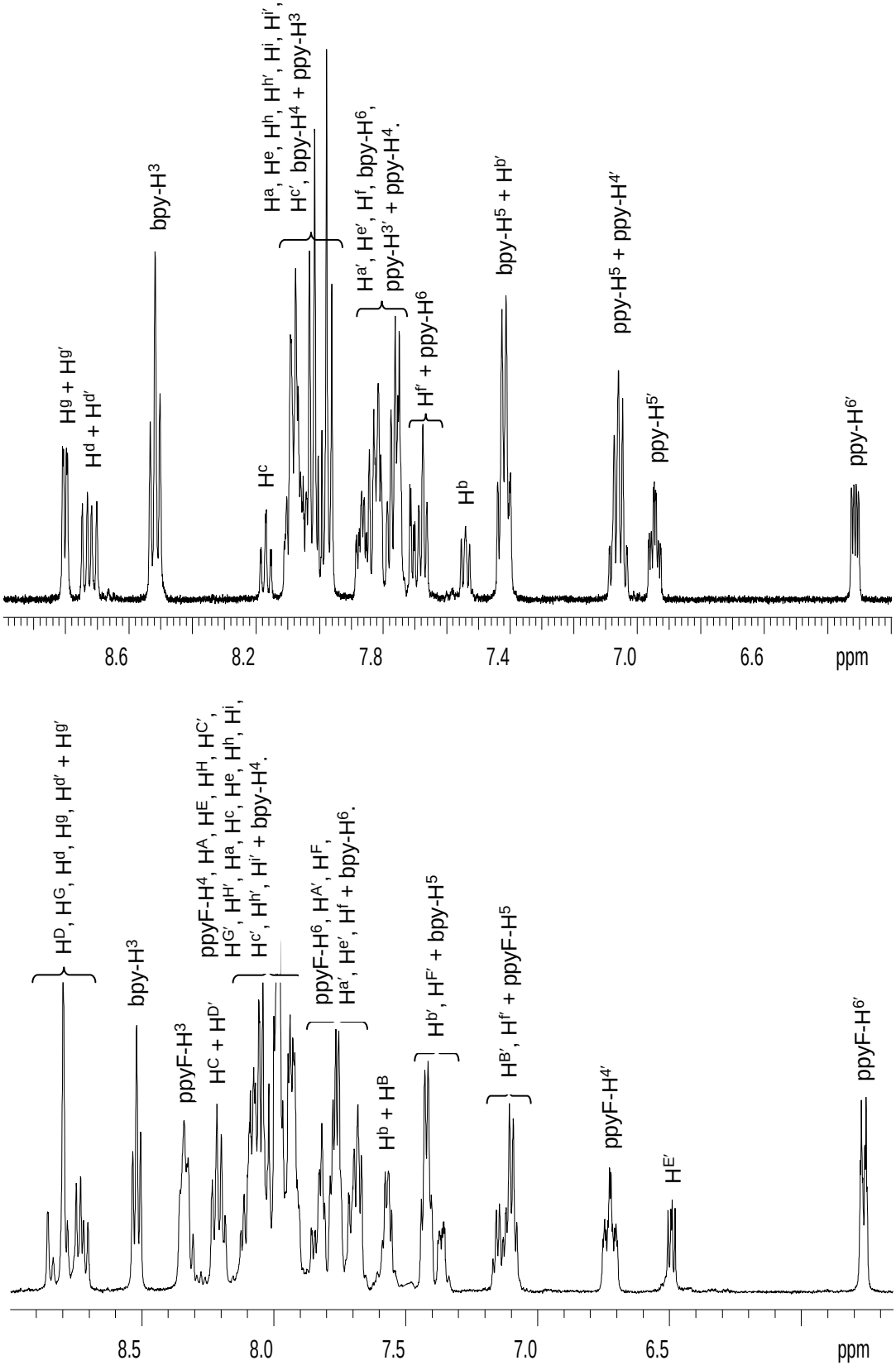
Ir–Ru



$(Ir^{F4})_2$–Ir–Ru



3. ^{1}H NMR data for the dimer (top) and tetramer (bottom) in CD_3CN at 295K.



4. UV-vis spectra of the tetramer and of the individual constituent building blocks, together with their sum [(2xIr^{F4}) + Ir + Ru] (in CH_3CN at 295 K).