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Recent Advances in the Synthesis and Applications of 2,6-Dipyrazolylpyridine Derivatives and their Complexes

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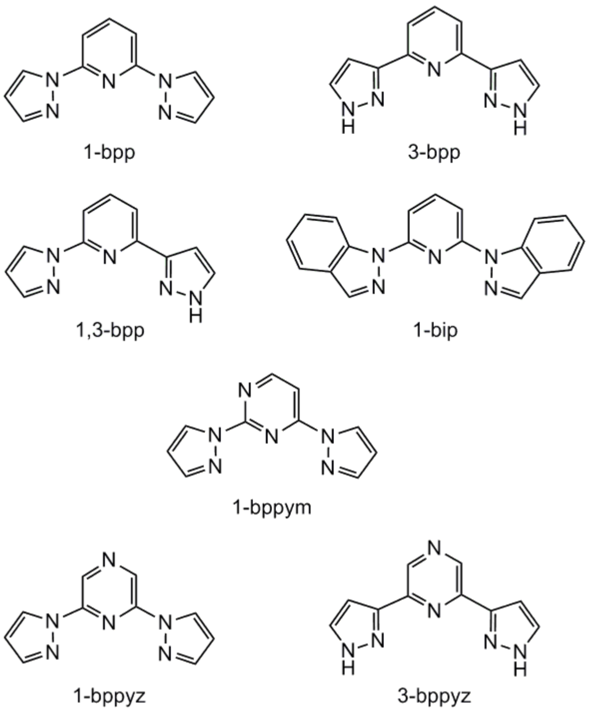
Developments in the chemistry of 2,6-di(pyrazol-1-yl)pyridine (1-bpp) and 2,6-di(pyrazol-3-yl)pyridine (3-bpp), their derivatives and their complexes are surveyed, with emphasis on the last eight years. Particular advances include the synthesis of multi-functional spin-crossover switches; the incorporation of emissive *f*-element podand centres into biomedical sensors; the self-assembly of a variety of functional soft materials and surface structures; and, the use of 3-bpp complexes in catalysis.

Introduction

Tris-heterocyclic ligands continue to be very widely used in transition metal chemistry, because of their synthetic flexibility, strong metal binding properties, and their ability to impart properties like luminescence or spin-crossover onto a coordinated metal ion. 2,2':6',2''-Terpyridine (terpy) and its derivatives are still the most widely used ligand of this type, and are important in supramolecular chemistry,[1] soft materials chemistry[2,3] and nanoscience[4] among other fields of research. However, other classes of *tris*-heterocycle such as 2,6-di(benzimidazol-2-yl)pyridines[3,5] and the 2,6-di(pyrazolyl)pyridines[6-8] have certain advantages over the terpyridines for some applications and are also well-studied in their own right. The coordination chemistry of 2,6-di(pyrazol-1-yl)pyridine (1-bpp) and 2,6-di(pyrazol-3-yl)pyridine (3-bpp, Scheme 1) was first developed in two particular areas: their iron(II) complexes which can show unusual, and useful, spin-crossover switching properties; and, a class of podands based on the 1-bpp skeleton which form strongly emissive lanthanide complexes.[6] While those areas have continued to expand, more recently the use of bpp derivatives in other areas of research has also been explored, including catalysis, solar cell photosensitisation and soft materials.

The synthesis and coordination chemistry of 1-bpp, 3-bpp and some related ligand classes were surveyed eight years ago,[6] and two more recent articles have reviewed spjn-crossover iron(II) complexes of the same ligand types.[7,8] This article updates these earlier reviews, and emphasises results published since 2005. After a description of current developments in the syntheses of these ligands, the discussion is then grouped according to their different applications. The types of *tris*-heterocycle to be considered, and their abbreviations, are shown in Scheme 1.



Scheme 1. The classes of ligand discussed in this article, and their abbreviations.

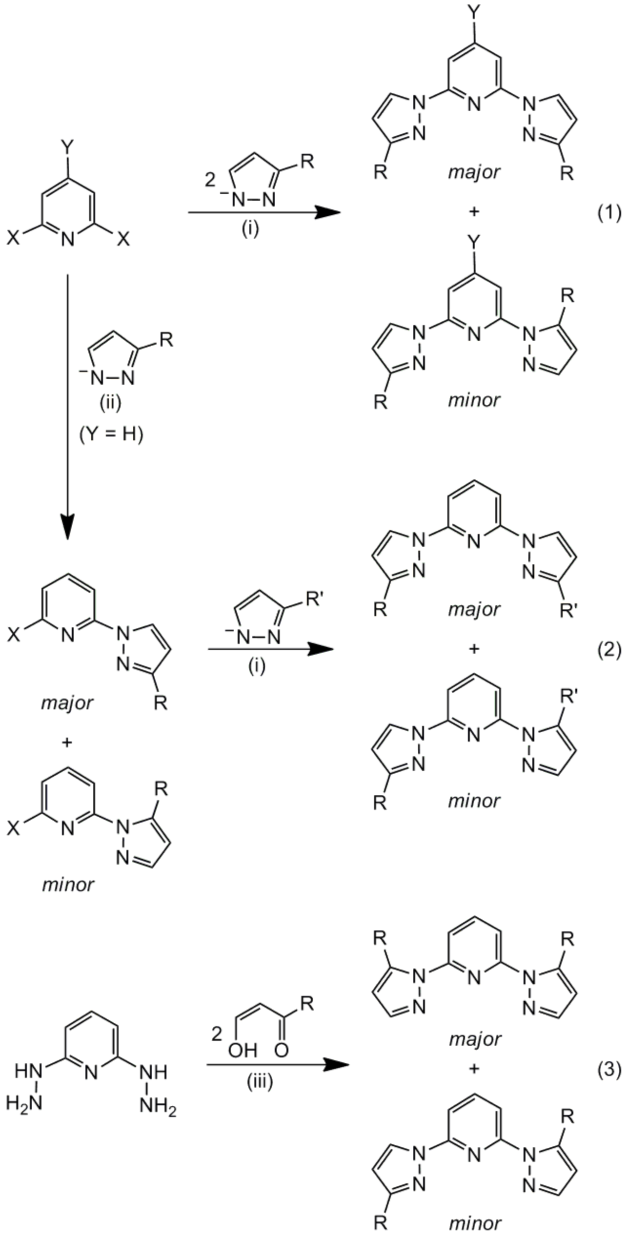
Synthesis of 1-bpp derivatives and related ligands

The first-reported method for synthesising 1-bpp derivatives is still the most commonly used one,[9] namely the nucleophilic coupling of pyrazolide anions with 2,6-dihalopyridines (eq 1, Scheme 2).[6] 2,6-Dibromopyridine precursors (X = Br) are usually used but dichloro- and difluoropyridines (X = Cl or F) can also work well, especially if the pyridine ring has additional electron-withdrawing 'Y' substituents (Scheme 2). The yield of the reaction can depend strongly on the presence of other substituents on the pyridine ring, and can be increased if required by using an excess of pyrazole reagent. The process is quite forgiving in other ways, however. For example, 1-bpp derivatives bearing protic pyridine substituents ($Y = CO_2H$,[10,11]) can be made by eq 1 without prior protection of the acidic function. Since attack by the second pyrazole equivalent requires more forcing conditions, preparation of unsymmetric 1-bpp derivatives by stepwise addition of two different pyrazoles is straightforward and works well (eq 2, Scheme 2).[9] No such unsymmetric ligand with $Y \neq H$ has yet been reported,[6,7] but the method should also work in that case. Only one study of catalysis of eq 1 has been published, reporting that palladium catalysts increase the rate of reaction, but do not give higher yields.[12] Although 1*H*-pyrazoles can be *N*-arylated under Ullmann conditions, for example,[13] that has not yet been applied to the synthesis of 1-bpp derivatives.

Where substituents are present on the pyrazole *C*3 positions, the less hindered 3’,3’’-disubstituted-1-bpp isomer is the major product of eqs 1 and 2[9] although small amounts of the 3’,5’’-disubstituted-1-bpp isomer(s) are also sometimes observed (Scheme 2).[6] If the pyrazole ‘R’ substituents are small and non-polar (*e.g.* methyl), the subsequent chromatographic purification of the desired 3’,3’’-disubstituted isomer can be challenging. A number of 1-bpp derivatives bearing simple alkyl or aryl substituents have been prepared in this way,[6,7,14-17] including chiral derivatives produced using optically pure pyrazole reagents.[6] An exception to this generalisation is where indazole reagents are used, when eq 1 yields the more hindered 2,6-di(indazol-1-yl)pyridine products (1-bip, Scheme 1) in moderate yield.[18,19] That reflects the usual reactivity pattern for deprotonated indazoles, which prefer electrophilic attack at *N*1.

A small number of 1-bpp ligands substituted at the pyridine ring can be accessed directly by eq 1,[6,7,10,11] but these can be converted into a wider range of 4-substituted-1-bpp products by subsequent functional group transformations (see below). Finally, eq 1 can also be extended to 1-bppyz analogues (Scheme 1), using 2,6-dichloropyrazine as starting material.[6,20,21] Much milder reaction conditions are employed in that case, because of the greater reactivity of the dichloropyrazine reagent.[20] However, this also means that unsymmetric 1-bppyz derivatives cannot be produced cleanly (*c.f.* eq 2).

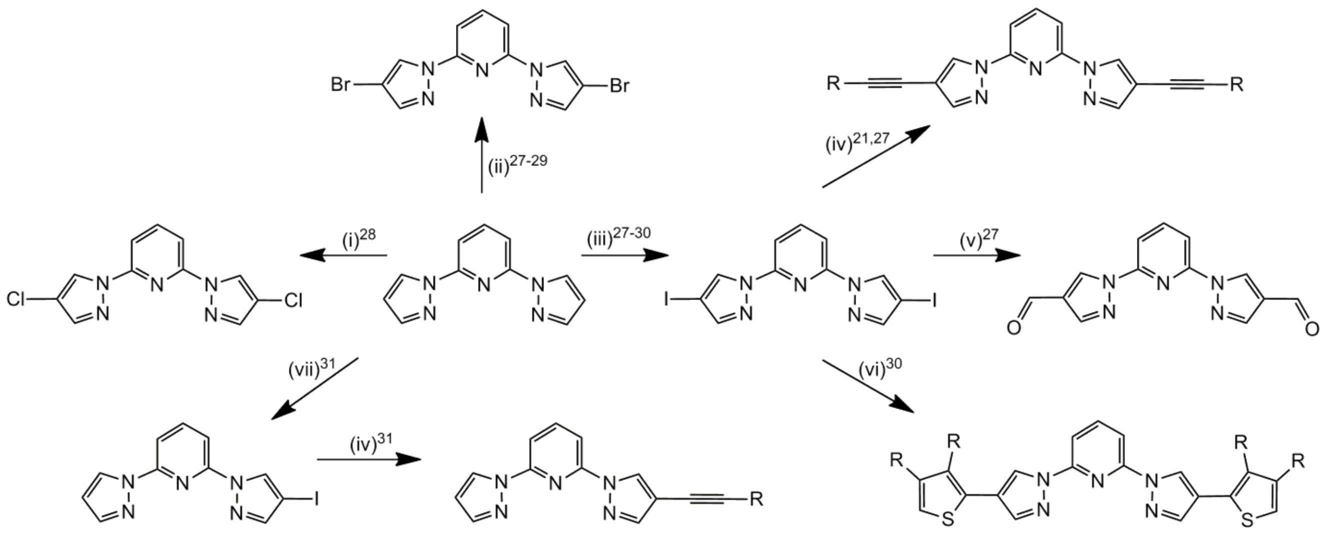
An alternative route to 1-bpp derivatives substituted at the pyrazole ring has been published by Garner *et al.*, by treatment of 2,6-di(hydrazino)pyridine with β–diketones (Scheme 2, eq 3).[22,23] This route has a potential advantage in giving the opposite regioselectivity to eq 1, since bulkier or more electron-donating pyrazole substituents tend to adopt the 5’,5’’-positions in the 1-bpp products (eq 3, Scheme 2). When applied to the 2,6-di(indazol-1-yl)pyridine system, the same 1-bip products afforded by eq 1 are also obtained by this route (Scheme 1).[24] The methods in eq 1 and eq 3 have also been used to prepare 1-bppym derivatives (Scheme 1), starting from the appropriate 2,6-dihalo- or 2,6-di(hydrazino)-pyrimidine.[25,26]



Scheme 2. Synthetic routes to 1-bpp derivatives (R, R’ = H, alkyl or aryl usually). Typical reaction conditions: (i) diglyme, 110-130º C, 3-5 days; (ii) diglyme or thf, 60º C, 2 days; (iii) thf, cat. H^+, reflux, 12-24 hrs.

Chemical modification of 1-bpp itself can be achieved by halogenation (Scheme 3). Mild electrophilic chlorination, bromination or iodination reagents lead to selective dihalogenation at the pyrazole *C*4 positions.[27-30] Selective mono-iodination at just one pyrazole ring has also been achieved by monitoring the reaction carefully,[31] while more forcing conditions lead to multiple halogenations of 1-bpp, at the pyrazole and pyridine rings.[29] Comparable halogenations of 1-bppyz were less successful, and 4’,4’’-dihalo-1-bppyz derivatives are more easily obtained by eq 1, using preformed 4-halopyrazole reagents.[21]

4’,4’’-Diiodo-1-bpp and -1-bppyz derivatives are good reagents for Sonogashira couplings, affording 4’,4’’-di(alkynyl)-1-bpp and -1-bppyz products.[21,27,31] There is also one report of a Stille coupling from the same precursor, yielding a 4’,4’’-di(thienyl)-1-bpp derivative,[30] but attempted Heck reactions were reportedly unsuccessful.[21] Attempted nitration of 1-bpp using HNO_3/H_2SO_4 led to a mixture of products, involving partial nitration of the pyridyl as well as the pyrazolyl rings.[28] 4’,4’’-Dinitro-1-bppyz was prepared by eq 1, however, starting from preformed 4-nitropyrazole.[22] 4’,4’’-Dinitro-1-bpp cannot be made by that route, because the more forcing conditions required leads to decomposition of the nitropyrazole reagents.



Scheme 3. Important methods for the post-synthetic modification of 1-bpp. Typical conditions used: (i) NaClO, aq CH_3CO_2H. (ii) Br_2, CH_3CO_2H then $Na_2S_2O_5$, H_2O. (iii) I_2, $[NH_4]_2[Ce(NO_3)_6]$, CH_3CN or I_2, HIO_3, CH_3CO_2H/H_2SO_4. (iv) RCCH, CuI, $[Pd(PPh_3)_4]$ (cat), NEt_3, dioxane. (v) EtMgBr, thf, –78 °C then dmf, 0 °C. (vi) 2-tributylstannylthiophene, $[PdCl_2(PPh_3)_2]$ (cat), CuI, dmf. (vii) I_2, HIO_3, CH_3CO_2H/H_2SO_4 (dropwise addition).

Preformed 1-bpp and 1-bppyz derivatives bearing chemically modifiable pyrazole substituents can be subsequently transformed into more complex structures.[16,21,27,30-33] One important example here is 3',3''-di(ethylcarboxy)-1-bpp (eq 1, R = CO_2Et), which can transformed into a series of podand derivatives for *f*-element complexation in three further steps.[6,32] These podands are described in more detail below.

Most syntheses of 4-substituted-1-bpp ligands (eq 1, $Y \neq H$, Scheme 2) begin from commercially available 2,6-dihydroxyisonicotinic acid. After a halogenation step, this is readily converted to 2,6-di(pyrazol-1-yl)pyridine-4-carboxylic acid by eq 1 (Y = CO_2H).[10,11] From there, a variety of functional group transformations are available, as shown in Scheme 4. This is the most common route for attaching additional functionality to the 1-bpp pyridine ring.[7,33-46] Recently, however, 4-bromo-2,6-difluoropyridine has been identified as an alternative starting material for 4-substituted 1-bpp derivatives. The fluoro groups of this precursor are selectively displaced in eq 1 (X = F, Y = Br), yielding a 4-bromo-1-bpp product that can be further modified by Sonogashira cross-coupling or substitution reactions.[47]

Synthesis of 3-bpp and 1,3-bpp derivatives

The only known synthetic route to 3-bpp derivatives is to construct the pyrazole rings about a pyridyl precursor, *via* Claisen condensation or a comparable acetylation reaction followed by hydrazinolysis (Scheme 5).[6] Compound 3-bpp itself is most conveniently prepared from 2,6-diacetylpyridine using dimethylformamide dimethylacetyl as formylating agent,[48] but 3-bpp derivatives substituted at the pyrazole *C*5 positions can also be accessed by more conventional Claisen condensations or other acetylation procedures.[6] A number of new derivatives of this type have been prepared in the last eight years,[49-62] and incorporation of electron-withdrawing substituents at the pyrazole *C*4 positions is also achievable by this method.[58-60]

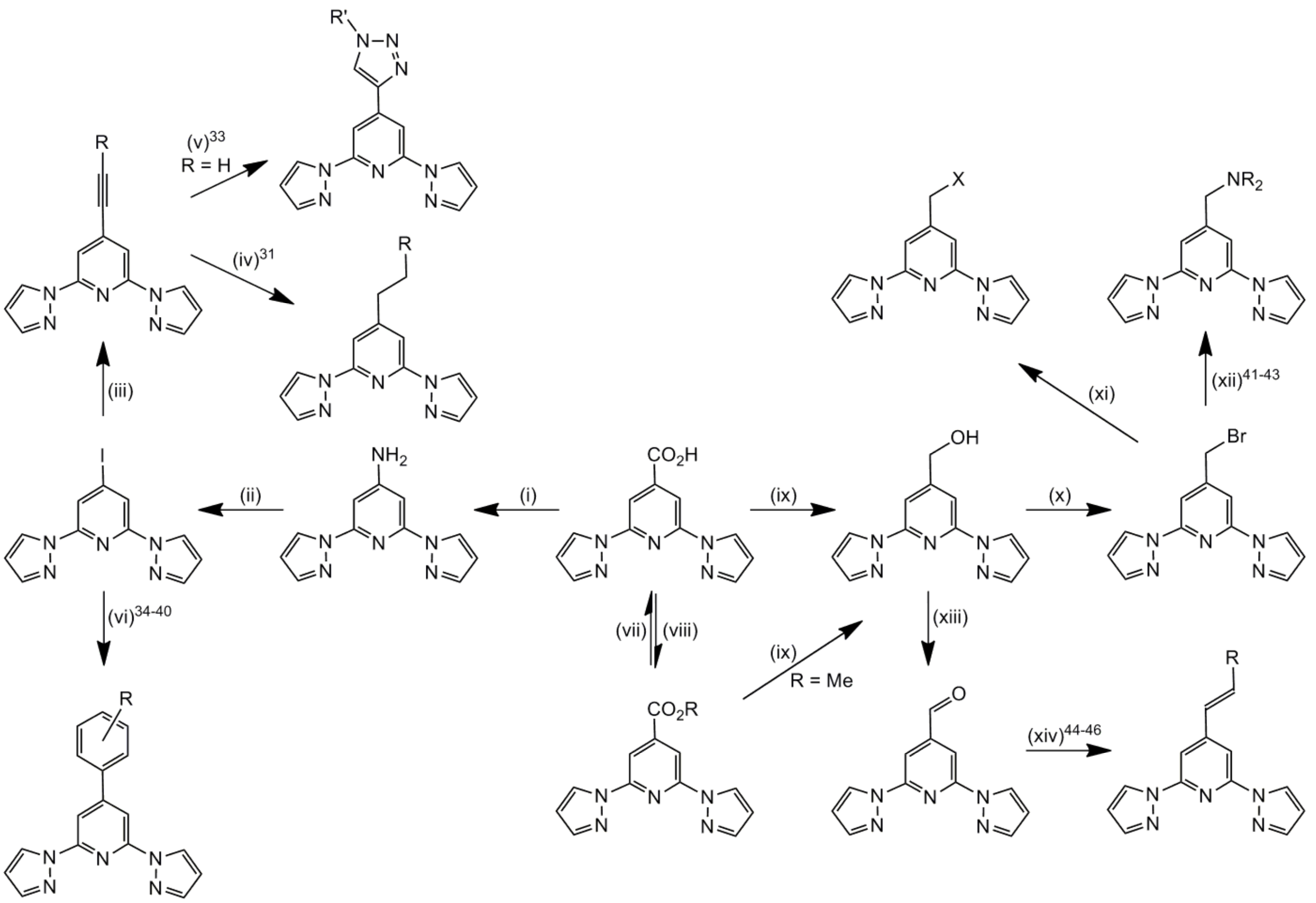
Preformed 3-bpp can be cleanly dialkylated at the pyrazole *N*1'/*N*1'' sites following deprotonation with NaH or another alkali metal-containing base (Scheme 5).[61-67] Chelation of the $[3\text{-bpp}{-}2H]^{2-}$ anion by the alkali metal ion directs the regiochemistry of the reaction by protecting the alternative pyrazole *N*2'/*N*2'' alkylation sites.[68] Alternatively, *N*,*N'*-dialkyl and *N*,*N'*-diaryl-3-bpp derivatives have sometimes been produced by performing the hydrazinolysis step of the 3-bpp synthesis using substituted hydrazines (Scheme 5).[6,51,69] The first 3-bpp derivative substituted at the pyridine ring was reported recently, from a series of transformations starting from 4-hydroxypyridine-2,6-dicarboxylic acid (cheladamic acid).[53] Finally, the pyrazinyl analogue 3-bppyz can also be accessed from 2,6-diacetylpyrazine, by the same route used for 3-bpp.[70]

Two different routes to 1,3-bpp or a dimethylated derivative of it have been reported, requiring four or five synthetic steps from available precursors.[71,72] They differ in their approach to the formation of a 2-acetyl-6-(pyrazol-1-yl)pyridine intermediate, which is then converted to a 1,3-bpp using the same conditions used to make unmodified 3-bpp (see above).

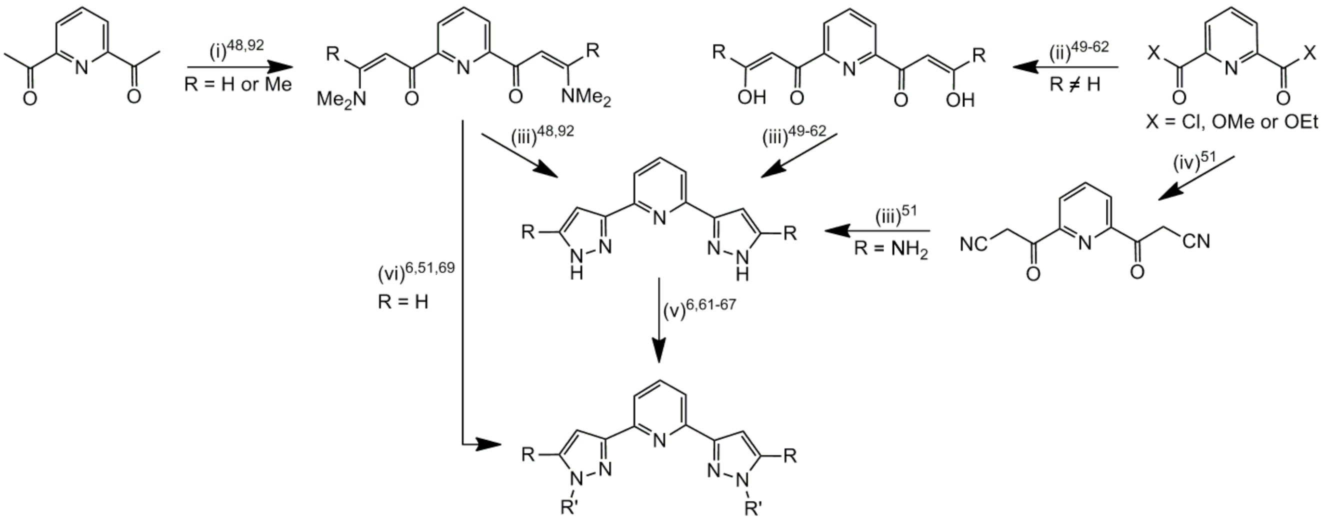
1-Bpp and related ligands in spin-crossover

Iron(II) complexes of 1-bpp derivatives continue to be heavily investigated by the spin-crossover community. Results on this topic published since 2009 are discussed here, and the reader is directed to ref. 7 for a discussion of earlier work.

The synthetic versatility of the 1-bpp pyridyl group (Scheme 4), and the tendency for $[Fe(1\text{-bpp})_2]^{2+}$ derivatives to exhibit spin-crossover near room temperature,[7] has led several groups to pursue multifunctional spin-crossover switches based on the $[Fe(1\text{-bpp})_2]^{2+}$ framework. Thus, $[Fe(L^1)_2]^{2+}$ contains two pendant electron-acceptor tetrathiafulvalene (TTF) moieties, which was crystallised with electron-donor anions in the double salt $[Fe(L^1)_2][Ni(mnt)_2]_2BF_4{\cdot}PhCN$. Partial electron transfer from the anions to the TTF pendant groups, which is evident in the crystal structure, afforded a semiconducting crystal whose resistivity



Scheme 4. Important methods for the production of 4-substituted-1-bpp derivatives. The procedures are referenced in ref. 7 unless otherwise stated. Typical conditions used: (i) $COCl_2$, thf; NaN_3, acetone/water; CF_3CO_2H, benzene; K_2CO_3, MeOH. (ii) $NaNO_2$, KI, HCl. (iii) RCCH, CuI, $[Pd(PPh_3)_4]$ (cat), NEt_3, thf. (iv) H_2, Pd/C (cat), ethyl acetate. (v) RN_3, $CuSO_4$, Na[ascorbate], dmf. (vi) $ArB(OH)_2$, $[Pd(PPh_3)_4]$ (cat), toluene or dioxane, Na_2CO_3. (vii) ROH, H_2SO_4 (cat). (viii) LiOH, thf then dil. HCl. (ix) $NaBH_4$, EtOH. (x) HBr, reflux or Br_2, PPh_3, CH_3CN, rt. (xi) NaX, CH_3CN. (xii) R_2NH, Na_2CO_3, KI (cat) or NBu_4Br (cat), CH_3CN, reflux or dmf, warm. (xiii) $C_2O_2Cl_2$, dmso, CH_2Cl_2, −78 °C, then NEt_3, rt. (xiv) $[RCH_2PPh_3]Br$, BuLi or KO*t*Bu, thf.



Scheme 5. Procedures for the synthesis of 3-bpp derivatives. Typical conditions used: (i) $Me_2NC(O)R$, reflux. (ii) RC(O)Me (2 equiv), NaH or NaOMe (2 equiv), MeOH, dme or CH_2Cl_2, reflux. (iii) $N_2H_4{\cdot}H_2O$ or $N_2H_4{\cdot}HCl$ (2-10 equiv), MeOH or EtOH, H^+ (cat) if required, reflux. (iv) MeCN, NaH (2 equiv), THF, reflux. (v) NaH or LiH (2 equiv), R'X (2 equiv), THF. (vi) $R'N_2H_3$ (2-10 equiv), MeOH or EtOH, reflux.

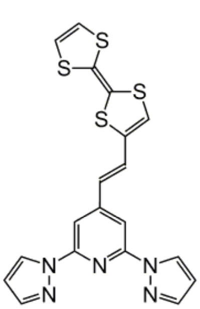
shows a distinct discontinuity in the region of the iron spin-transition.[46] Similarly, L^2 and L^3 are 1-bpp derivatives bearing fluorescent pyrenyl substituents. A solvate of $[Fe(L^3)_2][ClO_4]_2$ did exhibit spin-crossover and fluorescence, but no dependence between the iron spin state and the emission profile was observable in that case.[38] Mixed-metal complexes $[Fe(L^4)_2][BF_4]_4$ and $[Fe(L^5)_2][BF_4]_4$ were also prepared with fluorescence in mind, but no emission from pendant platinum centres was observed from the latter compound in the solid state.[41]

Styryl derivatives $[Fe(L^6)_2][BF_4]_2$[44,73] and $[Fe(L^7)_2][BF_4]_2$[45] were synthesised for studies of the ligand driven, light-induced spin-crossover (LD-LISC) effect, where *cis*/*trans* photoisomerism of the pendant styryl pendant groups induces a change in spin-state at the coordination iron centres.[74] Both complexes are effective in that regard, undergoing irreversible *cis*→*trans* isomerisation under visible light in solution and, unusually, in the solid state.[44,45] Notably, while the *trans* isomers of both complexes have similarly gradual spin-crossover profiles in the solid state, the *cis*-isomers are different; solid *cis*-$[Fe(L^6)_2][BF_4]_2$ is high-spin at room temperature, but *cis*-$[Fe(L^7)_2][BF_4]_2$ is predominantly low-spin. Thus, the LD-LISC effect in the two solids has an opposite effect on their iron spin-states.

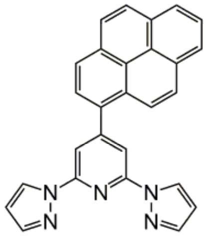
The compounds $[Fe(L^8)_2]^{2+}$ and $[Fe(L^9)_2]^{2+}$ have been introduced into single-molecule junctions, to investigate the relationship between conductivity through a single molecule and the spin-state at the central iron atom.[75,76] Although interpretation of the data is complicated by noise,[75] it was proposed that injecting two electrons onto the ligand-based LUMOs of $[Fe(L^9)_2]^{2+}$ triggers a low-spin→high-spin transition at the iron centre under the conditions of the experiment.[76] That might explain a splitting of the Kondo peak in the I/V response across the molecular junction. Interestingly, an opposing effect has since been reported in other studies, where single-electron charging of a ligand LUMO orbital induces a high-spin→low-spin state change in single molecules absorbed on a surface. While low-spin→high-spin switching could also be effected in those experiments, that was ascribed to the effect of local heating of the sample rather than to reduction of the molecule.[77]

The salt $[Fe(L^9)(L^9H)][ClO_4]_3{\cdot}MeOH$ has also been drop cast into polycrystalline thin films, which were subsequently manipulated into 200 nm striped patterns by wet lithography. Raman spectra at 393 and 170 K indicated that these films undergo spin-crossover at a comparable temperature to the bulk material.[78] Drop-casting $[Fe(L^{10})_2][BF_4]_2$ onto HOPG (graphite) surfaces instead yielded unusual patterns of bead nanostructures. Each bead was 2.5-4 nm in diameter, implying it contains approximately 5-10 molecules. Individual beads gave different responses under current image tunnelling spectroscopy, which may imply they may contain molecules in different spin states.[79] Thin electroluminescent films containing $[Fe(1\text{-}bpp)_2][BF_4]_2$ and chlorophyll have been incorporated into organic LED (OLED) devices, although modulation of the OLED emission by spin-crossover in the film was not observed.[80]

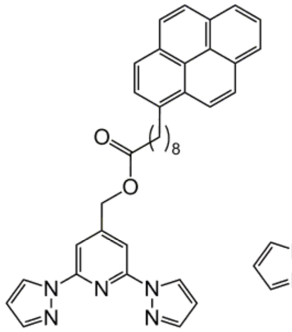
Solid solutions of $[Fe(1\text{-}bpp)_2][BF_4]_2$ doped with $[Cu(1\text{-}bpp)_2][BF_4]_2$,[81] $[Ru(terpy)_2][BF_4]_2$,[82] and $[Co(terpy)_2][BF_4]_2$[83] have been prepared, to investigate how the spin-transition of the $[Fe(1\text{-}bpp)_2][BF_4]_2$ host lattice at 260 K perturbs the electronic structure of the guest dopant. The materials



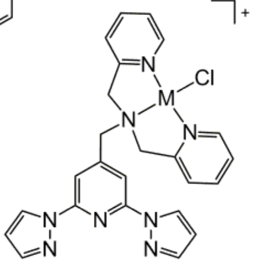
L^1



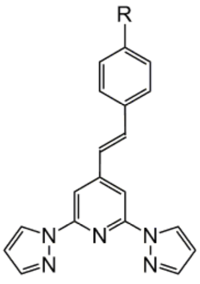
L^2



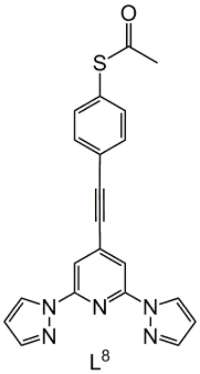
L^3



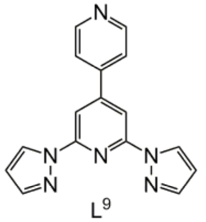
M = Pd, L^4
M = Pt, L^5



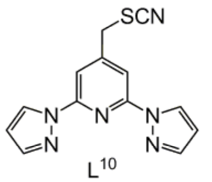
R = H, L^6
R = NO_2, L^7



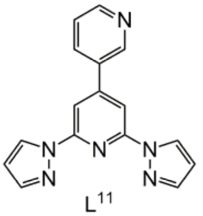
L^8



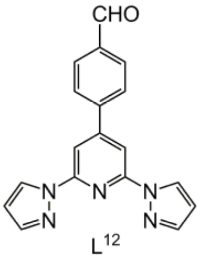
L^9



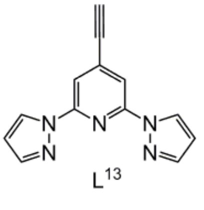
L^{10}



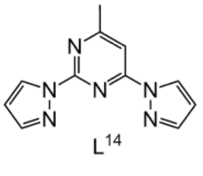
L^{11}



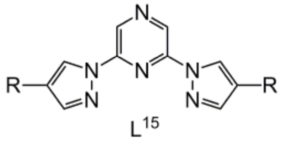
L^{12}



L^{13}



L^{14}



L^{15}
R = CH_3, Cl, Br, I, NO_2, NH_2, CCPh

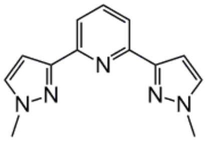
$[Fe(1\text{-}bpp)_2]_x[Co(terpy)_2]_{1-x}[BF_4]_2$ (x = 0.95-0.75) are of particular note, in that spin-crossover of the iron centres in the materials induces an allosteric spin-state switching in the cobalt dopant.[83,84]

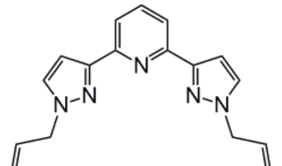
Other 1-bpp derivatives whose iron(II) complexes have been investigated for spin-crossover behaviour since 2009 include L^{11},[39] L^{12},[40] L^{13},[85] the 1-bppym ligand L^{14} [25] and the series of 1-bppyz derivatives collected as L^{15}.[21] Spin-crossover was observed in most of these examples, although some of them were complicated by polymorphism and solvate formation.[39,85] Light-induced spin-state trapping (LIESST effect)[86] studies were also performed in some cases,[21,40] which mostly followed the established behaviour of the $[Fe(1\text{-}bpp)_2]^{2+}$ series of complexes.[7] Finally, the use of $[Fe(L^9)_2]^{2+}$ as a temperature-sensitive probe for magnetic resonance imaging (MRI) has been patented.[87]

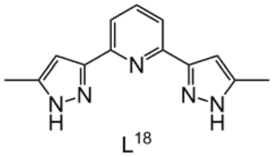
Solid $[Co(NO_3)_2(1\text{-}bppyz)]$ undergoes an unusual hysteretic magnetic discontinuity at 235 K. Rather than being spin-crossover, this reflects a change in zero-field splitting at the high-spin cobalt ion induced by a crystallographic phase transition.[88]

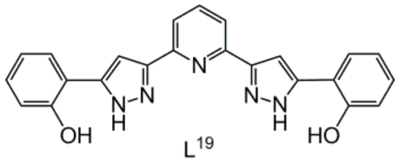
3-Bpp and related ligands in spin-crossover

Salts of $[Fe(3\text{-}bpp)_2]^{2+}$ have been heavily studied since the late 1980s.[6,8,89] That compound exhibits very variable spin-state behaviour that is highly dependent on the water content of the samples, the presence of lattice water tending to favour the low-spin state of the complex. Its utility is also enhanced because $[Fe(3\text{-}bpp)_2]^{2+}$ is stable in aqueous solution, in contrast to $[Fe(1\text{-}bpp)_2]^{2+}$ which decomposes in water. Those observations have been explained by solution-phase measurements, which showed that spin-crossover in $[Fe(3\text{-}bpp)_2]^{2+}$ shifts to *ca*. 60 K higher temperature in water compared to organic solvents.[90] That probably reflects increased polarisation of the $N^{\delta-}–H^{\delta+}$ groups in the molecule by strong N–H…O hydrogen bonding between the complex and the solvent. That would lead to more electron-rich 3-bpp ligands, which in turn would exert a larger ligand field at the iron atom. Similarly spin-crossover of different salts of $[Fe(3\text{-}bpp)_2]^{2+}$ in solution depends on the anion present, in that more associating halide ions increase the midpoint temperature by up to 20 K in acetone/water mixtures.[91]


L^{16}


L^{17}


L^{18}


L^{19}

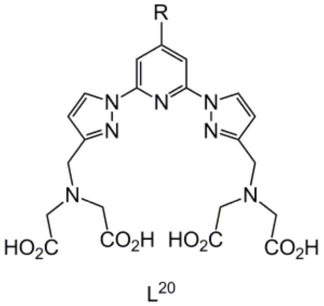
Despite the recent wider availability of substituted 3-bpp derivatives (see above), few of them have investigated in spin-crossover research so far. *N*,*N'*-Dialkylation of 3-bpp suppresses spin-crossover in complexes such as $[Fe(L^{16})_2][BF_4]_2$ and $[Fe(L^{17})_2][BF_4]_2$, probably on steric grounds.[67] However, iron(II) complexes of two *N*H-pyrazolyl 3-bpp ligands show more interesting behaviour. Hydrated and anhydrous forms of $[Fe(L^{18})_2][BF_4]$ and $[Fe(L^{18})_2][ClO_4]$ are isostructural under ambient conditions, but exhibit complicated and contrasting spin-crossover properties. The anhydrous BF_4^- salt exhibits a highly cooperative spin-transition near 205 K with a wide hysteresis loop,[92] but the ClO_4^- salt is simply high-spin.[93] Conversely, $[Fe(L^{18})_2][ClO_4]_2\cdot 2H_2O$ is spin-crossover active, but the hydrated BF_4^- salt is not. *X*-ray powder diffraction revealed that these differences reflect different sequences of phase changes that take place in the materials upon cooling.[92,93]

Solvates of $[Fe(L^{19})_2][ClO_4]_2$ have also proven fruitful.[94-97] The acetone solvate of this salt exhibits a spin-transition around 150 K, with a 40 K hysteresis loop.[94] The wide hysteresis does not involve a crystallographic phase change, but may be mediated by changes to anion disorder and ligand conformation. Spin-state trapping experiments by laser irradiation (LIESST[86]) or thermal quenching allow access to two different metastable high-spin states of the compound at low temperatures. The thermally quenched material resembles the thermodynamic high-spin phase, while following LIESST irradiation the ligand conformation is closer to that found in the low-spin phase. This has therefore allowed the spin-state change, and the accompanying conformational rearrangement, to be decoupled in this system.[95] The thf solvate of the same salt is isostructural with the acetone one, but only undergoes complete spin-crossover following solvent loss on exposure to air.[96] Other solvates of the same complex salt show more variable spin-state behaviour.[97] Salts of $[Fe(3\text{-}bppyz)_2]^{2+}$ (Scheme 1) are low-spin in the solid state.[70]

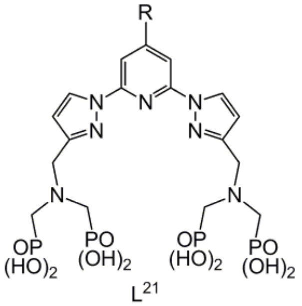
The dinuclear complex $[\{Fe(NCS)_2(3\text{-}bpp)\}_2(\mu\text{-}4,4'\text{-}bipy)]$ undergoes spin-crossover in just one of its iron centres on cooling under ambient conditions,[98] which is preceded by the higher temperature loss of a crystallographic centre of symmetry.[99] This crystallographic phase change is not reversed during LIESST irradiation, so the thermodynamic and kinetically trapped high-spin states of the compound are crystallographically distinct.[99] Under hydrostatic pressure, however, both iron atoms are gradually converted to the low-spin state as the pressure is raised.[100] A different dimeric complex with this ligand set, $[\{Fe(NCS)(\mu\text{-}NCS)(3\text{-}bpp)\}_2]\cdot 2(4,4'\text{-}bipy)$, has also been crystallised but is not spin-crossover active.[101]

f-Block complexes

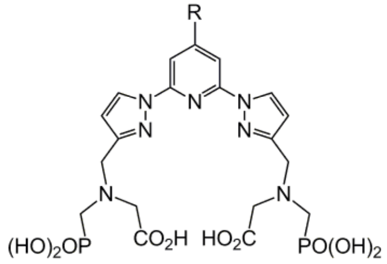
The other aspect of bpp research that has been heavily studied is their *f*-element chemistry.[6] Tetra-carboxylate podands of type L^{20} were first investigated in 1993.[32] They encapsulate lanthanide ions in aqueous solution (log K = 14-16) with hydration numbers ≤0.5, and are good sensitisers for several *f*-elements yielding emissions with ms lifetimes.[6,19,102] Functionalisation of the pyridyl 'R' group allows a range of targeting groups and receptors to be appended to the podand skeleton, such as streptavadin and biologically labelled silica particles.[6,19,47] The emission quantum yields of $[Ln(L^{20})]$



L[20]



L[21]



L[22]

complexes depend strongly on the nature of R,[19] making them responsive to the binding of substrates or changes in their environment. These conjugates have yielded fluorescent sensors for protein:protein interactions and DNA hybridisation, with sensitivities up to the pg range.[6]

More recent studies have developed these designs into sophisticated time-resolved sensors, for small molecule and biological analytes. Two $[Ln(L^{20})]$ podands bearing oxidisable 'R' substituents have been developed, where degradation of the side-chain leads to enhancement of the emission. One of these was employed as a "switch-on" sensor for H_2O_2, with ms time resolution and a nM detection limit. This allowed the monitoring of H_2O_2 production by biological saccharide degradation in leaf cells by fluorescence microscopy.[103] Another, slightly different design afforded an analogous fluorescent sensor for monitoring the $OH^{\bullet}$ radical in live cells.[104] Two different $[Tb(L^{20})]$ complexes bearing pendant chelate 'R' groups have been designed as fluorescent sensors for Zn^{2+} and Hg^{2+} ions.[42,43]

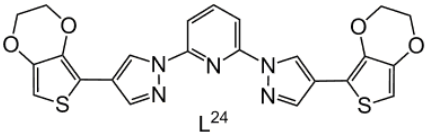
Silica particles coated with a $[Ln(L^{20})]$ podand were further modified with antibodies or binding proteins for the hepatitis B virus. The resultant particles had good chemical stability and were able to detect hepatitis B antigens at sub-μM limits, with improved hit rates compared to a commercial diagnosis method.[105] In another study, $[Ln(L^{20})]$ podands were tethered to polymer beads, which were subsequently labelled with another antibody. The resultant beads were able to detect a cancer antigen with improved sensitivity over a commercial kit.[19] A $[Tb(L^{20})]$ derivative bearing a targeting substituent at a podand side-arm, rather than the pyridine ring, was used as a reporter group in a protein/antibody conjugate sensor for trace pesticides.[106]

Analogous phosphonate (L^{21}) and mixed phosphonate/carboxylate podands (L^{22}) have also recently been reported.[107-109] The $[Ln(L^{21})]$ and $[Ln(L^{22})]$ complexes have comparable solution structures and emission properties to their $[Ln(L^{20})]$ analogues, but have improved chemical stability. For example, $[Eu(L^{21})]$ exhibits $\log K = 20.4$ in aqueous solution.[107] Two groups have patented the use of these phosphonated podands in biological imaging,[110] and in medical diagnostics and phototherapy.[111]

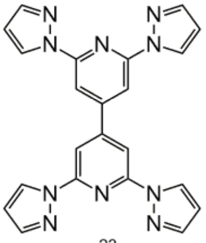
The tridentate 1-bpp framework itself is also an efficient antenna for lanthanide ions, which has been exploited to make fluorescent materials. The back-to-back derivative L^{23} self-assembles into hollow nanotubes in water:thf mixtures. The nanotubes are blue-emissive, and doping their surfaces with $[Eu(tta)_3]$ (Htta = 1-thienyl-3-trifluoromethylpropane-1,3-dione) introduces a second red-emissive centre. The resultant hybrid nanostructures exhibit three colour red/blue/purple emission under a fluorescence microscope.[36] In a comparable approach, a green-emitting benzothiadiazole dye was decorated with blue-emitting 1-bpp fragments using Click chemistry. The product forms 500 nm vesicles in water:thf, which were doped with red-emitting $[Eu(tta)_3]$. The resultant assembly exhibits combined red/blue/green/yellow emission.[34] Finally, a 1-bpp/fluorene copolymer that was assembled through multiple Sonogashira couplings (Scheme 3), spin-coated onto quartz then doped with $[Eu(tta)_3]$ as before, yields an almost perfect white-emitting polymer film.[31]

An $[Eu(L^{20})]$ derivative bearing a branched R substituent forms a fluorescent gel in dodecane.[47] The adduct $[Eu(hfac)_3(L^{24})]$ is emissive in solution,[112] and has been electropolymerised into luminescent conducting thin films.[113] Lastly, polymeric *catena*-$[Pr(1\text{-bpp})Ag_3(SCN)_6(H_2O)_x]_n$ (x = 0 or 1) exhibit a strong praesodynium-based emission in the solid state.[114]

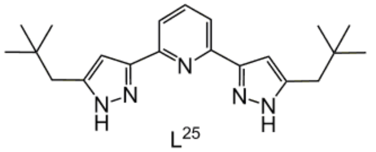
The 3-bpp fragment is also an antenna for europium and terbium emission,[49,54,58,115,116] but has not been exploited to the same extent as the 1-bpp series. However, one recent study introduced L^{25} as a reagent for the fractional separation of lanthanide/actinide mixtures. The ligand showed a strong selectivity for americium in liquid:liquid extraction experiments from nitric acid, with a superior selectivity over *4f* ions compared to other *tris*-heterocycle extractants.[54]



L[24]



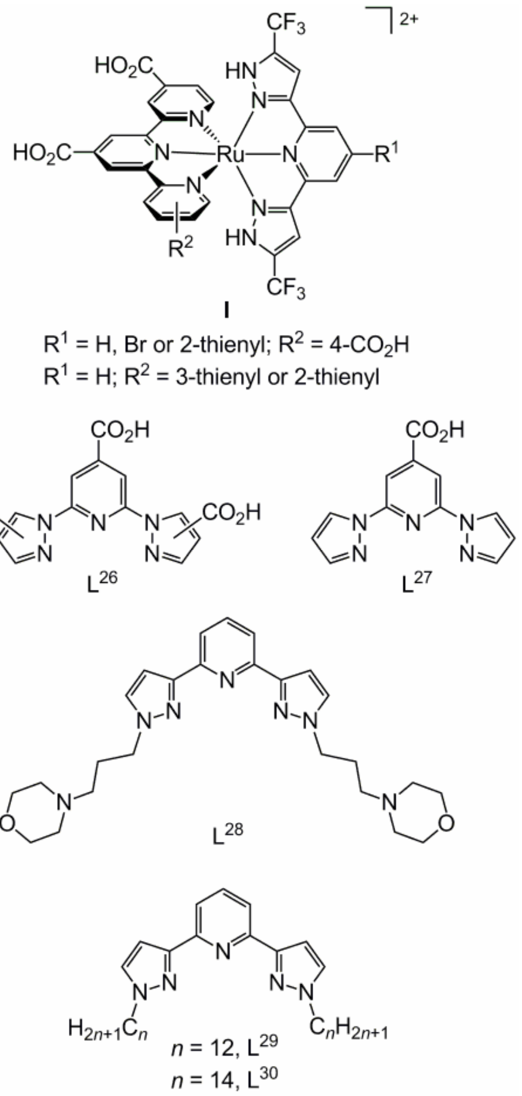
L[23]



L[25]

Emissive *d*-block complexes

While $[Ru(1\text{-bpp})_2]^{2+}$[117] and $[Ru(3\text{-bpp})_2]^{2+}$[118] are not emissive, luminescent centres of type $[Ru(bpp)(terpy)]^{2+}$ and $[RuX(bpp)(bipy)]^{+}$ ($X^{-} = Cl^{-}$ or NCS^{-}) have been reported for the 1-bpp[6,30,119,120] and 3-bpp[53,121] ligand series. Some of these have been investigated as dyes for dye-sensitised solar cells (DSCs[122]). The most success has been achieved with complexes related to **I**, bearing thienyl substituents at either the 3-bpp ligand (R^1) or the terpy derivative (R^2).[53,121] Conjugation of the acceptor ligand to the thienyl group red-shifts the complexes' absorption across the full visible spectrum. Using **I**, DSCs with photoconversion efficiencies of up to 10.7 % have been prepared, comparable to those using $[Ru(NCS)_3(terpy)]$ or $[Ru(NCS)_2(bipy)_2]$ derivatives



but avoiding the problematic thiocyanate ligation.[53]

A theoretical study implied that $[RuCl(bipy)(L^{26})]^+$, with a poly-carboxylated 1-bpp derivative, should show superior DSC performance to an analogue with the carboxy groups on the bipy co-ligand.[123] A ligand of type L^{26} has yet to be synthesised, although $[RuCl(dcbpy)(L^{27})]Cl$ (dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid) is moderately effective in DSCs,[124] and comparable to [RuCl(dcbpy)(1-bpp)]Cl.[119] A theoretical study of the use of $[Co(1\text{-}bpp)_2]^{2+}$ derivatives as redox mediators in DSCs has also been published.[125] Interestingly, L^{27} has also been employed as a dopant in a DSC polymer electrolyte. In this case, however, L^{27} improves the DSC performance by reducing the polymer crystallinity, and by interacting with the TiO_2 electrode surface rather than the soluble ruthenium complex dye.[126,127]

Electropolymerisation of $[Ru(terpy)(L^{24})][PF_6]_2$ yields a luminescent, semiconducting polymer film whose broad visible absorption may make it suitable for photovoltaic applications.[30] A $[ReBr(CO_3)]$ adduct of a related dithienyl-3-bpp derivative, whose 3-bpp fragment is only bidentate, is also strongly emissive.[61]

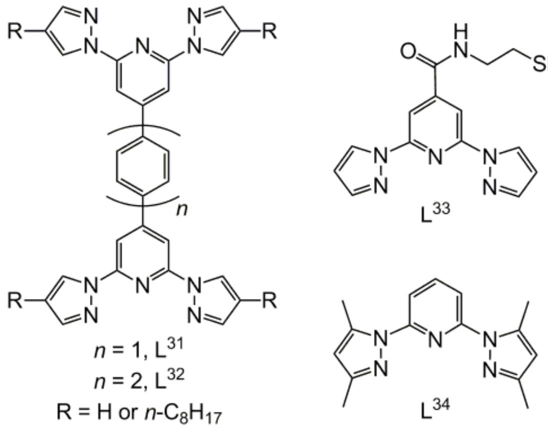
Platinum(II) complexes supported by bpp derivatives can also be fluorescent in solution and/or the solid state, and have found increasing use.[65,71,128-130] Single crystals of [PtCl(L)]Y (L = 3-bpp, 1,3-bpp or L^{16}; Y^- = Cl^- or ClO_4^-) show high charge-carrier mobilities in field-effect transistor devices, with $[PtCl(L^{16})]ClO_4$ showing a performance comparable to pentacene crystals.[71] The conductivity of the crystals correlates with the distance between the adjacent bpp ligands in the molecular stacks in the lattice. In a different application, $[PtCl(L^{28})]CF_3SO_3$ inhibits DNA expression in hepatocarcinoma cells and, unusually, shows a ten-fold selectivity for G-quadruplex DNA over the standard duplex form. NMR data imply that $[PtCl(L^{28})]^+$ binds G-quadruplex DNA by stacking at the 3'-terminal.[65] The complexes $[MCl(L^{29})]^+$ (M^{2+} = Pd^{2+} and Pt^{2+}) have been used as probes for host:guest interactions with molecular tweezers containing face-to-face $[Pt(terpy)]^{2+}$ units,[129] while $[PtX(L^{30})]PF_6$ (X^- = Cl^- or $PhC{\equiv}C^-$) have been assembled into luminescent Langmuir-Blodgett films.[130] Some related complexes bearing steroidal substituents, including $[Pt(C{\equiv}CCH_2OCO_2\{cholesteryl\})(L^{30})]CF_3SO_3$, form supramolecular gels in cyclohexane.[131]

Copper(I) and silver(I) clusters supported by deprotonated $[L^{18}–2H]^{2-}$ are strongly emissive in the solid state. The emissions are metal-centred, and mediated by $d^{10}\ldots d^{10}$ interactions.[62,132] Another emissive silver complex has also been reported, based on a hybrid 3-bpp/*N*-heterocyclic carbene ligand.[64]

Dipyrazolylpyridines in self-assembly

Spin-crossover thin films and nanostructures,[78,79] luminescent assemblies[31,34,36] and soft materials[30,47,113,130] formed from 1-bpp derivatives have been described above. Other 1-bpp moieties have been reported to self-assemble in the absence of a metal ion. Thus, L^{31} and L^{32} (R = H) assemble into nanoscale structures when drop-cast from CH_2Cl_2 solutions, with tape and tubular morphologies respectively. Both assemblies yield the same violet emission exhibited by the crystalline compounds.[35] The corresponding L^{31} derivative with R = *n*-octyl yields a soluble, emissive coordination polymer when treated with $Zn[ClO_4]_2$. The polymer has a molecular weight *ca.* 9600 g mol^{-1}, corresponding to 8-9 $[Zn(\mu\text{-}L^{31})]^{2+}$ repeat units, and was drop-cast into patterns on a silica surface.[33] The thiolated derivative L^{33} forms monolayers when dropcast onto Au(111) in which the 1-bpp skeleton lies flat on the gold surface in a regular 2D array.[133] L^{34} adsorbs onto steel surfaces with a Langmuir isotherm, and is an efficient inhibitor against acid corrosion.[134]

Alternatively, 3-bpp and its derivatives are useful scaffolds for polymetallic complexes, by bridging between metal ions through



deprotonated pyrazolate groups.[135] For example, treatment of L^{18} with silver salts in the presence of base affords clusters of formula $[Ag_6(\mu_3\text{-}\{L^{18}\text{–}H\})_6]X_6$, whose topology varies depending on the anion X^-.[62] Reaction of L^{18} or L^{35} with Cu_2O affords octanuclear $[Cu_8(\mu_4\text{-}\{L\text{–}2H\})_4]$ (L = L^{18} or L^{35}), with four di-copper fragments arranged in a ladder-type array.[132] Both these cluster types are strongly emissive in the solid state. The following have also been prepared: a hexanuclear iron(III) complex $[Fe_6(\mu_3\text{-}\{3\text{-bpp–}2H\})_4(\mu_3\text{-}O)_2(\mu\text{-}OMe)_3(\mu\text{-}OH)Cl_2]$;[136] copper(II) adducts $[M_2(\mu\text{-}\{L^{36}\text{–}2H\})_2]$ and $[M_4(\mu\text{-}\{L^{36}\text{–}2H\})_4]$ (M^{2+} = Ni^{2+}[57] or Cu^{2+}[137,138]); a related dimer $[Cu_2(NO_3)_2(\mu\text{-}\{3\text{-bpp–}H\})_2]$;[139] the sulfate complexes $[M_2(\mu\text{-}\{L\text{–}2H\})_2(\mu\text{-}SO_4)]$ (M^{2+} = Co^{2+} or Zn^{2+}; L = L^{18} or L^{35}) and $[Zn_4(\mu\text{-}\{L^{35}\text{–}2H\})_4(\mu_4\text{-}SO_4)][OH]_2$;[140] and, dinuclear $[Ru_2(\mu\text{-}\{L^{35}\text{–}H\})_2(\mu\text{-}Cl)(P\{C_6H_4CF_3\}_3)_2]Cl$.[141] Other polymetallic complexes where a 1-bpp or 3-bpp derivative acts as a simple capping ligand are also known.[52,101,142-149]

Appending extra donor groups onto the 3-bpp skeleton gives further scope for high-nuclearity complex formation. Thus, the di-phenoxo derivative L^{19} has afforded Ni_3,[150] Mn_4 and Mn_{10}[151] clusters in which deprotonated $[L^{19}\text{–}3H]^{3-}$ or $[L^{19}\text{–}4H]^{4-}$ ligands exhibit a variety of coordination modes. Treatment of the dipyridyl-3-bpp L^{38} with $Co[BF_4]_2$ yields cyclic $[Co^{II}_8(\mu_3\text{-}\{L^{38}\text{–}2H\})_4(OH)_4(MeOH)_{16}][BF_4]_4$; and, the mixed-valent 3x3 grid $[Co^{III}Co^{II}_8(\mu_3\text{-}\{L^{38}\text{–}2H\})_6][BF_4]_7$, containing a central cobalt(III) site surrounded by a square of alternating high-spin and low-spin cobalt(II) ions.[152] A similar complexation using a 1:1 mixture of iron(II) and cobalt(II) reagents led to an alternative 3x3 structure $[Fe^{III}Fe^{II}_4Co^{II}_4(\mu\text{-}L^{38})_6(\mu\text{-}OH)_{12}(OH_2)_6][BF_4]_7$, where iron(II) sites occupy the corners of the grid and the iron(III) ion is at the centre.[153] The two grid motifs differ, in that the metal ions are directly linked by $[L^{38}\text{–}2H]^{2-}$ ligands in the all-cobalt example. In contrast, the L^{38} ligands in the mixed-metal grid are protonated, and the metal ions are bridged by hydroxo groups. An intermediate $[Fe^{III}_2Co^{II}_5(\mu\text{-}O)_6(\mu\text{-}L^{38})_4(H_2O)_6][BF_4]_4$ was also isolated from the mixed-metal complexation, and its conversion to the grid product was monitored by ES mass spectrometry.[153]

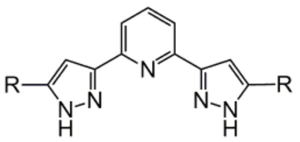
The corresponding copper complex can be isolated in two different oxidation levels, $[Cu^{II}_9(\mu_3\text{-}\{L^{38}\text{–}2H\})_6][BF_4]_6$ and $[Cu^{I}_2Cu^{II}_7(\mu_3\text{-}\{L^{38}\text{–}2H\})_6][PF_6]_4$. The copper(I) sites in the latter compound occupy opposite corners of the 3x3 grid, while the central copper(II) site in both structures has an unusual Jahn-Teller-compressed octahedral configuration.[154] A hydrogen-bonded grid-like assembly $[\{Co(L^{35})_2\}(L^{35})_4][BF_4]_2$ has also been reported, in which the mononuclear complex cation associates with four additional L^{35} ligands through N–H…N interactions.[155]

Copper(I) and silver(I) complexes of 1-bpp, 1-bppyz and 3-bpp exist as dimeric molecules or coordination polymers, in which the ligands adopt a helical conformation.[20,62,156-158] Several bpp derivatives bearing pendant pyridyl groups, including L^{39} and L^{40}, have been used to make extended helicate complexes.[6,63,159-161]

Dipyrazolylpyridines in catalysis and small molecule activation

When ref. 6 was written in 2005, only a handful of catalysis studies involving a bpp derivative had been published. There have been several new investigations since then, particularly involving cross-coupling reactions,[17,69,162] transfer hydrogenation[66,72,141,163-168] and alkene polymerisation.[14,56,139,158,169,170] Individual reports of 1-bpp complexes as oxime dehydrogenation[171] and alkane photooxidation catalysts have also been published.[172] The most notable results from this list are two reports of nickel/1-bpp catalysts for sp^3/sp^3 Negishi couplings,[17,162] and the consistently high catalytic activity shown by complexes of type $[RuCl_2(bpp)(PPh_3)]$ towards transfer hydrogenation.[66,72,163-165] None of these studies used a chiral bpp derivative as co-ligand, although those are easily accessible for the 1-bpp series.[6]

Bubbling O_2 or N_2 through a solution of $[Ru(L^{37}\text{–}2H)(PPh_3)_2(HOMe)]$ rapidly affords $[Ru(L^{37}\text{–}2H)(PPh_3)_2(N_2)]$ or $[Ru(L^{37}\text{–}2H)(PPh_3)_2(O_2)]$, containing end-on bound N_2 and side-on O_2.[55] The iron analogue $[Fe(L^{37})(PMe_3)_2(NCMe)][CF_3SO_3]_2$ catalyses the disproportionation of hydrazine into ammonia and dinitrogen, with almost complete conversion after 18 hrs. [173] The reaction can be partially arrested using phenylhydrazine as substrate, allowing $[Fe(L^{37})(PMe_3)_2(HN{=}NPh)][CF_3SO_3]_2$ to be isolated from the mixture. The ability of L^{37} to act as a proton shuttle during the reaction may be important to the catalytic mechanism.[173] A theoretical study investigated the efficacy of rhodium complexes of L^{34}, among several other tridentate ligands, for the insertion of CO_2 into Rh–C bonds. Neutral chelates like L^{34} were predicted to be less effective for this step than pincer ligands with negatively charged central atoms, however.[174]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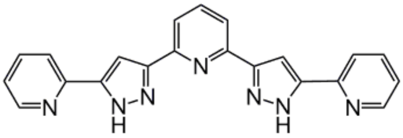
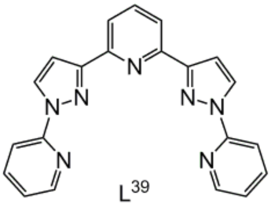
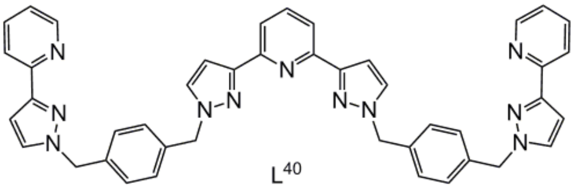
R = *t*Bu, L^{37}


L^{38}


L^{39}


L^{40}

Other complexes

In addition to those already discussed, many other complexes of 1-bpp and 3-bpp derivatives have been characterised since 2005.[6] Most of these are adducts of 1-bpp derivatives with divalent metal salts from groups 8,[14,169,170,175] 9,[169,176] 10,[171,175-178] 11[176,179-185] and 12,[186-192] although individual titanium(IV),[193] iron(III)[15] and rhenium(I)[194] examples are also included. An IR study showed that L^{34} forms adducts in methanol solution with $CuCl_2$, $NiCl_2$ and $CoCl_2$, but not with $MgCl_2$ or $CaCl_2$.[195] The number of miscellaneous complexes of 3-bpp derivatives is much smaller but more varied,[196-199] and includes manganese(II),[196] samarium(III)[198] and gold(III)[199] compounds.

Conclusion

The coordination chemistry of bpp and terpy derivatives is complementary in many ways. The weaker ligand field exerted on a metal ion by bpp makes its complexes more labile in solution than corresponding complexes of terpy derivatives.[6] For this reason, terpy derivatives are still more widely used in metal/organic materials chemistry and self-assembly, because their complexes are more robust.[1-5] However, introducing additional metal-donor groups into the bpp ligand skeleton, which is synthetically facile, overcomes that disadvantage. That has allowed lanthanide complexes of the podands L^{20}-L^{22} to find use in bioanalytical chemistry and fluorescent materials. Lanthanide complexes of bpp derivatives can be more emissive that their terpy counterparts, reflecting an improved match between the *f*-orbital energies and the bpp π-acceptor levels.[6]

The importance of $[Fe(bpp)_2]^{2+}$ derivatives in spin-crossover research also reflects the balance of heterocyclic donor groups in the bpp framework.[6-8] Corresponding $[Fe(terpy)_2]^{2+}$ complexes are nearly always low-spin. Thus, although a wider range of terpy ligands bearing pendant functionality is available than for the bpp series, functionalised $[Fe(bpp)_2]^{2+}$ complexes can afford switchable multifunctional materials and nanoscale devices that are not accessible with terpy ligands. Lastly, the 3-bpp framework in its iron complexes, or elsewhere, has additional possibilities for supramolecular chemistry and self-assembly that are not possessed by 1-bpp, or by terpy.

In conclusion, recent studies have further developed the established uses of bpp derivatives in spin-crossover and lanthanide chemistry. They have also introduced new directions for bpp research, particularly in self-assembly and nanoscience.

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Notes and references

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