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Ru(II) and Ir(III) complexes containing ADA and DAD triple hydrogen bonding motifs: Potential tectons for the assembly of functional materials.

Aidan P. McKay, Joseph I. Mapley, Keith C. Gordon and David A. McMorran*^[a]

Abstract: The synthesis and characterisation of series of [Ru(II)(bpy)₂L] and [Ir(ppy)₂L] complexes containing ligands L with the potential to engage in triple hydrogen bonding interactions is described. L1 and L2 comprise pyridyl triazole chelating units with pendant diaminotriazine units, capable of donor-acceptor-donor (DAD) hydrogen bonding, while L3 and L4 contain ADA hydrogen bonding units proximal to N^N and N^O cleating sites, respectively. X-ray crystallography shows the L1 and L2 containing Ru(II) complexes to assemble via $R_2^2(8)$ hydrogen bonding dimers, while [Ru(II)(bpy)2L4] assembles via extended hydrogen bonding motifs to form one dimensional chains. By contrast, the expected hydrogen bonding patterns are not observed for the Ru(II) and Ir(III) complexes of L3. Spectroscopic studies show that the absorption spectra of the complexes result from combinations of MLCT and LLCT transitions. The L1 and L2 complexes of Ir(III) and Ru(II) complexes are emissive in the solid state and it seems likely that hydrogen bonding to complementary species may facilitate tuning of their ³ILCT emission. Low frequency Raman spectra provide further evidence for ordered interactions in the solid state for the L4 complexes, consistent with the results from X-ray crystallography.

Introduction

Crystal engineering has been described as the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties.^[1] While the reliable prediction of the observed three-dimensional assembly of a given compound, or pair of compounds, in the solid state, which requires accounting for all the myriad weak interactions present between the compound(s) (commonly called packing forces), remains elusive, the use of relatively strong and directional intermolecular forces as a driver for the assembly process provides a way to limit the variability of the observed interactions. For this reason hydrogen bonding has become the most popular interaction studied.^[2] The incorporation of synthons such as carboxylic acid and amide groups leads to the observation of the expected $R_2^2(8)^{[3]}$ dimers in a large percentage of the resulting crystal structures and, for organic molecules at least, hierarchies of double hydrogen bond synthons have been developed.[4] Based on these developing sets of rules, modification of properties such as solubility and mechanical strength of

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crystalline compounds, or co-crystals of pairs of compounds, is now an area of intense research.^[5]

By comparison, the development of such understandings for triple hydrogen bonding synthons are less explored, and, in particular, reports of the assembly of transition-metal containing systems in this way are rare.^[6] We have recently reported examples of Ni(II),^[7] Pd(II) and Pt(II)^[8] complexes incorporating deprotonated 1,5-diarylbiguanide ligands. These ligands possess a donoracceptor-donor (DAD) triple hydrogen bonding motif and cocrystallization of these with organic molecules containing the complementary acceptor-donor-acceptor (ADA) motif was shown to result in the expected assemblies in the solid state. Unfortunately, the complexes displayed limited solubility in solvents other than DMF and DMSO, and this solubility was only due to the hydrogen-bonding ability of the solvents to break up the $R_2^2(8)$ dimeric homosynthons that assembly the complexes with each other in the solid state. However, these solvents also compete with the complementary organic molecules for the hydrogen bonding sites and so triple hydrogen bond-directed heterosynthon assembly in solution was not observed. The metalbiguanide complexes were neutral and all contained squareplanar metal centers, and we supposed that better solubility might be obtained by moving to charged complexes containing octahedral metal centers. To that end, and in light of their desirable photophysical properties, we looked to prepare Ru(II) and Ir(III) based complexes.

The feasibility of using hydrogen bonding to mediate electron or energy transfer between Ru(bpy)₃ and Ir(ppy)₃ – type systems has been explored.^[9] In particular, studies on Ru(II) and Os(II)containing bpy ligands derivatized by nucleobases have been shown to form triple hydrogen bonded heterosynthons within which the emission of the ruthenium center is quenched by the osmium center.^[10] Triple hydrogen bonding interactions have also been shown very recently to be able to non-covalently tune the emission properties of an Ir(III)-based system.^[11] Another recent report has also highlighted the ability of hydrogen bonding to facilitate photocatalysis reactions in Ir(III) complexes.^[12] There are fewer reports concerning the incorporation of such centers into functional materials. For example, while metal-organic frameworks (MOFs) have become a much studied area of materials chemistry, examples where Ru(bpy)₃ and Ir(ppy)₃ – type centers have been incorporated into the MOF framework are relatively rare,^[13] although the few systems that have been reported show that such incorporation leads to the MOF gaining desirable photophysical and/or catalytic properties. It seemed to us that the triple hydrogen-bond directed assembly of suitable Ru(II)- and Ir(III)-containing tectons with complementary organic or metal-containing species might provide an alternate way to prepare solid state structures with interesting properties.

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Herein we therefore describe a family of $[Ru(bpy)_2L]$ and $[Ir(ppy)_2L]$ complexes where L is a bidentate ligand which incorporates either a DAD or an ADA triple hydrogen bonding motif. Ligands L1 and L2 incorporate a DAD diaminotriazine (DAT) synthon^[6c, 14] which is remote from the metal ion, whereas L3 and L4 contain ADA motifs (based on hydantoin^[15] and orotic acid^[16] synthons, respectively) which are more proximal to the metal ion. Furthermore, L1 and L2 bind as neutral ligands to the respective metal centers, whereas L3 binds as a monoanion and L4 as a dianion: the resulting metal complexes therefore have charges ranging from +2 to -1.



Scheme 1. The ligands discussed in this work.

We report here the characterisation of these complexes and an assessment of their suitability as tectons for the construction of functional assemblies.

Results and Discussion

The 5-(2-pyridylmethylene)hydantoin ligand, HL3, was prepared as described in literature by reacting 2-pyridinecarboxaldehyde with a slight excess of hydantoin in a piperidine solution,^[15b] and the orotic acid ligand, H₂L4, was used as purchased. The two pyridyl triazole based ligands L1 and L2 are new in this work and were prepared through a three-step synthesis (Scheme 2). In each case. 2-bromo-5-cyanopyridine was initially converted to the trimethylsilane protected acetylene through standard Sonogashira techniques, give the known product 2-(2trimethylsilyl)acetyl-5-cyanopyridine product which gave spectra consistent with reported literature.[17] The benzyl and hexyl substituted 1,2,3-triazoles were then synthesized from the deprotected acetylene and the appropriately substituted azide, which was formed in situ from the substituted bromide and sodium azide, through a CuAAC type "click" reaction.[18] Finally the cyanogroup underwent cyclisation with dicyandiamide in DMSO at 190°C under sealed tube microwave conditions to give the 2,4diamino-1,3,5-triazine moiety as has been observed for other cyano- substituted heterocycles.[19]

When the benzyl substituted pyridyltriazole underwent the cyclisation reaction in deuterated solvent (DMSO- d_6) exchange of the triazole and methylene protons for deuterons occurred giving

L1-*d*₃ as product. The compositions of the new ligands were confirmed by elemental analysis and HRESI-MS. ¹H NMR were consistent with the expected structures and the deuterated ligand L1-*d*₃ had absent triazole and methylene signals when compared to L1, consistent with deuteration at these locations. NH signals were observed as a broadened singlet at about 6.9 ppm. Both ligands show limited solubility in common organic solvents so DMSO-*d*₆ was used for NMR characterisation.



Scheme 2. Syntheses of ligands L1 and L2. (i) TMS acetylene, [Pd(PPh₃)₂Cl₂], Cul, THF/DIPA, N₂ (ii) (a) Na₂CO₃, MeOH (b) R-Br, NaN₃, CuSO₄, Na ascorbate, DMF/H₂O (iii) dicyandiamide, DMSO, 190°C (microwave).

Complexes of the type [Ru(bpy)₂L] were prepared by the reaction of a slight excess of the appropriate ligand with one equivalent of [Ru(bpy)₂Cl₂] in ethanol which was heated to 125°C under sealed tube microwave conditions for 2 hours. The cationic complexes of L1 - L3 were precipitated from solution as their respective hexafluorophosphate salts by addition of aqueous NH₄PF₆ and then further purified through recrystallization from diffusion of diethyl ether into acetonitrile solution giving orange (L1 - L2) or red (L3) crystals. The complex of L4 is neutral and therefore could not be precipitated with aqueous NH₄PF₆, and instead the ethanol of the reaction solution was removed via rotary evaporation and the resulting solid was recrystallized from a warm 1:5 solution of methanol in water to give the pure product as black/purple crystals. The compositions of the complexes were confirmed by HRESI-MS, elemental analysis and ¹H and ¹³C NMR spectroscopies. Due to the unsymmetrical nature of the tertiary ligand the ¹H NMR spectrum contains individual peaks for all protons. The signals of the non-bpy ligands were fully assigned by means of COSY, HSQCAD, and HMBCAD 2D spectroscopies but the symmetry of the two bipyridine ligands resulted in significant overlap of their respective proton signals and with a lack of resolved NOSEY cross peaks mean the individual protons could not be assigned but conformation of the ligands could be inferred by the number and types of signals present. The complexes of L1 - L3 had reasonable solubility so CD3CN was used for NMR characterisation (spectra in DMSO-d6 solutions contained significant overlapping of signals, complicate analysis) while the complex of L4 was much less soluble so DMSO-d6 was used for characterisation. In acetonitrile the NH signals appear as broadened singlets at about 5.5 ppm for complexes of L1 and L2 and at about 8.0 ppm for the complex of L3. In DMSO-d₆ the NH signal appears as a much sharper peak and in the case of the complex of L4 a doublet at 9.76 ppm, which is coupling with the other proton of the orotic acid ligand. The NH signals of L3 and

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L4 are more deshielded than L1 and L2 due to both the proximity of the carboxyl groups and coordination of the ruthenium ion to the same ring as the amine moiety. While we might expect the complexes to self-assemble *via* hydrogen bonding in solution, no concentration dependence is observed in any of the complexes in CD₃CN or DMSO- d_6 . The complexes were not soluble in common chlorinated solvents so the concentration dependence could not be assessed in less hydrogen bonding solvents.

Complexes of the type fac-[lr(ppy)2L] were prepared from the reaction of the [(Ir(ppy)2-µ2-Cl2] dimer with two and a half equivalents of the appropriate ligand and an excess of sodium carbonate in dry DMSO solution under Ar at 125°C for 6 hours. The cationic complexes of L1 and L2 were precipitated from the reaction solution by slow addition of aqueous NH₄PF₆ and the isolated solid was purified by filtration through celite as a dichloromethane solution and precipitated by addition of diethyl ether to give the products as yellow solids. The neutral complex of L3 was extracted from a solution of the DMSO reaction solution and water:brine solution with chloroform and the combined organic extracts were repeatedly washed with water to remove residual DMSO. The resulting oil was taken up in minimum chloroform and the product precipitated as an orange solid by addition of excess petroleum ether. The anionic complex of L4 precipitated overnight as the tetrabutylammonium salt after the addition of an aqueous solution of tetrabutylammonium chloride and then acetone to the reaction solution. The compositions of the complexes were confirmed by HRESI-MS, elemental analysis and ¹H and ¹³C NMR spectroscopies. Due to the unsymmetrical nature of the ligands the ¹H NMR spectrum contains individual peaks for all protons but as expected from the [(Ir(ppy)₂-µ²-Cl₂] dimer only the fac- isomers of the complexes are observed where the coordinated C atoms are trans to the tertiary ligand.^[20] The proton signals of all the ligands are assigned by means of COSY, NOSEY, HSQCAD, and HMBCAD 2D spectroscopies with the cross peaks between the coordinated carbon of the ppy ligands and the protons of the same ring as well as to the proton para- to the coordinated nitrogen allowing the full assignment of the ligands (although the two ppy ligands cannot be differentiated).

The iridium complexes show better solubility than the ruthenium complexes but DMSO-d₆ was still used for NMR characterisation, both for giving clearer, less overlapped, signals than other solvents and to give sharper NH signals for assignment. For the complexes of L1 and L2 these signals are still broadened and both appear at about 6.4 ppm. For the complexes of L3 and L4 the NH signals appear as very sharp singlets at 10.17 and 9.52 ppm, respectively. As for the ruthenium complexes the complexes of L3 and L4 have downfield shifted NH signals compared to L1 and L2 because of both the close proximity to carbonyl groups and coordination of the metal ion to the same ring as the amine is contained in. Also like the ruthenium complexes, no concentration dependent peak shifting was observed in DMSO-d6 nor was it observed in the less hydrogen bonding solvent CDCl₃ although in this solvent the NH peaks, which are the most likely to shift due to self-assembly through hydrogen bonding, cannot be observed likely due to proton exchange with the solvent.

The absorption spectra for all complexes are shown in Figure 1 and it can be seen that the Ru complexes have a lower band gap than their Ir counterparts. The spectra for $[Ru(bpy)_2(L1)]^{2+}$ and $[Ru(bpy)_2(L2)]^{2+}$ are comparable to $[Ru(bpy)_2(pytri)]^{2+}$ which displays an ¹MLCT absorption at 440 nm, but has reduced absorption between 340 and 390 nm.^[21] This higher energy absorption process, which is also present in the free ligand, is attributed to a charge transfer transition from the DAT unit to the pyridyl-triazole unit (Figure S1). At lower energy a weak absorption is observed which is attributed to the spin-forbidden ³MLCT transition.^[21a]

L3 and L4, unlike L1 and L2, differ from bpy due to the σ coordinating nitrogen and, in the case of L4, coordinating oxygen. This induces a splitting of the Ru d orbitals and a clear separation of the MLCT transitions is observed. For $[Ru(bpy)_2(L4)]$ a shoulder on the low energy MLCT is observed at 480 nm which is attributed to the degeneracy of the Ru d orbitals being lifted. This perturbation is not observed for $[Ru(bpy)_2(L3)]^+$ which is consistent with calculations (*vide infra*)(Tables S1-S12). The overall splitting is relatively similar for both ligands with a difference in energy between the highest and lowest MLCT bands of 0.99 eV for $[Ru(bpy)_2(L3)]^+$ and 1.04 eV for $[Ru(bpy)_2(L4)]$. At lower energies than the MLCT bands ligand to ligand charge transfer (LLCT) transitions are observed for both $[Ru(bpy)_2(L3)]^+$ and $[Ru(bpy)_2(L4)]$.



Figure 1. UV-Vis spectra for all complexes. Ru complexes measured in DMSO and Ir complexes measured in DCM.

The absorption spectra of $[Ir(ppy)_2(L1)]^+$ and $[Ir(ppy)_2(L2)]^+$ displays a weaker absorption spectrum as expected for Ir-ppy systems.^[22] The lowest energy transitions are assigned as spin forbidden ³MLCT transitions with ¹MLCT transitions occurring at higher energies. The Ir to ppy MLCT transitions are not perturbed compared to the previously reported methyl-pytri analogue $[Ir(ppy)_2(Me-pytri)]^+$.^[22c] For the Ir complexes with L3 and L4 ligands some spectral differences are observed. For $[Ir(ppy)_2(L4)]^$ similar MLCT transitions are present with an additional transition

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occurring at 460 nm that is attributed to a LLCT from L4 to ppy. There is a redshift of the MLCT transitions for $[lr(ppy)_2(L3)]$ indicating that the accepting MOs are located on the L3 instead of ppy ligands which consistent with calculations. The absorption profile for all compounds were independent of concentration indicating that negligible dimerisation occurs in solution.

Optimised geometries were calculated using the B3LYP method with a split basis set which has previously been shown to provide a good model for other Ru and Ir complexes.^[23] A LanL2DZ basis set was employed for Ru and Ir with 6-31G(d) for all other atoms.^[24] As L1 and L2 complexes are structurally similar only the L1 complexes were calculated. Raman spectra were measured to validate the optimised geometries and it was found that the measured Raman bands differed from predicted values with a mean absolute deviation of less than 10 cm⁻¹ (Figures S2-S4). This value does not take into account the carbonyl bands, for which frequencies are often overestimated in these types of calculations.^[25] The optimised geometries show good correlation to structures obtained from X-ray crystallography (*vide infra*) with differences in bond lengths of less than 2.2 pm.

Once the optimised geometries were validated time dependantdensity functional theory (TD-DFT) calculations were performed to model the complexes electronic properties. The calculated molecular orbitals (MOs) and electronic transitions are shown in Tables S1-S12. The predicted transitions are in good agreement with the absorption spectra and are consistent with the assignments made above. For the Ru complexes the LUMO is consistently located on the bpy ligands. This is unsurprising as both the anionic ligands (L3 and L4) as well as the electron rich triazole containing ligands (L1 and L2) are expected to be higher energy than that of bpy.^[21, 26] In Ru(bpy)₂(L1)]²⁺ the HOMO was predicted to be located on the DAT unit of L1 however, due to the isolation of the HOMO from the bpy based LUMOs, the lowest energy transition with appreciable oscillator strength occurs from HOMO-1 which is located on the Ru. For both [Ru(bpy)₂(L3)]⁺ and [Ru(bpy)₂(L4)] the HOMO is located on the anionic ligand with lower energy MOs based on the Ru which show splitting based on the asymmetric ligand field. Thus the lowest energy transitions are LLCT from L3 or L4 with MLCT transitions to bpy occurring at higher energy. The MLCT transitions for [Ru(bpy)₂(L4)] include notable LLCT contribution from L4.

In the Ir complexes the energy of the ppy ancillary ligands is higher than that of the bpy ligands in the Ru complexes. This results in a blueshifting of the absorption spectra and increased influence of the accompanying ligand.^[27] For $[Ir(ppy)_2(L1)]^+$ the LUMO is located on L1 while the HOMO is delocalised over Ir and ppy, thus the lowest energy transition is a mixed MLCT/LLCT from Ir and ppy to L1. The HOMO and HOMO-1 of $[Ir(ppy)_2(L3)]$ are spread across all three ligands and the Ir while the unoccupied MOs are mostly located on either ppy or L3 which results in the transitions having mixed MLCT, LLCT and ligand centred (LC) character. The lowest energy transition results in population of the LUMO, which is located primarily on L3 (87%), with higher energy transitions populating ppy based MOs. The Ir to L3 MLCT/LLCT

transition results in $[Ir(ppy)_2(L3)]$ having greater absorption above 350 nm than the other Ir complexes. The predicted transitions for $[Ir(ppy)_2(L4)]$ show mixed MLCT and LLCT from Ir and L4 to ppy which are similar to those of $[Ru(bpy)_2(L4)]$, despite occurring at higher energy although there is increased LLCT contribution from L4 to all transitions.

In summary the lowest energy chromophores for these complexes are: (a) MLCT from Ru to bpy for $Ru(bpy)_2(L1)]^{2+}$ and $Ru(bpy)_2(L2)]^{2+}$, (b) LLCT from L3 or L4 to bpy for $[Ru(bpy)_2(L3)]^+$ and $[Ru(bpy)_2(L4)]$, (c) MLCT/LLCT from Ir and ppy to L1 for $[Ir(ppy)_2(L1)]^+$ and $[Ir(ppy)_2(L2)]^+$, (d) MLCT/LLCT from Ir and ppy to L3 for $[Ir(ppy)_2(L3)]$ and (e) MLCT/LLCT from Ru and L4 to ppy.

The emission spectra for the Ir complexes are shown in Figure 2. No emission was observed for the Ru complexes which is partially due to the presence of a lower energy ³metal centred (MC) states being thermally accessible from the ³MLCT state.^[26] It has previously been reported that the inclusion of the pytri unit improves the overlap of the ³MLCT and ³MC states of Ru which results in a quenching of emission even when the emissive state is not located on the pytri moiety. [21a, 28] The emission processes exhibited by [Ir(ppy)2(L3)] and [Ir(ppy)2(L4)] display vibronic progressions. These features are consistent with a ppy based mixed MLCT/LC states which is seen in other Ir-ppy complexes.^[22c, 26] Emission is observed from both triplet (~500 nm) and singlet (~400 nm) states with the singlet state displaying considerably lower intensity which is consistent with the rapid intersystem crossing observed in other Ir(III) complexes.^[29] The measured lifetimes (Table 1) are consistent with the assignments of the states as singlet and triplet for the high and low energy emission, respectively. [Ir(ppy)2(L3)] displays considerably shorter triplet state lifetime than the other Ir complexes. This may be attributable to the methylene linker between the pyridine and hydantoin components of L3. Similar lifetimes were reported for an analogous Ir complex with a ligand containing a pyridine and triazole linked via a methylene bridge; [Ir(ppy)2(py-Me-tri)], τ = 200 ns. $^{[22b]}$ As the emissive state is ppy based this suggests that emission is not occurring from the lowest energy state for [Ir(ppy)₂(L3)], which is L3 centred, and this is consistent with excitation emission map (Fig S7) which shows that the lowest energy transitions leads to a dark state. The shorter triplet lifetime alongside the presence of a dark state can be used to rationalise the decreased quantum yield observed for [lr(ppy)2(L3)]. The excitation emission map also revealed that the ¹MLCT emission only occurred upon direct excitation to that state (320 to 350 nm) which supports the assignment of the lower energy transitions as having L3 or L4 involvement.

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Figure 2. Normalised emission spectra for Ir complexes in DCM with an excitation at 325 nm.

The emission spectra for $[Ir(ppy)_2(L1)]^+$ and $[Ir(ppy)_2(L2)]^+$ display a redshifted emission with a loss of vibronic features. This is in stark contrast with the previously reported, DAT lacking derivative, $[Ir(ppy)_2(pytri-Me)]^+$ which displayed a similar triplet emission as $[Ir(ppy)_2(L3)]$ and $[Ir(ppy)_2(L4)]^-$.^[22c] This suggests the emission is occurring from a ³ILCT state which is consistent with the measured lifetimes. While the ³ILCT state is lower in energy than the ³MLCT state the ¹ILCT state is higher in energy than the ¹MLCT indicating that there is either improved spin-orbit coupling for the ILCT state or that there is a shift in excited state geometry which lowers the energy of the ILCT states below the MLCT states.

Table 1. Emission properties for all complexes in degassed dichloromethane.An excitation of 325.4 nm was used for all measurements.								
	λ_{Em} / nm	τ / ns	Φ					
[lr(ppy) ₂ (L1)] ^a	586	655	0.03					
[lr(ppy) ₂ (L2)] ^a	582	730	0.03					
[lr(ppy) ₂ (L3)] ^a	496	254	0.01					
	398	8.1						
[lr(ppy) ₂ (L4)] ^{- a}	496	790	0.05					
	398	8.4						
L1	389	2.3	0.02					
L2	389	2.1	0.02					

[a] Highest energy emission reported for processes with vibronic structure.

Solid state emission spectra are shown in Figure S9. $[Ir(ppy)_2(L1)]^+$ and $[Ir(ppy)_2(L2)]^+$ display similar solution and solid state emission indicating that the solid is amorphous. The slightly broadened emission of $[Ir(ppy)_2(L2)]^+$ implies that it has a greater disorder in the solid than $[Ir(ppy)_2(L1)]^+$ which is consistent with low frequency Raman measurements (*vide infra*). The solid state emission of $[Ir(ppy)_2(L3)]$ and $[Ir(ppy)_2(L4)]^-$ display a small bathochromic shift compared with the solution phase emission which is consistent with other Ir(|II|) complexes.^[30]

Solid state emission is also observed for the all Ru complexes except for $[Ru(bpy)_2(L3)]^+$. The emission for $[Ru(bpy)_2(L1)]^{2+}$ and $[Ru(bpy)_2(L2)]^{2+}$ is similar but slightly redshifted to their Ir counterparts indicating the same ³ILCT emission is occurring. The emission for $[Ru\{bpy)_2(L4)]$ is considerably redshifted compared with its Ir counterpart. This is unsurprising as $[Ir\{ppy)_2(L4)]^-$ is emitting from a ppy based MLCT/LC state while the lowest energy states for $[Ru\{bpy)_2(L4)]$ are MLCT and LLCT. The occurrence of solid state emission for the Ru complexes, which is not observed in solution, is attributed to a loss of non-radiative decay pathways, due to restriction of their geometries in the solid state. The flexibility of the methylene bridge in $[Ru(bpy)_2(L3)]^+$ allows for access to these pathways which explains the lack of emission for this complex.

Crvstals [Ru(bpy)₂(L1-d₃)](PF₆)₂·CH₃CN of and [Ru(bpy)₂(L2)](PF₆)₂·CH₃CN suitable for X-ray analysis were grown from diffusion of diethyl ether into acetonitrile solutions of $[Ru(bpy)_2(L1-d_3)](PF_6)_2$ and $[Ru(bpy)_2(L2)](PF_6)_2$, respectively. While crystals of the non-deuterated L1 complex were obtained, none were found to be suitable for X-ray analysis. However, the deuterated complex was serendipitously crystallised and these crystals, which were suitable for X-ray analysis, possessed the same unit cell and was found for the crystals of the non deuterated version. Both complexes crystallize in the triclinic space group P-1 with the asymmetric unit containing one complex unit with the accompanying hexafluorophosphate anions and one acetonitrile solvent molecule. (Figure 3) In the structure of $[Ru(bpy)_2(L2)](PF_6)_2$ the second PF_6^- anion (P2 and F7-F12) is disordered with the major component being 70% present. The ruthenium ions are octahedral with the pyridyltriazole ligands coordinating N^N as expected through the pyridine and N-1 of the triazole. The octahedral coordination geometry of both structures is partially distorted with the three chelate rings having bond angles at Ru1 ranging from 78.0° to 79.1°. Each structure contains a racemic mixture of the Λ - and Δ - enantiomers which, in pairs, form hydrogen bonded dimers where the two DAT rings hydrogen bond to each other in an offset manner with supporting interactions from the PF₆ anions. (Figure 4)

In the structure of $[Ru(bpy)_2(L1-d_3)](PF_6)_2$ the hydrogen bonding forms a $R_3^3(10)R_2^2(8)R_3^3(10)$ motif with a strong hydrogen bonds between N9 and N6 of the adjacent molecule (H···N 2.24 Å, NH···N 165°) as well as between N8 and F10, while the bond observed between N9 and F9 is weaker (H···F 2.17 and 2.36 Å, NH···F 158° and 125° respectively). In the structure of $[Ru(bpy)_2(L2)](PF_6)_2$ however the PF6° anions are arranged differently and have more interactions with the amines of the DAT moiety giving a $R_1^2(4)R_3^2(8)R_2^2(8)R_3^2(8)R_1^2(4)$ motif with a strong hydrogen bond between N9 and N6 of the adjacent molecule (H···N 2.17 Å, NH···N 157°) and a series of weaker bonds from N8 to F7A and F8A as well as N9 to F8A (H···F 2.37, 2.39, 2.42 Å, NH···F 134°, 161°, 117° respectively).

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Figure. 3 X-ray crystal structure of $[Ru(bpy)_2(L1-d_3)](PF_6)_2$ (top) and $[Ru(bpy)_2(L2)](PF_6)_2$ (bottom). Ellipsoids are drawn at 50% and only major components of disorder shown.

In the structure of [Ru(bpy)₂(L1-*d*₃)](PF₆)₂ a L1-*d*₃ ligand overlays the hydrogen bonding DAT moieties between two other complexes with the benzyl ring offset π - π stacking with one DAT ring (centroid–N6 3.50 Å) and the triazole deuteron hydrogen bonding to an amine of the other DAT ring (D…N 2.62 Å, CD…N 152°) supported by an additional offset π - π interaction between two pyridines (centroid–C3 3.62 Å), overall forming a chain of complexes down the crystallographic *b* axis (Figure 4).^[5] The structure of [Ru(bpy)₂(L2)](PF₆)₂ has a similar arrangement of complexes although in a more extended manner, relying more on bridging interactions through the PF₆ anions (H…F 2.27 – 2.63 Å, 115° - 180°) and not displaying any significant π -stacking interactions. (Figures S10-S11)



Figure 4. (top) X-ray crystal structure of $[Ru(bpy)_2(L1-d_3)](PF_6)_2$ showing the $R_3^2(10)R_2^2(8)R_3^3(10)$ motif hydrogen bonding pairs. (bottom) X-ray crystal structure of $[Ru(bpy)_2(L2)](PF_6)_2$ showing the $R_1^2(4)R_3^2(8)R_2^2(8)R_3^2(8)R_1^2(4)$ motif hydrogen bonding pairs.

Crystals of [Ru(bpy)₂(L3)](PF₆)·CH₃CN suitable for X-ray analysis were grown from diffusion of diethyl ether into an acetonitrile solution of [Ru(bpy)₂(L3)](PF₆). The complex crystallizes in the monoclinic space group P21 with the asymmetric unit containing a single enantiomer of the complex, with a Λ configuration, its accompanying hexafluorophosphate anion and one acetonitrile solvent molecule. (Figure 5) The ruthenium ion is octahedral with the singly deprotonated L3 ligand coordinating N^N to form a six membered chelate ring and an overall 1+ complex. The octahedral coordination geometry is partially distorted with the three chelate rings having bonding angles at Ru1 ranging from 78.9° to 89.3°. Unexpectedly, the hydrogen bonding observed in the structure is merely a series of discrete single hydrogen bonds. N3 of the hydantoin singly hydrogen bonds to N8 of the acetonitrile solvate (H···N 2.25 Å, NH···N 162°). Both O1 and O2 engage in non-classical CH···O hydrogen bonding with aromatic protons from adjacent bi-pyridine moieties (H···O 2.55, and 2.34 Å, CH…O 142°, and 175° for O1 and O2 respectively) but otherwise do not show any strong interactions, consistent with the results of the low frequency Raman studies. This is also observed from the PF6- anion which also shows a series of CH…F interactions (H…F 2.43 – 2.61 Å, 127° – 164°).

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It is noted that, where $R_2^2(8)$ dimers are found, the two component molecules are generally spanning a center of inversion – in this case, the symmetry of the adopted space group may be what precludes the formation of the expected hydrogen bonding motifs.



Figure 5. X-ray crystal structure of $[Ru(bpy)_2(L3)]PF_6$. Ellipsoids are drawn at the 50% probability level.

Crystals of $[Ru(bpy)_2(L4)]$ suitable for X-ray analysis were obtained from an aqueous solution of the complex. The complex crystallises in the monoclinic space group $P2_1/c$ with the asymmetric unit containing one complex unit and two full water molecules with a third in partial (40%) occupancy (Figure 6). The ruthenium ion is octahedral with the doubly deprotonated orotic acid ligand coordinating N^O bidentate, as expected, to give an overall neutral complex. The octahedral coordination geometry is partially distorted with the three chelate rings having bonding angles at Ru1 ranging from 78.3° to 79.6°.



Figure 6. X-ray crystal structure of $[Ru(bpy)_2(L4)]$. Ellipsoids are drawn at the 50% probability level and water solvates O6 and O7 are omitted for clarity.

The structure contains a racemic mixture of the Λ - and Δ enantiomers and the orotate ligand forms an $R_2^2(8)$ hydrogen bond to the orotate ligand of an adjacent molecule between N2 and O2 (H···O 2.15 Å, NH···O 157°). This is supported by

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additional hydrogen bonds from the carbonyl oxygens to the O5 and O6 water molecules (H···O 2.10, 2.05, and 2.07 Å, OH···O 171°, 171°, and 167° for H6A, H6B, and H5A respectively) to form an overall $R_4^3(10)R_2^2(8)R_4^3(10)$ motif. The packing of the molecules is further facilitated by weak non-classical hydrogen bonds between H3 and O4 (H···O 2.73 Å, CH···O 162°) of an adjacent molecule forming a second $R_2^2(10)$ like motif, and is supported by O5 which hydrogen bonds to the carboxylic acid (H…O 1.89 OH…O 163°). Thus, Å. а $\{R_4^3(10)R_2^2(8)R_4^3(10)R_3^2(8)R_2^2(10)R_3^2(8)\}_{\infty}$ motif assembles the complexes into infinite one-dimensional chains along the crystallographic a axis. (Figure 7) The extensive hydrogen bonding that the carbonyl groups enjoy is consistent with the results of the low frequency Raman studies (vide infra). The partial occupancy water solvate has a weak non-classical hydrogen bond to C6 (H···O 2.52, CH···O 135).



Figure 7. X-ray crystal structure of $[Ru(bpy)_2(L4)]$ showing hydrogen bonding chains down the crystallographic a axis with repeating $\{R_4^3(10)R_2^2(8)R_4^3(10)R_3^2(8)R_2^2(10)R_3^2(8)\}_{\infty}$ motif.

Crystals of *fac*-[Ir(ppy)₂(L3)] suitable for X-ray were grown from diffusion of diethyl ether into a chloroform solution of the complex. The complex crystallizes in the monoclinic space group C2/c with the asymmetric unit containing one complex and half a disordered diethyl ether solvate. (Figure 8) The iridium ion is octahedral with the singly deprotonated L3 ligand coordinating N^N and the coordinated C atoms of the ppy ligands both *trans*- to the L3 ligand giving the *fac*- geometry^[20] and an overall neutral complex as expected. The octahedral coordination geometry is partially distorted with the three chelate rings having bonding angles at Ir1 ranging from 80.2° to 88.3°.

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The crystal contains a racemic mix of the Λ - and Δ - enantiomers which for hydrogen bonded pairs *via* O3 of the ether solvate (H···O 1.99 Å, NH···O 175°) with the angle of the hydrogen bonding through the oxygen (N···O···N) and the overall angle between the two complexes being 113°. These pairs of complexes then stack into chains down the *b* axis supported by a series of weak non-classical hydrogen bonds from C18 and C19 to O1 (H···O 2.997 and 2.965 Å, CH···O 127° and 126°, respectively). (Figure 9) As was the case with [Ru(bpy)₂(L3)](PF₆), no $R_2^2(8)$ hydrogen bonding motif is observed.



Figure 8. X-ray crystal structure of *fac*-[$Ir(ppy)_2(L3)$]. Ellipsoids are drawn at the 50% probability level and with only the major components of disorder shown.



Figure 9. X-ray crystal structure of $fac-[Ir(pp)_2(L3)]$ showing how two complexes hydrogen bond (blue) *via* the diethyl ether solvate, then the hydrogen bonded complexes stack down the crystallographic *b* axis with support from weak non-classical hydrogen bonds (green).

The Raman spectra for all compounds are shown in Figure 10 and it can be observed from the low frequency region that there is a range of crystallinity among the compounds. [lr(ppy)2(L1)]+ and [lr(ppy)₂(L2)]⁺ are the most amorphous and display a single broad band in the LFR region. Some crystallinity is observed for $[Ir(ppy)_2(L3)]$, which is made apparent by the resolution of low frequency bands, but even greater crystallinity is seen for the remaining complexes. Further information is revealed in the mid frequency region. (Figure S4) Carbonyl bands can be clearly resolved for [Ru(bpy)₂(L3)]⁺ but only a broad band is observed for [lr(ppy)₂(L3)] consistent with the low frequency region which indicates that [Ir(ppy)2(L3)] is more amorphous. The carbonyl bands for the L4 complexes could not be resolved. The lack of carbonyl bands is also observed with an excitation of 1064 nm. (Figures S2, S3) Alongside the crystallinity of the L4 complexes, this suggests that the carbonyls are occupied with intramolecular bonds in a crystalline lattice which is consistent with the X-ray crystallography data.



Figure 10. Low and mid frequency Raman spectra for all compounds with a 785 nm excitation in solid state.

Hirshfeld Analysis^[31] provides further insight into the relative importance of the various intermolecular interactions found in the crystal structures. In particular, the fingerprint region plots $d_i vs.$ d_e , graphically depict the distances from the calculated Hirshfeld surface to the nearest nuclei inside and outside the surface, respectively, with the colours changing from blue to green as the frequency with which a particular (d_i/d_e) increases. Figures S12-S16 show the fingerprint plots for the five complexes.

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Figure 11 shows the relative amounts of the major interaction types observed in the structures, obtained from the fingerprint plots. Comparison of the plots for $[Ru(bpy)_2(L1)](PF_6)_2$ and $[Ru(bpy)_2(L2)](PF_6)_2$ shows that the percentage of H-H interactions for the L2 complex is larger than for the L1 complex, due to the hexyl chains, while the percentage of C-C interactions is greater for the L1 complex due to the benzyl substituent being able to engage in π - π stacking interactions.

[Ru(bpy) ₂ (L1)](PF ₆) ₂		■ C-H	H -H	■N-H	■ O-H	F-H	C-C		Other
14.2	25.3	10.0			38.8			4.8	6.9
[Ru(bpy) ₂ (L2)](PF ₆) ₂									
15.5	30.9		14.0			30.6		2.1	6.9
[Ru(bpy) ₂ (L3)]PF ₆									
19.9	29.5		6.3	11.8		25.	6	1	.5 5.3
[Ru(bpy) ₂ (L4)]									
11.6	37.7		2.0		35.1			8.2	5.4
[lr(ppy) ₂ (L3)]									
29.2			53	.0			2.5	11.3	1.7 2.3

Figure 11. Quantification of intermolecular interactions in the crystal structures from HIrshfeld fingerprint analysis.

The percentage of N-H interactions are similar between them, and the large percentage of H-F interactions reflects the hydrogen bonding interactions to the PF₆⁻ anions. The plots for the two L3 complexes show very similar percentages of H-O interactions, but differ in that the [Ru(bpy)₂(L3)]PF₆ complex has 25.6% of the interactions as H-F hydrogen bonds to the anion. By comparison, the plot for [Ru(bpy)₂(L4)] shows that over one third of all the interactions are H-O hydrogen bonds, as expected given the extensive hydrogen bonding interactions observed.

Conclusions

The aim of the work was to prepare transition metal complexes that could act as potential tectons for triple hydrogen bonddirected assembly. The new ligands and the Ru(II) and Ir(III) complexes described here were able to be readily synthesized and while they display good solubility in low-donicity solvents, ¹H NMR studies disappointingly showed no evidence of appreciable homosynthon assembly in solution. In the solid state, [Ru(bpy)₂(L1)](PF₆)₂ and [Ru(bpy)₂(L2)](PF₆)₂ assemble into dimers via the expected $R_2^2(8)$ motifs, supported by NH-F hydrogen bonding to the PF6⁻ anions, and [Ru(bpy)2(L4)] assembles into one-dimensional chains via hydrogen bonding interactions between the coordinated orotate ligands (again as expected) supported by water solvate molecules. However, the solid-state structures of [Ru(bpy)2(L3)]PF6 and [Ir(ppy)2(L3)] do not show the five-membered hydantoin ring displaying the hydrogen bonding patterns seen in other systems. These results suggest that, while the L1, L2, and L4-containing complexes have

promise for the formation of the desired heterosynthon assemblies, use of the L3 complexes might be less successful.

The measured emission spectra of the complexes show that there is limited scope for using hydrogen bonding through the L ligand to tune the emission of the Ru(II) complexes in solution (as they are non-emissive) nor for the [lr(ppy)₂(L3)] and [lr(ppy)₂(L4)]⁻ complexes, as these emit from ppy-based states. However, the Ru(II) and Ir(III) complexes of L1 and L2 do show promise, particularly in the solid state, as in these the emissive state lies on the L ligand.

The low frequency Raman studies support what is observed in the X-ray crystallography, specifically that the assembly of the compounds in the solid-state structures of the L3-containing complexes does not significantly involve the carbonyl groups while the opposite is true for the L4-containing complexes. This, for these complexes at least, the LFR spectra provide a non-crystallographic guide to the nature of the hydrogen bonding interactions present.

With these results in hand, work on preparing co-crystals of these complexes with each other and with other suitable organic species is underway and these results will be reported in due course.

Experimental Section

Experimental details, crystal structures, Hirshfeld Analysis and spectroscopic data are provided in the Supporting Information.

Acknowledgements

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Keywords: Hydrogen bonding • crystal engineering • ruthenium • iridium • X-ray crystallography

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

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Ru(bpy)2(L)] and [Ir(ppy)2(L)] complexes, where L is a ligand containing either a DAD or ADA triple hydrogen bonding motif, have been prepared and characterised and their potential to act as components in supramolecular assembles assessed, through analysis of their solid-state structures and their spectroscopic properties.

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Ru(II) and Ir(III) complexes containing ADA and DAD triple hydrogen bonding motifs: Potential tectons for the assembly of functional materials.