The synthesis of 4′-aryl substituted terpyridines by Suzuki cross-coupling reactions: substituent effects on ligand fluorescence

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Several 4′-aryl-substituted 2,2′:6′,2″-terpyridines (tpy-C_6H_4R) have been prepared by palladium-catalysed cross-coupling of 4′-bromoterpyridine or 4′-triflate-terpyridine (triflate = trifluoromethylsulfonyloxy) with aryl boronic acids or esters, $RC_6H_4B(OR')_2$ (R = H, *m*-NH_2, *p*-CHO, -NO_2, -CN, -NMe_2, -NPh_2). The new ligand 4′-mesityl-terpyridine (mesityl = 2,4,6-trimethylphenyl) was prepared in the same way. Similarly, 4′-bromophenylterpyridine (tpy-ϕ-Br) has been cross-coupled with aryl halides to generate several new biaryl-substituted terpyridines (tpy-ϕ-C_6H_4R where R = H, *p*-CN, NMe_2, NPh_2), together with two related compounds with pendent 3- or 4-pyridyl groups (tpy-ϕ-C_6H_4-py). For selected compounds, the alternative coupling strategy of reaction of a terpyridine-4-boronate or terpyridine-4-phenylboronate with the appropriate aryl halide has also been investigated (*e.g.* to prepare tpy-ϕ-$C_6H_4NO_2$), but was generally found to be less satisfactory. All of the compounds are fluorescent in the UV region of the spectrum, the biaryl-substituted compounds being only slightly red-shifted compared to the monoaryl systems, but with the further red-shift that accompanies protonation being more significant for the former. Fluorescence lifetimes in solution are in the range 1–5 ns. The emission spectra of the aminobiphenyl-substituted compounds (tpy-ϕ-$C_6H_4NR''_2$, where R″ = Me or Ph) display a large red-shift with increasing solvent polarity, suggesting the involvement of an intramolecular charge transfer state, as found previously for the two analogues omitting the phenyl ring (tpy-$C_6H_4NR''_2$). In contrast to the latter, however, protonation or binding of a Lewis acidic metal ion to the aminobiphenyl compounds serves to quench almost completely their emission.

Introduction

The complexation chemistry of polypyridyl ligands has been a vibrant area of research for several years. The intense interest in such ligands and their complexes with transition metal ions is due especially to their potential utility in a range of applications, for example as luminescent chemosensors, as photocatalysts, as components of devices for the conversion of light into electrical energy, in new electroluminescent materials, and even in information processing and storage in the germinating area of molecular electronics and photonics.[1a–e] Apart from the ubiquitous bidentate ligands 2,2′-bipyridine and 1,10-phenanthroline, the ligand 2,2′:6′,2″-terpyridine has been employed in a large number of studies, usually binding as a tridentate ligand. The structural simplicity of bis-terpyridyl complexes compared to their tris-bipyridyl analogues has been widely noted[2,3] (*e.g.* the absence of complicating factors such as chirality or facial and meridional isomers), and this simplicity is retained upon introduction of substituents into the 4′-positions of the terpyridines, which are necessarily disposed in a *trans* configuration to one another along a C_2 axis.

Aryl substituents at the 4′-position exert a profound influence on the luminescence of bis-terpyridyl ruthenium(II) complexes, and their effect on the wavelength and lifetime of emission has been investigated in some detail.[4] More recently, the photophysical properties of uncomplexed terpyridines have also begun to attract interest.[4c,5,6] Whilst the majority of those studied to date emit in the near ultra-violet region of the spectrum, terpyridines substituted with electron-donating aminophenyl substituents have been shown to possess low-energy intramolecular charge transfer (ICT) excited states, leading to highly solvent-dependent emission in the visible region.[5,6] We have demonstrated recently that complexation of metal ions (*e.g.* Zn^{2+} or Cd^{2+}) to such terpyridines leads to a stabilisation and red-shift of the ICT state and hence to intriguing potential as sensory systems for these metals.[6] Complexes incorporating electron-rich terpyridines of this type have also been reported recently to offer interesting non-linear optical properties,[7] whilst the incorporation of a biphenyl substituent into the 4′-position has been used to influence π-stacking interactions in the solid state.[8] Clearly then, strategies for the incorporation of aryl substituents into the 4′-position of the terpyridine core are of considerable interest with respect to many of the applications discussed above.

The "traditional" routes to 4′-aryl terpyridines are based on the Tschitschibabin pyridine synthesis, involving the condensation of two equivalents of 2-acetylpyridine with the appropriate aryl aldehyde, with formation of the central pyridine ring being effected by reaction of the diketone intermediate with ammonia (or a source thereof) at elevated temperatures.[9] A number of variations have been reported over the 50 years since 4′-phenyl-terpyridine was first prepared in this way,[10a] some involving isolation of the intermediate enone or diketone,[10b,c] others employing mild or solvent-free conditions for parts of the synthesis,[10c] but almost all relying on a common step in which the central pyridine ring is formed. Such methodology relies on the availability of the appropriate aryl aldehyde, and is not compatible with base-sensitive functionality. Distinctly different synthetic approaches, in which all three pyridine rings are present in the starting materials, include the reaction of 2,2′-bipyridine with 2-pyridyl-lithiums and the Stille coupling of 2,6-dibromopyridines with 2-trialkyltin pyridines.[11] Although this latter procedure has proved popular for 6,6″- and 4′-(non-aryl)-substituted systems,[11] it has not been used to provide access to 4′-arylterpyridines, probably owing to the relative inaccessibility of 4-aryl-2,6-dibromopyridines.[12]

This report describes some investigations into the utility of the Suzuki cross-coupling reaction of aryl boronic acids with

aryl bromides in derivatising terpyridines at the 4′ position.† Recently, we reported on the preparation of terpyridine-4′-phenylboronic acid, and on cross-coupling reactions of metal complexes of this ligand with aryl bromides; complexes incorporating 4′-bromoterpyridine similarly underwent coupling with aryl boronic acids.[14] Here, results on free terpyridines are presented, offering access to a range of new and established ligands, and the relative merits of the two distinct coupling strategies considered (*i.e.* which of the two coupling partners carries the boronic acid). The photophysical properties of the series of substituted ligands so prepared are also described.

Results and discussion

Synthesis of ligands by cross-coupling

A Couplings with 4′-triflate-terpyridine. 4′-Triflate-terpyridine is readily prepared from 2,6-bis(2-pyridyl)-4(1*H*)-pyridone in around 70% yield.[13b] Initial investigations focused on the use of this compound in cross-couplings with aryl boronic acids or esters. Although sometimes more capricious than their bromo or iodo analogues, many aryl triflates have been employed successfully in cross-couplings of the Suzuki type.[15] Conditions frequently used for triflate couplings were adopted, namely tetrahydrofuran as the solvent, $Pd(PPh_3)_4$ as catalyst, and the presence of sodium carbonate to favour formation of the boronate anion (added as a saturated aqueous solution). For example, these conditions have been reported to give good results for a triflate-substituted pyrrole.[16]

Although ligands L^1–L^4 were successfully prepared in this way from 4′-triflate-terpyridine (Scheme 1), the yields of crude product, as estimated from ^{1}H NMR, were, at best, modest, and reaction times for complete consumption of starting material were long (24–72 h). Moreover, the contaminating materials included significant amounts of triphenylphosphine and, apparently, mixtures of tetraarylphosphonium salts, which proved troublesome to separate from the terpyridine products, both by crystallisation and by chromatography. The final isolated yields were, therefore, disappointing, as evident from Table 1. Purification could be achieved more readily in the case of L^2, since acidification led to a water-soluble tricationic compound: impurities were removed by washing an acidic aqueous solution with dichloromethane, and the terpyridine subsequently isolated by basicification and back-extraction into dichloromethane.

Although frequently well-behaved, unsatisfactory behaviour of triflates in cross-couplings is not uncommon. A number of studies on a variety of substrates have reported problems, often attributed to decomposition of the catalyst and irreversible reaction of the liberated triarylphosphine with the triflate substrate, leading to phosphonium salts.[17] In some instances, phosphine-free palladium catalysts, including palladium acetate and derivatives, are able to catalyse cross-coupling reactions efficiently, whilst eliminating the problems of phosphine-derived side-products.[18] However, there was no evidence for the formation of the desired products when such conditions were employed for reactions of 4′-triflate-terpyridine (reaction in acetone in the presence of 0.2 mol% palladium acetate[18]).

Only for the *p*-dimethylamino-substituted ligand, L^6, was a satisfactory yield obtained using triflate-terpyridine (Table 1). The reaction proceeded more rapidly in this case, as monitored by consumption of tpy-OTf on TLC, and the product was amenable to purification using an acidification–wash–basicification sequence. It is likely that the electron-donating group on the boronic acid increases the nucleophilicity of the boron and hence the rate of transmetallation, making it more competitive with the side-reactions discussed above. There was no evidence for aryl–aryl exchange between the palladium centre and the triphenylphosphine ligand to give 4-(dimethylamino)biphenyl, although such competing reactions have sometimes been reported to become significant in the presence of electron-donating substituents in the aryl boronic acid.[15,19]

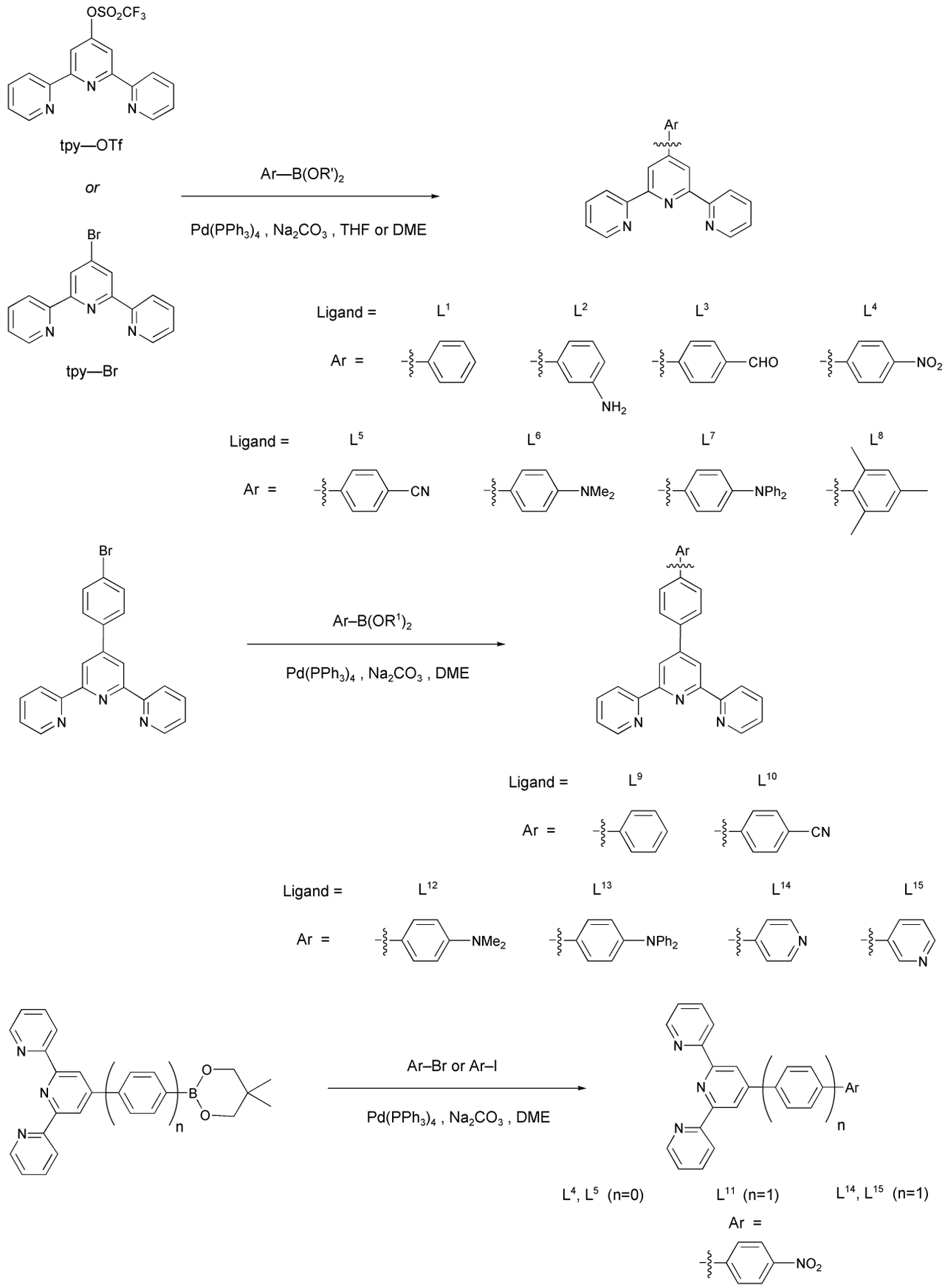
B Couplings with 4′-bromoterpyridine. Given the poor results with 4′-triflate-terpyridine, attention was turned to the use of 4′-bromoterpyridine in its place: bromo-aromatics are usually more reactive and more robust than their triflate analogues. 4′-Bromoterpyridine (tpy-Br) may be prepared directly from 2,6-bis(2-pyridyl)-4(1*H*)-pyridone by bromination with $POBr_3$;[20] in our hands, however, this reaction required large quantities of the brominating agent, long reaction times and rarely gave a yield of more than 50% (significantly lower upon scaling-up). In contrast, we have found that treatment of 4′-triflate-terpyridine with a solution of HBr in acetic acid at 110 °C leads to complete conversion into 4′-bromoterpyridine within 4 h, and this procedure was therefore used preferentially.

As is evident from Table 1, 4′-bromoterpyridine gave greatly superior results in cross-couplings with aryl boronic acids compared to the triflate. Fewer side-products were formed, facilitating purification. In line with several reports that strong bases favour couplings with sterically crowded boronic acids,[21] barium hydroxide was employed in place of sodium carbonate in the preparation of the novel mesityl-substituted ligand L^8, which was obtained in 61% yield after recrystallisation from ethanol. The same strategy was also successful in preparing the 4′-biphenyl-substituted ligand, L^9, and *p*-substituted biaryl analogues, L^{10}–L^{15}, by using 4′-(4-bromophenyl)terpyridine in place of 4′-bromoterpyridine (Scheme 1).

C Couplings with terpyridine-boronic esters. Although access to many aryl boronic acids is straightforward by the "classical" methodology of lithiation of the analogous bromo-aromatic and subsequent reaction with a trialkoxyboron {usually $B(OMe)_3$ or $B(O^iPr)_3$}, this procedure is unsuitable for aryl groups incorporating sensitive functionality (for example, those which would react with BuLi). In contrast, palladium-catalysed coupling of the bromo-aromatic with tetraalkoxydiboron compounds offers valuable entry to such systems, a procedure which has rapidly gained popularity since its inception by Miyaura in 1995 (Scheme 2).[22] The method tends to be less reliable in the presence of strongly electron-withdrawing groups, however, as they often favour competitive homo-coupling of the starting bromo-aromatic to generate biphenyl side-products. This undesirable effect was encountered in this work in the preparation of the *p*-nitrobenzeneboronate ester required in the synthesis of L^4 (Table 1): *p*-nitroiodobenzene consistently gave a 3 : 1 mixture of the desired compound and 4,4′-dinitrobiphenyl. The synthesis of pyridine boronates (for L^{14} and L^{15}) by this method was similarly affected. Moreover, these boronic esters, once prepared, did not undergo coupling as efficiently as those with electron-donating substituents, as is evident from the isolated yields (*e.g.* entries L^4 and L^{14} in Table 1), probably due to a lower stability of the electron-deficient boronic acids with respect to deboronation.[23]

The "reverse" coupling strategy as a route to aryl-substituted terpyridines was therefore investigated, namely use of a terpyridine-4′-boronate (or terpyridine-4′-phenylboronate) as a common synthon for reaction with bromo-aromatics, to avoid reliance on the availability of boronic acids or an efficient pathway to them. We have previously reported the synthesis of 4′-(4-neopentylglycolatoboron)terpyridine (tpy-B_{neo}) and its analogue with an interposed phenyl group, (tpy-ϕ-B_{neo}), using the Miyaura coupling with bis(neopentylglycolato)diboron (B_2neo_2).[14] Subsequent work with different batches of B_2neo_2

† Related Sonogashira couplings have been reported by others for the introduction of alkynyl functionality into the 4′ position,[13a] as have Stille coupling reactions of 4′-triflate-terpyridine; *e.g.* with vinyltributyltin to give 4′-vinylterpyridine,[13b] and with tetramethyltin to provide 4′-methylterpyridine.[13c]

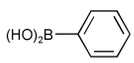
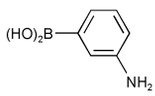
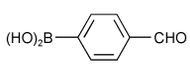
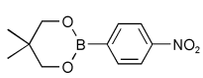
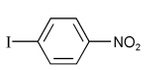
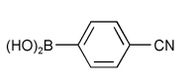
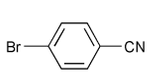
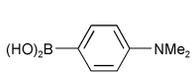
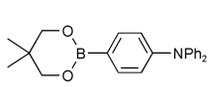
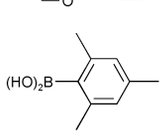
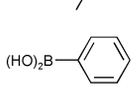
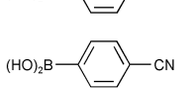
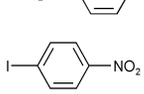
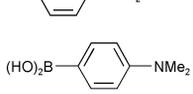
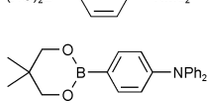
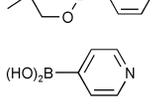
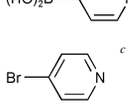
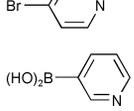
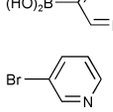


Scheme 1

and of the Pd(dppf)Cl_2 catalyst has revealed that formation of tpy-ϕ-B_{neo} may frequently be accompanied by a small amount of the homo-coupled, "back-to-back" bis-terpyridine (Scheme 2), sometimes up to 10 mol%. Again, as for the bromopyridines, this is probably due to the inductively electron-withdrawing nature of the pyridine ring. In an attempt to suppress this undesirable side-reaction, some alternative conditions were assessed for the preparation of tpy-B_{neo}:

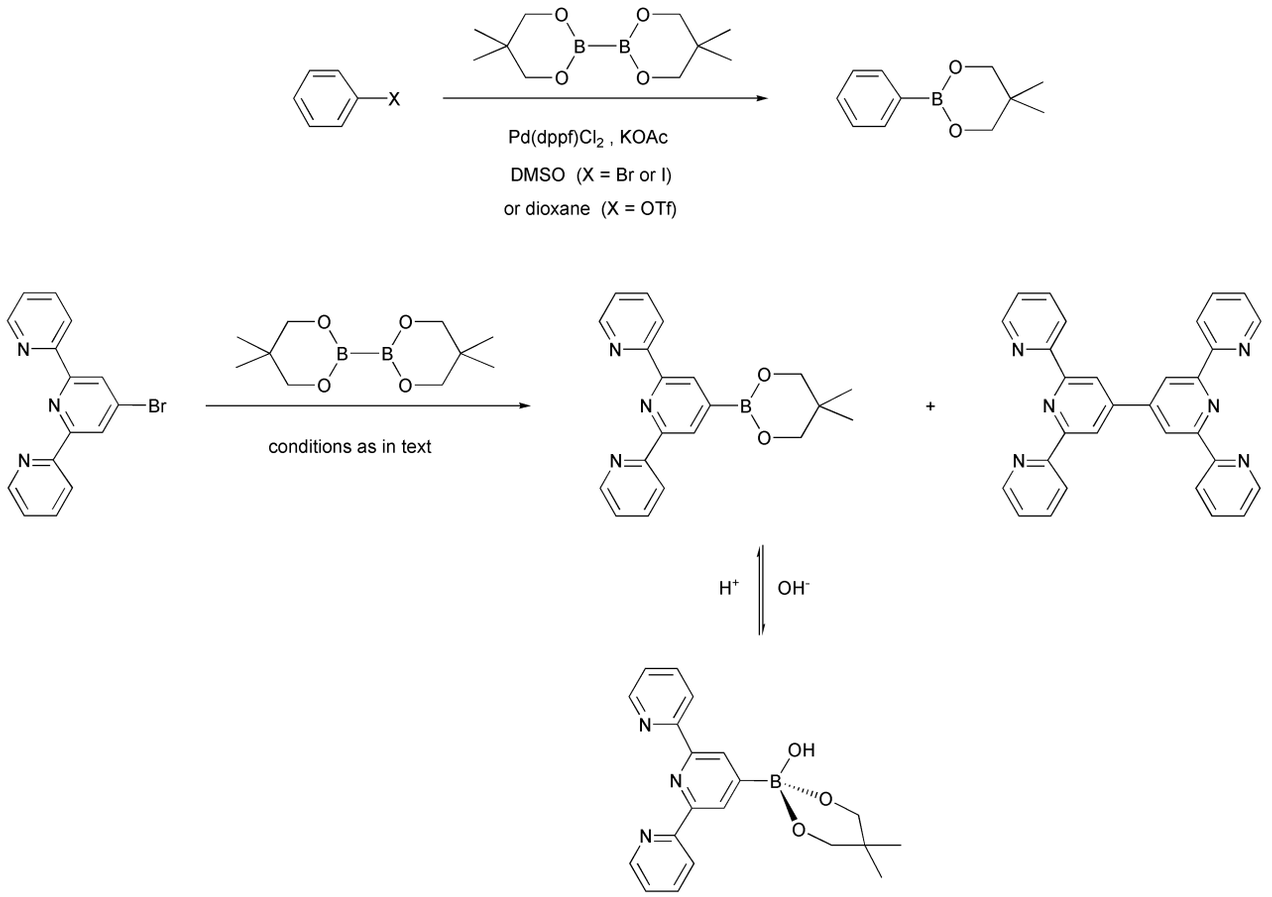
(a) Use of dioxane as the solvent, in place of dimethyl sulfoxide. Dioxane is generally found to be a less active solvent in

Table 1 Routes to terpyridines L^1–L^{15}: coupling partners, solvent and isolated yields[a]

Ligand	Starting terpyridine	Reacting aryl partner	Solvent	Isolated yield (%)
L^1	tpy-OTf		THF	10
	tpy-Br		THF	80
L^2	tpy-OTf		THF	14
L^3	tpy-OTf		THF	13
	tpy-Br		DME	75
L^4	tpy-OTf		THF	9[b]
	tpy-Br		DME	30
	tpy-Bneo		THF	64
L^5	tpy-Br		THF	80
	tpy-Bneo		THF	34
L^6	tpy-OTf		THF	65
L^7	tpy-Br		DME	59
L^8	tpy-Br		DME	61
L^9	tpy-ϕ-Br		DME	60
L^{10}	tpy-ϕ-Br		DME	57
L^{11}	tpy-ϕ-Bneo		DME	28
L^{12}	tpy-ϕ-Br		DME	43
L^{13}	tpy-ϕ-Br		DME	60
L^{14}	tpy-ϕ-Br		DME	36
	tpy-ϕ-Bneo	 [c]	DME	4
L^{15}	tpy-ϕ-Br		DME	67
	tpy-ϕ-Bneo		DME	46

[a] Solvent employed was tetrahydrofuran (for the couplings involving triflates) or dimethoxyethane (for most reactions employing aryl bromides or iodides). The catalyst was $Pd(PPh_3)_4$, and sodium carbonate was used as the base in each case, except for L^8 where barium hydroxide was employed. [b] Traces of PPh_3 (< 5%) remained in the product, despite repeated recrystallisations. [c] The hydrochloride salt was used; immediate conversion into the free pyridine is expected under the basic conditions employed.

cross-couplings, but has been used successfully in the reaction of aryl triflates with bis(pinacolato)diboron.[22b] In the present instance, no reaction was observed at reflux (100 °C), whilst a reaction temperature of 150 °C under pressure led to a mixture of the desired product, the homo-coupled terpyridine and unsubstituted terpyridine, the latter presumably formed by hydro-dehalogenation of the starting material under these forcing conditions.



Scheme 2

(b) Use of $Pd(CH_3CN)_2Cl_2$–tri-*o*-tolylphosphine as catalyst. This, too, led to contamination of the desired product by the homo-coupled terpyridine, and proved to be inferior to $Pd(dppf)Cl_2$ in that only partial conversion of the starting material was achieved, even after a reaction time of 24 h.

(c) Reaction in methanol in the presence of lithium methoxide and $Pd(dppf)Cl_2$. At room temperature, these conditions have been reported to suppress the homo-coupling of aryl halides containing electron-withdrawing substituents, whilst allowing the cross-coupling with the tetraalkoxodiboron to proceed.[24] However, no reaction was observed in the present instance after 24 h. Increasing the temperature to 55 °C (18 h) led to a complex mixture of the starting 4′-bromoterpyridine, the desired product, the homo-coupled terpyridine, methoxyterpyridine, and unsubstituted terpyridine.

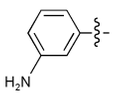
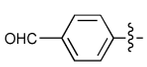
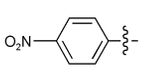
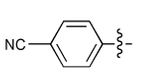
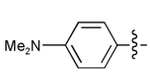
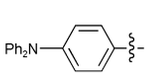
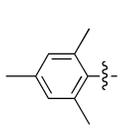
Of the conditions investigated, therefore, none offered any advantage over those originally employed and, indeed, were less successful. In fact, we have found that separation of the contaminating bis-terpyridine can be effected readily by exploiting the water solubility of the boronate anion formed upon addition of aqueous base (Scheme 2), and consequently the original procedure clearly remains the preferred, with high conversions and shorter reaction times (typically 5–6 h).

Subsequent cross-couplings of the terpyridine boronates with aryl halides were successful. In the case of the 4′-nitrophenyl compound (L^4), a higher yield was obtained in this way (Table 1). In general, however, this strategy did not offer improvements in terms of yields or reaction times; for example, the 4′-cyanophenyl and 4′-(*p*-nitrobiphenyl) compounds (L^5 and L^{11}) and the pyridyl-substituted compounds L^{14} and L^{15} (pairs of entries in Table 1). In fact, in the case of L^{14}, coupling of the terpyridine-4′-phenylboronate with 4-bromopyridine gave a very poor isolated yield, whereas the reverse coupling with pyridine-4-boronic acid gave a satisfactory result, despite the electron-withdrawing nature of the pyridine. Based on these results, together with the problems in synthesising the terpyridine boronates and their tendency to pick up iron from the dppf catalyst during their formation, the couplings of the 4′-bromo and 4′-bromophenylterpyridines are clearly the more attractive, in general.

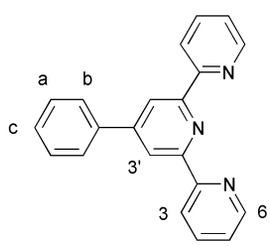
NMR characterisation of the terpyridine products

^{1}H NMR data for the ligands synthesised are collated in Tables 2 and 4 (for aryl- and biaryl-substituted ligands respectively). Data for ligands L^1–L^4, L^6 and L^9 (which have been prepared previously by conventional methodology[9]) were consistent with the literature values, but our data at 500 MHz are included for comparative purposes. Partial assignment of the spectra was possible on the basis of splitting patterns and coupling constants, whilst ^{1}H–^{1}H NOESY spectra proved most informative in providing an unambiguous assignment of the resonances of the pendent ring(s), owing to NOE between $H^{3'}$ and H^b (and not H^a) (numbering system employed is shown in footnotes to Tables 2 and 4). In none of the compounds was NOE observed between H^6 and $H^{3'}$, which is consistent with a *transoid* arrangement of the pyridine rings about the interannular C–C bonds, in line with earlier observations and several solid-state structures, including those of L^6 and L^8 obtained during this work. A NOESY spectrum also allowed the two equally intense singlets in the mesityl-substituted compound L^8, namely those due to $H^{3'}$ and H^a, to be distinguished. Thus, $H^{3'}$ displayed a single cross-peak to the *ortho* methyl groups only (2.03 ppm, 6H), whereas H^a showed coupling to both the *ortho* and *para* methyl groups. The resonances of the lateral pyridine rings (H^2, H^3, H^4, H^5) and of the central pyridine ring ($H^{3'}$) are scarcely affected by changes in the substitution pattern in the 4′-aryl pendent group, with the exception of the 4′-mesityl compound L^8, for which there is a large shift in the $H^{3'}$ resonance of about 0.5 ppm to low frequency. This may be rationalised in terms of

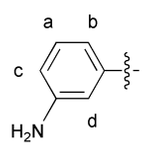
Table 2 ^{1}H NMR data for the phenyl-substituted ligands L^1–L^8 [a]

Ligand	H^3	H^4	H^5	H^6	$H^{3'}$	H^a	H^b	H^c	Other
L^1 	8.68 d 8.0	7.90 t 7.5	7.37 dd 7.5, 5.0	8.74 d 6.5	8.76 s —	7.52 t 7.5	7.92 d 7.0	7.46 t 7.0	—
L^2 	8.67 d 10.0	7.87 td 9.5, 1.5	7.34 dd 9.5, 6.0	8.73 d 6.0	8.70 s —	7.28 [b] 1H, m [b]	7.29 [b] 1H, m [b]	6.77 1H, dt 9.0, 2.5	7.22 1H, br s $H^{d'}$
L^3 	8.69 d 8.1	7.90 td 7.5, 2.0	7.37 ddd 7.5, 5.0, 1.5	8.73 d 4.5	8.77 s —	8.06 [b] d 8.0	8.02 [b] d 8.0	—	10.05 (1H) s (CHO)
L^4 	8.67 d 7.5	7.90 td 7.5, 2.0	7.32 ddd 7.5, 4.5, 1.0	8.73 d 4.5	8.74 s —	8.36 d 8.0	8.04 d 8.0	—	—
L^5 	8.69 d 8.0	7.90 td 7.5, 2.0	7.32 ddd 6.0, 5.0, 1.5	8.73 d 5.0	8.74 s —	7.82 d 10.0	8.00 d 8.5	—	—
L^6 	8.68 d 8.0	7.88 td [c]	7.36 ddd 7.5, 5.0, 1.0	8.75 d 5.0	8.74 s —	6.83 d 9.0	7.90 d [c]	—	3.05 (6H) s (CH_3)
L^7 	8.67 d 7.5	7.87 td 8.0, 2.0	7.35 ddd 7.5, 5.0, 1.0	8.72 d 4.0	8.71 s	7.17 d [c]	7.79 d 8.5	—	7.30 (4H) 7.17 (4H) 7.07 t (*m*-Ph) d (*o*-Ph) t (*p*-Ph) 7.5 [c] 7.5
L^8 	8.64 d 7.5	7.83 td 7.5, 1.5	7.28 dd 7.0, 5.5	8.62 d 4.5	8.26 s —	6.90 s —	—	—	2.29 (3H) 2.03 (6H) s (*p*-CH_3) s (*o*-CH_3) —

[a] All spectra acquired in $CDCl_3$ at 500 MHz and assigned using ^{1}H–^{1}H NOESY. δ in ppm relative to residual $CHCl_3$ at 7.26 ppm; J in Hertz. All signals integrate to two protons except where stated otherwise. [b] Signals too close to allow unambiguous assignment and, for L^2, determination of coupling constant. [c] Overlap of resonances prohibits reliable determination of coupling constants. Key to numbering:



L^1, L^3 - L^8



L^2

the deshielding effect of the π-cloud of the 4′-pendent ring, normally significant, being reduced as the mean torsion angle between the pendent aryl ring and the central pyridine ring increases. That the *ortho* methyl substituents of the pendent mesityl group induce such a twisting is evident from the solid state structure of L^8, which reveals a torsion angle of 67.52(4)°, compared to typical values of about 30° in most biphenyl structures omitting *ortho* substituents.‡ The effect is apparently also transmitted to H^6 and H^5 to some extent, which appear at slightly lower frequency than in the other compounds; indeed, only for this compound does H^6 appear to low frequency of H^3.

The relative shifts of the protons in the pendent aryl group are governed by the aryl substituent. For the unsubstituted phenyl ligand L^1 and all the biaryl systems L^9–L^{15}, the proton *ortho* to the terpyridine (H^b) appears to high frequency of the *meta* proton (H^a), reflecting the more strongly electron-withdrawing nature of the terpyridine unit compared to a phenyl group, with the difference being amplified by electron-donating substituents at the *para* position (L^6 and L^7). In contrast, the situation is reversed for the *p*-nitro substituted compound, indicating that the electron-withdrawing influence of the terpyridine is weaker than that of a nitro group. The substituent and terpyridyl effects are almost balanced in the formyl-substituted compound L^3, where the chemical shifts are approximately coincident. A similar trend is seen in the distal ring of the biaryl-substituted compounds (Table 4), with $H^{b'}$ at higher frequency in all cases, except for the electron-withdrawing 4-nitro and 4-pyridyl systems, L^{11} and L^{14}; the balance between electron withdrawal by the substituent and the 4′-phenylterpyridine fragment is attained in this case in the cyano system (L^{10}).

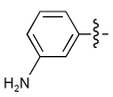
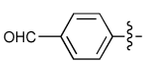
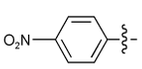
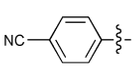
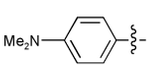
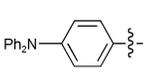
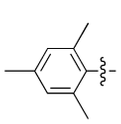
The ^{13}C spectra, assigned with the aid of ^{1}H–^{13}C correlation spectroscopy, revealed a similar striking homology in the resonances of the pyridyl carbons; the most significant deviation was again found in the mesityl system L^8, in which the $C^{3'}$ resonance displayed a modest shift of 4 ppm to high frequency compared to the other compounds.

Absorption and fluorescence properties of the terpyridines

2,2′:6′,2″-Terpyridine itself absorbs strongly below about 320 nm, but is only weakly emissive, with a fluorescence

‡ Full details of the crystal structures of L^8 and L^6, determined by X-ray diffraction, will be reported shortly elsewhere.

Table 3 ^{13}C NMR data for ligands L^1–L^8 [a]

Ligand	C^3	C^4	C^5	C^6	C$^{3'}$	C^a	C^b	C^c [b]	Quaternaries	Other
L^1 	121.4	137.0	123.9	149.0	119.0	128.9	127.4	129.0	156.1, 155.8, 150.4, 138.4	—
L^2 	121.4	136.9	123.7	149.1	118.9	117.7 [c]	129.8 [c]	115.7	156.3, 155.8, 150.5, 146.9, 139.5	113.8 (C$^{d'}$)
L^3 	121.4	137.0	124.0	149.1	119.0	128.0 [c]	130.3 [c]	—	156.2, 155.8, 148.9, 144.4, 136.4	192.0 (CHO)
L^4 	121.4	137.0	124.2	149.2	118.9	124.2	128.3	—	156.3, 155.6, 147.8, 144.9, 148.1	
L^5 	121.3	137.0	124.1	148.3	118.6	132.7	128.0	—	156.3, 155.7, 143.1, 118.7 [d]	112.6 CN
L^6 	121.5	137.2	123.7	150.1	117.7	112.4	128.1	—	156.3, 155.3, 151.1, 148.8, 125.0	40.4 (CH_3)
L^7 	121.4	136.8	123.8	148.7	118.3	129.4	128.0	—	156.3, 155.8, 149.7, 149.2, 147.4, 131.8	124.8, *m*-Ph 123.3, *o*-Ph 123.1, *p*-Ph
L^8 	121.1	136.7	123.6	149.1	121.9	128.0	—	—	156.2, 155.5, 151.6, 137.0, 136.6, 134.9	20.9 (*p*-CH_3) 20.6 (*o*-CH_3)

[a] Spectra recorded in $CDCl_3$ at 125.7 MHz; assigned using ^{1}H–^{13}C COSY, observing ^{1}H at 499.8 MHz and decoupling ^{13}C at 125.7 MHz. δ in ppm relative to $CDCl_3$ at 77.0 ppm. Numbering system employed as in footnote to Table 2. [b] C^c assigned only for L^1 and L^2 (Table 3) and C$^{c'}$ only for L^9 and L^{15} (Table 5), where these are secondary carbon atoms. [c] C^a and C^b (Table 3) and C$^{a'}$ and C$^{b'}$ (Table 5) not assignable unambiguously, due to coincidence or near-coincidence of corresponding protons in the ^{1}H spectrum. [d] *ipso* C–CN not detected. [e] Overlap of ^{1}H resonances of *ortho*-Ph and H$^{a'}$ prohibits unambiguous assignment of these resonances by ^{1}H–^{13}C correlation spectroscopy.

maximum of 338 nm.[4c] As discussed recently by Araki and co-workers,[5] the introduction of aryl substituents into the 4′ position of the terpyridine unit can lead to quite dramatic effects on the fluorescence intensities and, in some cases, the wavelength of emission. In line with their observations, the 4′-aryl-substituted terpyridines prepared here display longer wavelength and more intense emission than those of unsubstituted terpyridine (apart from the nitro-substituted system L^4, which is scarcely emissive). The absorption and emission properties in solution in ethanol are collated in Table 6. Fluorescence lifetimes have been recorded where possible, with values in the range 1–5 ns, quite typical of conjugated aromatic molecules. Comparison of the behaviour of 4′-phenylterpyridine L^1 with the newly prepared 4′-mesityl analogue L^8 provides very strong evidence in support of the need for attainment of an approximately coplanar conformation in the excited state in order to favour fluorescence, as the emission of L^8 is less intense than that of L^1 by a factor of 20.

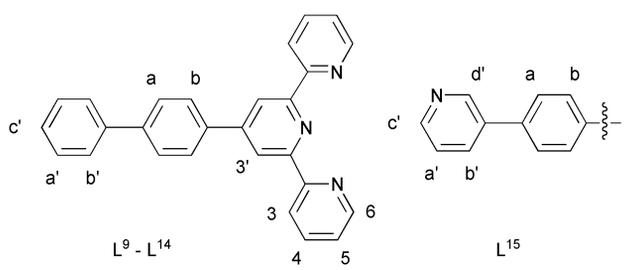
The introduction of a *p*-formyl (L^3) or *m*-amino substituent (L^2) leads to a large reduction in the intensity of the emission relative to 4′-phenylterpyridine, though with no significant effect on the excited state energy, whilst a *p*-cyano substituent (L^5) gives rise to a small red-shift in absorption and emission, and an increase in the emission intensity. Interest in the photophysics of the biphenyl-substituted terpyridine L^9 and its metal complexes has been awakened following the recognition of different possible π-stacking interactions in the solid-state, leading to distinct effects on the excited states.[8] The additional phenyl ring in L^9 compared to L^1 leads to only a small red-shift in the emission, although the intensity is significantly enhanced. Again, a *p*-nitro substituent has a deleterious effect on emission (L^{11}), although to a lesser extent than in L^4. The *p*-cyanophenyl and 4- and 3-pyridyl substituted analogues (L^{10}, L^{14} and L^{15}) reveal a small blue-shift in the emission maximum and somewhat longer fluorescence lifetimes.

The fluorescence properties of the amino-functionalised ligands L^6, L^7, L^{12} and L^{13} are quite different from those of the other ligands. The strong solvent dependence of emission from L^6 was reported recently by Araki,[5] and interpreted in terms of an intramolecular charge transfer (ICT) excited state: polar solvents are able to stabilise such charge-separated excited states, leading to large red shifts in the emission, as observed. These observations were reinforced by the results of a semi-empirical MO calculation, which showed the influence of the amino substituent in raising the energy level of the pendent phenyl to such an extent that the π_{Ph}—π^*_{tpy} excited state occurs at lower energy than the "locally excited" π_{tpy}—π^*_{tpy} state.[5] We have reported that the diphenylamino substituted system L^7 displays comparable behaviour but that, in contrast to L^6, the intensity of emission remains high in ethanol (Table 7).[6] This effect was attributed to the much lower basicity of the diphenylamino pendent, and hence its weaker capacity to act as a hydrogen bond acceptor from ethanol solvent molecules.[6] The newly prepared ligands L^{12} and L^{13} incorporate the same pair of units as L^6 and L^7 (terpyridine unit and an amino-substituted phenyl group) but with an interposed phenyl ring. In fact, the data in Table 7 reveal strikingly that the two new systems behave in a manner which is fully in line with the earlier analogues. The absorbance maxima are again almost independent of solvent, consistent with initial excitation to a locally excited state as normally observed for ICT compounds. In a given solvent, the emission maximum of both L^{12} and L^{13} occurs at rather longer wavelength than for the corresponding analogue L^6 or L^7 respectively in the same solvent, indicative of stabilisation of the excited state (of the order of 1000 cm^{-1}) as a result of the additional phenyl ring. However, a very similar pattern to the effect of increasing polarity emerges. The dimethylamino-substituted compounds experience the larger overall effects (*e.g.* L^{12} shifts from 395 nm in cyclohexane to 567 nm in ethanol, compared to 404 to 545 nm for L^{13}), with the change

Table 4 ^{1}H NMR data for the biphenyl-substituted ligands L^9–L^{15} [a]

Ligand	H^3	H^4	H^5	H^6	H$^{3'}$	H^a	H^b	H$^{a'}$	H$^{b'}$	H$^{c'}$	Other
L^9	8.69 d 7.9	7.89 td 7.6, 1.7	7.37 dd 6.4, 4.5	8.74 d 4.0	8.80 s —	7.75 d 8.3	8.01 d 8.4	7.49 t 7.5	7.68 t 7.5	7.39 t, 1H 7.5	—
L^{10} NC	8.68 d 8.0	7.89 t 7.5	7.37 dd 7.0, 5.0	8.74 d 4.5	8.77 s —	7.72 d 8.5	8.01 d 8.5	7.74 s (4H) —		—	—
L^{11} O_2N	8.69 d 7.9	7.92 td 7.8, 1.8	7.38 ddd 7.4, 4.9, 1.1	8.75 d 4.7	8.79 s —	7.77 d 8.4	8.04 d 8.6	8.33 d 8.8	7.82 d 6.8	—	—
L^{12} Me_2N	8.68 d 7.9	7.89 t 7.4	7.36 dd 6.8, 5.0	8.75 d 4.5	8.79 s —	7.71 d 8.2	7.97 d 8.2	6.84 d 8.5	7.60 d 8.7	—	3.02 (CH_3) s (6H) —
L^{13} Ph_2N	8.69 d 8.0	7.89 td 8.0, 2.0	7.36 ddd 7.5, 5.0, 1.0	8.74 d 4.0	8.79 s —	7.72 d 8.5	7.99 d 8.0	7.17 d 7.5	7.56 d 8.5	—	7.17, 4H, d 7.0[c], *o*-Ph 7.29, 4H, t 8.5, *m*-Ph 7.05, t 7.0, *p*-Ph
L^{14} N	8.70 d 8.0[c]	7.90 td 7.5, 1.5	7.38 dd 7.5, 4.5	8.75 d 4.5	8.79 s —	7.80 d 8.0	8.05 d 8.0	8.71 d 5.5[c]	7.60 d 4.5	—	—
L^{15} N	8.70 d 7.8	7.90 td 7.8, 1.5	7.38 ddd 7.5, 4.8, 1.2	8.75 ddd 4.8, 1.8	8.80 s —	7.75 d 8.7	8.05 d 8.4	7.42 dd (1H) 8.1, 4.5	7.97 dd (1H) 7.8, 2.4, 1.8	8.64 dd, 1H 4.8, 1.5	8.94 (H$^{d'}$) d (1H) 2.4

[a] Spectral details as in footnote *(a)* to Table 2. Key to numbering:

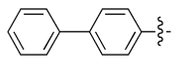
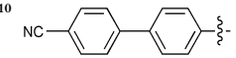
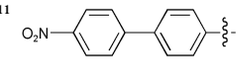
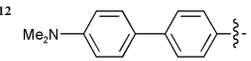
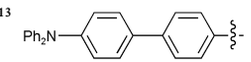
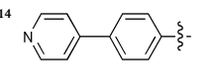
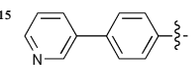


from cyclohexane to THF leading to an especially pronounced effect for the former. Significantly, the intensity of emission of the dimethylamino-substituted compound L^{12}, just like its analogue L^6, is greatly reduced in ethanol compared to the other solvents (factor of about 30 in ϕ_f), whereas both of the diphenylamino compounds retain strong emission in ethanol. This reinforces our view that the weak emission of the former pair may be related to the capacity of the –NMe_2 nitrogen to act as a good hydrogen bond acceptor from ethanol solvent molecules, inhibiting the twisting of the diakylamino group which is thought to accompany formation of the ICT state. The trend in lifetimes of emission is similar for each compound, increasing from cyclohexane through THF to DCM and then decreasing in ethanol.

Effect of protonation on emission. It is well-established that terpyridine itself normally undergoes two successive protonation processes upon acidification in solution, and that the mono- and diprotonated species formed are characterised by red-shifted and more intense emission compared to the free-base.[4c,27] Addition of trifluoroacetic acid (> 2 equiv.) to the 4′-monoaryl-substituted compounds (L^1–L^5) leads to small red-shifts in the emission, with variable effects on intensity (an initial increase at low concentrations of acid was pronounced only for ligands L^2 and L^3, with all compounds displaying a reduction in intensity under highly acidic conditions). This red-shifting effect is more pronounced for the 4′-biaryl compounds L^9, L^{11}, L^{14} and L^{15}, where the maxima are shifted to 410–440 nm with an increase in intensity, leading to strong, blue emission (Fig. 1), and corresponds to the recently reported effect of coordination of Lewis acidic metal ions to L^9.[8]

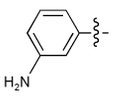
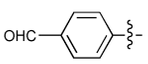
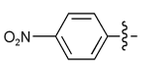
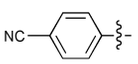
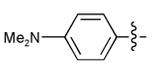
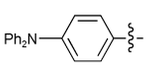
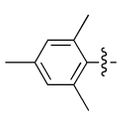
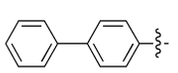
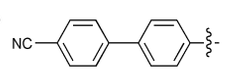
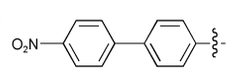
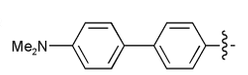
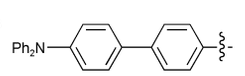
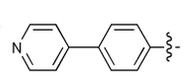
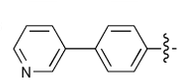
The behaviour of the amino-functionalised systems to protonation is again very different from that of the other compounds. Protonation of L^6 and L^7 leads to the appearance of a new, long wavelength band in the absorption spectrum (430 nm), as reported previously, whilst coordination of zinc leads to a very similar effect.[6] Emission is further red-shifted (by about 100 nm), attributed to stabilisation of the ICT state by the coordinated metal ion, with a moderate decrease in intensity. In contrast, acidification of the newly prepared analogues, L^{12} and L^{13}, leads to a long tail in the absorption spectrum, extending to about 500 nm, rather than a well-defined, new long wavelength band. Binding of zinc ions, on the other hand, does lead to such a band (Fig. 2). For both Zn^{2+} and H^+, the emission intensity is greatly reduced, though again red-shifted, with a scarcely detectable signal centred around 700 nm. Presumably, the additional rotations and vibrations that are possible in these biaryl systems lead to much more efficient non-radiative deactivation of the low-energy ICT state. In terms of potential applications as sensors or in photoactive metal complexes, therefore, the new amino-functionalised ligands incorporating the additional phenyl ring appear to be less attractive than those previously described.[6]

Table 5 ^{13}C NMR data for the biphenyl-substituted ligands L^9–L^{15} [a]

Ligand	C^3	C^4	C^5	C^6	$C^{3'}$	C^a	C^b	$C^{a'}$	$C^{b'}$	$C^{c'b}$	Quaternaries	Other
L^9 	121.4	136.9	123.9	149.2	118.7	127.6	127.7	128.9	127.2	127.6	156.3, 156.0, 149.8, 141.9, 140.5, 137.3	—
L^{10} 	121.4	136.9	123.9	149.1	118.7	127.7	128.0	132.6[c]	127.6[c]	—	156.1, 156.0, 149.2, 144.8, 139.6, 138.7[d]	111.2 (–CN)
L^{11} 	121.4	137.0	123.9	149.2	118.7	127.9	128.1	124.2	127.9	—	156.1, 156.0, 149.1, 147.2, 146.8, 139.2, 139.0	—
L^{12} 	121.3	136.8	123.8	149.1	118.5	126.5	127.6	112.7	128.2	—	156.3, 155.9, 150.2, 149.9, 141.9, 135.7, 127.7	40.5 (–CH_3)
L^{13} 	121.4	136.9	149.8	149.1	118.6	127.0	127.5	124.5[e]	126.7	—	156.3, 155.9, 149.8, 147.5, 141.3, 136.9, 136.7, 134.1	129.3, *m*-Ph 123.8, *o*-Ph[e] 123.0, *p*-Ph
L^{14} 	121.6	137.0	124.0	149.2	118.7	127.5	128.1	121.6	121.4	—	156.1, 150.3, 149.4, 147.6, 139.3, 138.6	—
L^{15} 	121.4	136.9	124.0	149.4	118.6	127.5	128.0	123.6	134.3	149.1	156.1, 156.0, 148.8, 138.5, 138.2, 135.9	148.2 ($C^{d'}$)

[a] Spectral details as in footnote to Table 3 and atom numbering as in footnote to Table 4.

Table 6 Photophysical data for the ligands L^1–L^{15} [a]

Ligand	Absorption λ_{max}/nm ($\log_{10}\varepsilon$)	Emission λ_{max}/nm	I/I_{phtpy} [b]	τ/ns [c]
L^1 	282 (4.57)	339, 351	1.00	1.2
L^2 	280 (4.52) 308(sh) (4.12)	348	0.03	—[d]
L^3 	283 (4.56)	339, 352	0.10	—[d]
L^4 	289 (4.49)	368	< 0.01	—[d]
L^5 	277 (4.62) 320(sh) (3.98)	365	1.59	3.0
L^6 	291 (4.56) 348 (4.48)	531[e]	0.11[e]	2.6[e]
L^7 	290 (4.59) 360 (4.41)	513[e]	3.12[e]	2.5[e]
L^8 	284 (4.74)	339	0.05	—[d]
L^9 	289 (4.80)	374	2.92	1.5
L^{10} 	294(4.93)	346(sh) 359	2.16	1.9
L^{11} 	288 (4.80) 318 (4.61)	367 382(sh)	0.20	0.80
L^{12} 	287 (4.81) 344 (4.28)	567[e]	0.24[e]	—[d]
L^{13} 	284 (4.50) 347 (4.32)	545[e]	1.88[e]	1.5[e]
L^{14} 	287 (4.53)	346(sh) 358	2.40	2.8
L^{15} 	287 (4.59)	346(sh) 358	1.90	2.0

[a] In solution in ethanol at 293 ± 3 K. [b] Integrated emission intensity relative to L^1, upon excitation at 285 nm for isoabsorbant solutions, except for those marked *(e)*, which were excited at 350 nm. Spectra were acquired using excitation and emission band-passes of 2.5 nm in each case, and were corrected for the wavelength dependence of the photomultiplier tube. The quantum yield of L^1 was measured to be 0.08 ± 0.02, using 2-aminopyridine in 0.05 M H_2SO_4(aq) as standard, for which $\phi = 0.60 \pm 0.05$ for excitation at 285 nm.[25] [c] Estimated uncertainty ± 0.2 ns. [d] Emission too weak to allow measurement of the fluorescence lifetime using the available instrumentation. [e] For excitation at 350 nm.

Summary

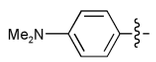
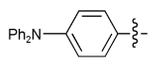
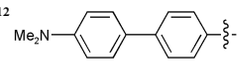
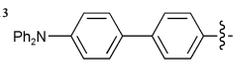
In conclusion, palladium-catalysed, Suzuki-type cross-coupling of aryl boronic acids with 4′-bromoterpyridine (or 4′-bromophenylterpyridine) has been shown to be a viable and versatile method for the preparation of 4′-aryl-substituted terpyridines. Although compounds with simple aryl substituents are more readily prepared using conventional Kröhnke methodology, the cross-coupling procedure allows the use of a common synthon, to provide facile, divergent access to a range of systems under mild conditions. In particular, 4′-biaryl-substituted systems are also accessible in this way, overcoming the relative inaccessibility of the appropriately functionalised biphenyl carboxaldehydes which would be required for a conventional approach. The biaryl compounds have similar fluorescence properties to their mono-aryl analogues, and display a significant red-shift in emission upon protonation. The four amino-functionalised ligands investigated all display evidence of an emissive ICT excited state but the response to acid or metal binding is very different according to the presence or absence of the interposed phenyl ring.

Experimental

Synthetic details

2,6-Bis(2′-pyridyl)-4(1*H*)-pyridone was prepared by base-catalysed condensation of acetone with ethyl picolinate followed by ring closure with ammonium acetate,[28] and subsequently converted to 4′-triflate-terpyridine upon reaction with trifluoromethanesulfonic anhydride in pyridine.[13b] 4-(Diphenylamino)benzeneboronic acid neopentyl ester was prepared as described previously,[6] as were the terpyridine boronates.[14] Tetrakis(triphenylphosphine)palladium(0) was

Table 7 The effect of solvent on the photophysical properties of the amino-functionalised ligands L^6, L^7, L^{12}, L^{13}

		Cyclohexane	THF	DCM	EtOH
L^6 	λ_{max}/nm (abs)[a]	337	346	348	348
	λ_{max}/nm (em)[b]	369, 385(sh)	469	470	531
	τ_f/ns[c]	1.7	5.2	5.2	2.6
	ϕ_f[d]	0.31[e]	0.22	0.27	0.01
L^7 	λ_{max}/nm (abs)[a]	356	360	361	362
	λ_{max}/nm (em)[b]	392, 414(sh)	453	472	513
	τ_f/ns[c]	1.2	3.4	4.0	2.5
	ϕ_f[d]	0.36	0.51	0.58	0.25
L^{12} 	λ_{max}/nm (abs)[a]	335	350	350	348
	λ_{max}/nm (em)[b]	395, 413(sh)	496	504	567
	τ_f/ns[c]	1.2	2.5	2.7	—[f]
	ϕ_f[d]	0.60[e]	0.52	0.64	0.02
L^{13} 	λ_{max}/nm (abs)[a]	354	352	353	347
	λ_{max}/nm (em)[b]	404, 425(sh)	472	494	545
	τ_f/ns[c]	1.2	2.3	2.9	1.5
	ϕ_f[d]	0.60	0.40	0.43	0.15

[a] Position of longest wavelength absorption band. [b] Wavelength of maximum emission upon excitation into the lowest energy absorption band, obtained after correction for the wavelength dependence of the photomultiplier tube. [c] Estimated uncertainty ± 0.2 ns. [d] Fluorescence quantum yields were measured using an excitation wavelength of 350 nm and excitation and emission band-passes set to 2.5 nm in each case; quinine sulfate was used as the standard ($\phi = 0.546$ in 1 M H_2SO_4);[26] estimated uncertainty ± 25%. [e] Measured using an excitation wavelength of 340 nm: a steeply decreasing absorbance profile at 350 nm in cyclohexane prohibits the reliable use of this wavelength. [f] Emission too weak to allow reliable determination of lifetime.

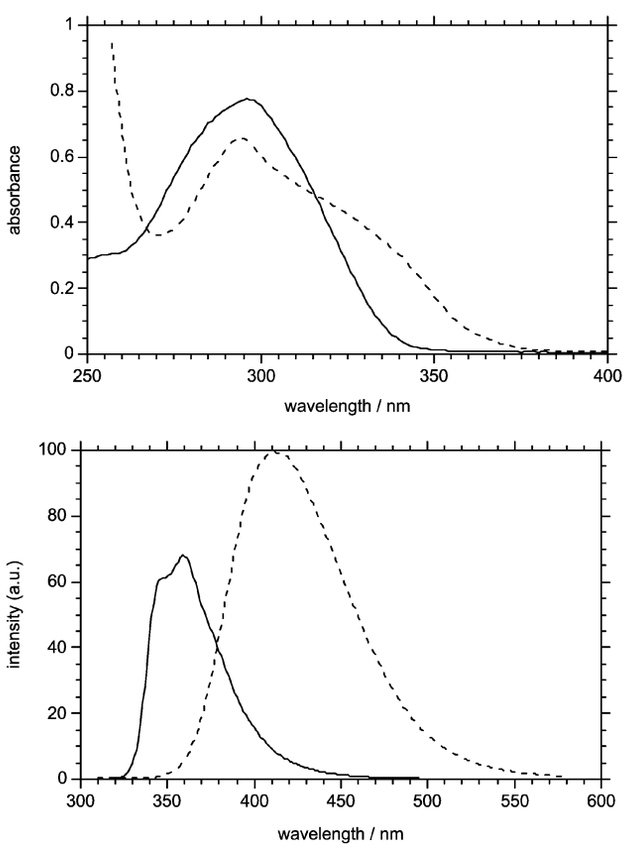


Fig. 1 The effect of protonation on the absorption and emission spectra of the cyanobiphenyl-substituted terpyridine L^{10}. (a) *Upper:* absorbance spectrum of L^{10} (10^{-5} mol dm^{-3} in ethanol) in the absence of acid (solid line) and in the presence of trifluoroacetic acid at 10^{-4} mol dm^{-3} (dashed line). (b) *Lower:* corrected fluorescence emission spectra of L^{10} (10^{-6} mol dm^{-3} in ethanol) in the absence of acid (solid line) and in the presence of acid (dashed line), upon excitation at the isosbestic point (315 nm).

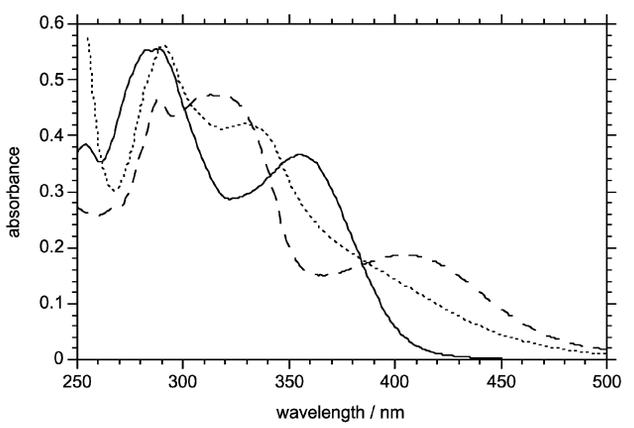


Fig. 2 Absorption spectrum of L^{13} in ethanol (solid line), in the presence of trifluoroacetic acid (10^{-2} mol dm^{-3}, dashed line) and in the presence of zinc triflate (5 equiv., dotted line); [L^{13}] = 1.7 × 10^{-5} mol dm^{-3}.

obtained by hydrazine reduction of a DMSO solution of $PdCl_2$ in the presence of triphenylphosphine.[29] Other reagents were used as supplied from commercial sources. DMSO was dried over 4 Å molecular sieves for at least 24 h before use and dimethoxyethane was dried over sodium wire. Proton and ^{13}C NMR spectra were recorded on a Varian 500 MHz instrument (500 and 125.7 MHz respectively). Electron ionisation (EI) and desorbed chemical ionisation (CI) mass spectra were measured using a Micromass Autospec instrument. High resolution spectra for accurate mass determinations were carried out by electrospray ionisation at the EPSRC National Mass Spectrometry Service Centre, Swansea.

Representative procedure for coupling of 4′-bromoterpyridine or 4′-bromophenylterpyridine with an aryl boronic acid; L^5 as the example. 4′-Bromoterpyridine (583 mg, 1.87 mmol), 4-cyanobenzeneboronic acid (302 mg, 2.06 mmol, 1.1 equiv.) and dimethoxyethane or tetrahydrofuran (12 mL) were placed in an oven-dried Schlenk tube. The solution was degassed *via* three freeze–pump–thaw cycles (final $p < 0.1$ mm Hg), and then placed under nitrogen. Sodium carbonate (590 mg, 5.57 mmol, 3.0 equiv.) was dissolved in the minimum volume of water in a separate small Schlenk and degassed similarly. The catalyst, $Pd(PPh_3)_4$ (90 mg, 0.08 mmol, 0.043 equiv.) was added to the first Schlenk, followed immediately by the sodium carbonate solution, transferred using a cannula. After stirring at room temperature for 1 h, the temperature was increased to 85 °C for

Table 8 Mass spectral data for terpyridines synthesised[a] and elemental analyses for new compounds

L^1 309 (M^+), 231 ($M^+ - py$), 78 (Ph^+). L^2 324 (M^+), 246 ($M^+ - py$); HRMS (EI): 324.1374 (M^+); calc. for $C_{21}H_{16}N_4$, M: 324.1375. L^3 337 (M^+). L^4 354 (M^+), 324 ($M^+ - NO$), 308 ($M^+ - NO_2$). L^5 334 (M^+), 256 ($M^+ - py$). L^6 352 (M^+), 308 ($M^+ - NMe_2$); HRMS (EI): 352.1686 (M^+); calc. for $C_{23}H_{20}N_4$, M: 324.1683; found C, 76.71, H, 5.58, N, 16.32; calc. for $C_{23}H_{20}N_4 \cdot 0.5H_2O$: C, 76.43, H, 5.86, N, 15.50%. L^7 (using CI) 477 ($M + H^+$). L^8 351 (M^+), 350 ($M^+ - H$), 335 ($M^+ - CH_3$), 273 ($M^+ - py$); HRMS: 352.1812 ($M + H^+$); calc. for $C_{24}H_{21}N_3$, $M + H^+$: 352.1813; found C, 78.95, H, 5.90, N, 11.74; calc. for $C_{24}H_{21}N_3 \cdot H_2O$: C, 78.00, H, 6.27, N, 11.37%. L^9 385 (M^+), 307 ($M^+ - py$). L^{10} 410 (M^+), 332 ($M^+ - py$); HRMS: 411.1609 ($M + H^+$); calc. for $C_{28}H_{18}N_4$, $M + H^+$: 411.1609; found C, 80.24, H, 4.35, N, 13.38; calc. for $C_{28}H_{18}N_4 \cdot 0.5H_2O$: C, 80.17, H, 4.57, N, 13.36%. L^{11} 430 (M^+), 400 ($M^+ - NO$), 384 ($M^+ - NO_2$), 352 ($M^+ - py$), 322 ($M^+ - NO - py$); HRMS: 431.1501 ($M + H^+$); calc. for $C_{27}H_{18}N_4O_2$, $M + H^+$: 431.1508; found C, 74.46, H, 4.09, N, 12.65; calc. for $C_{27}H_{18}N_4O_2$: C, 75.34, H, 4.21, N, 13.02%. L^{12} 428 (M^+), 308 ($M^+ - C_6H_4NMe_2$); HRMS: 429.2079 ($M + H^+$); calc. for $C_{29}H_{24}N_4$, $M + H^+$: 429.2079; found C, 75.01, H, 5.43, N, 11.63; calc. for $C_{29}H_{24}N_4 \cdot 2H_2O$: C, 74.98, H, 6.08, N, 12.05%. L^{13} (using CI) 553 ($M + H^+$). L^{14} 386 (M^+), 308 ($M^+ - py$); HRMS: 387.1610 ($M + H^+$); calc. for $C_{26}H_{18}N_4$, $M + H^+$: 387.1609; found C, 71.88, H, 5.18, N, 12.03; calc. for $C_{26}H_{18}N_4 \cdot 3H_2O$: C, 70.89, H, 5.49, N, 12.72%. L^{15} 386 (M^+), 308 ($M^+ - py$); HRMS: 387.1609 ($M + H^+$); calc. for $C_{26}H_{18}N_4$, $M + H^+$: 387.1609.

[a] Low resolution mass spectral data are provided for all compounds and were obtained by electron ionisation, except where stated otherwise. Accurate mass data are provided for those compounds which have not been reported previously, and were obtained by electrospray ionisation, except where marked EI, indicating electron ionisation. Elemental analyses are given for new compounds; small deviations from calculated values are consistent with the presence of retained water molecules, confirmed by the ^1H NMR spectra in anhydrous $CDCl_3$.

24 h. The progress of the reaction could be monitored readily by thin layer chromatography on alumina, eluant 70% hexane–30% ethyl acetate, allowing consumption of the 4′-bromoterpyridine ($R_f = 0.6$) and formation of product ($R_f = 0.2$) to be followed. (Gas chromatography was also suitable, except for the terpyridines carrying amino functionality). After complete consumption of starting material, the solvent was removed under reduced pressure, and the crude residue dissolved in a mixture of dichloromethane and water (25 mL of each). The organic layer was separated, washed with dilute aqueous sodium hydroxide (0.1 M, 3 × 30 mL) and dried over anhydrous potassium carbonate. Removal of solvent led to a green-brown residue which, after recrystallisation from ethanol, led to the required product as a colourless solid (497 mg, 80%). ^1H and ^{13}C NMR data are given in Tables 2–5.

The 'reverse' coupling procedure, involving the reaction of the terpyridine-4-boronate ester, or terpyridine-4-phenylboronate ester, with an aryl halide, was carried out in the same way, using a 10% excess of the boronate. Those reactions which employed 4′-triflate-terpyridine in place of 4′-bromoterpyridine were also performed similarly, but using tetrahydrofuran as the solvent in place of dimethoxyethane.

Characterisation data for the terpyridines are given in Tables 2–5 (nuclear magnetic resonance) and Table 8 (mass spectra and elemental analyses).

Absorbance and emission spectra and lifetimes

UV–visible absorbance spectra were recorded using a Bio-Tek Instruments Uvikon-XS spectrometer using quartz cuvettes of 1 cm pathlength. Steady-state emission spectra were recorded in 1 cm pathlength cuvettes, using an Instruments S.A. Fluromax equipped with a Hamamatsu R928 photomultipler tube; spectra were corrected for the wavelength dependence of the detector. Fluorescence lifetimes were measured using an Instruments S.A. Fluorolog τ-3 instrument, by global fitting of the demodulation and phase shift of the emission, following excitation with sinusoidally-modulated light over the frequency range 10–250 MHz. A suspension of Ludox® in water was used as the standard, which acts as a scattering sample of τ 0.0 ns.

Acknowledgements

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References

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