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New approaches to sugar-functionalised 2,2′:6′,2″-terpyridines based upon tetrafluorophenoxy spacers; crystal and molecular structures of 4′-(tetrafluoro-4-hydroxyphenyl)-2,2′:6′,2″-terpyridine and 4′-(4-methoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine

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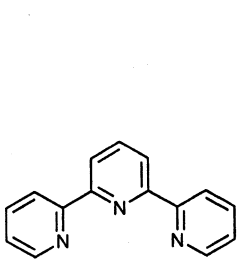
Abstract

The new ligand 4′-pentafluorophenyl-2,2′:6′,2″-terpyridine (**2**) has been prepared with a view to utilising the electrophilic reactivity at the 4-position of the substituent to provide access to sugar-functionalised compounds. Although **2** reacts cleanly with simple alcohols, attempts to incorporate spacers or to attach sugars were unsuccessful. However, dealkylation of the 4′-(4-alkoxytetrafluorophenyl)-2,2′:6′,2″-terpyridines gave the corresponding phenol in good yield. Solid state structures of 4′-(tetrafluoro-4-hydroxyphenyl)-2,2′:6′,2″-terpyridine (**5**) and 4′-(4-ethoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine (**4**) are reported; the former compound has an extremely unusual *cis, trans* configuration of the pyridine rings as a result of intermolecular hydrogen bonding involving the phenol. Iron(II) complexes of **2** and **4** have been prepared; the compounds behave as typical tpy ligands and the fluorinated phenyl substituents are strongly electron-withdrawing. The reaction of the phenol **5** with electrophiles allows access to new 4′-(4-alkoxytetrafluorophenyl)-2,2′:6′,2″-terpyridines and by using 2-bromoethyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside as electrophile, the glucose-functionalised ligand **9** and the iron(II) complex $[Fe(\mathbf{9})_2][PF_6]_2$ were prepared.

Keywords: Ironglucose; 2,2′:6′,2″-terpyridine; sugar; X-ray

1. Introduction

Metal-directed self-assembly of functionalised ligands is a well-established methodology that is being applied to the preparation of a wide variety of topologically and topographically novel species [1–3]. In the first generation of such systems, the primary role of any functionality within the ligands was to control the coordination behaviour and spatial or electronic characteristics. Second generation supramolecular systems are those in which the self-assembly algorithms are better understood and have been designed with the aim of building molecular level devices [4]. In such systems, the role of the functionality is to introduce some additional and desirable property into the self-assembled system.



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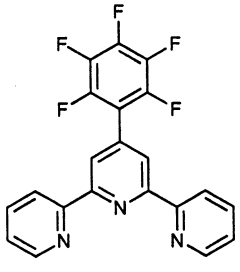

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We have adopted the 2,2′:6′,2″-terpyridine (tpy, **1**) metal-binding motif as an assembly principle for the synthesis of numerous novel metallosupramolecular systems and have recently developed approaches to a range of tpy-functionalised biomolecules which may be

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subsequently aggregated through interactions with metal centres [5]. One aim of this study is the development of metal-ion based delivery systems for biomolecules. In the course of this work we developed a series of strategies for the attachment of tpy domains to target motifs through various linker groups. In particular, we have prepared a series of ligands in which a glucose or galactose residue is attached either directly or through an oxyethyl spacer to a tpy metal-binding domain [6]. In this paper, we describe approaches to new generations of sugar-functionalised tpy ligands with an aromatic spacer. Specifically, we report the synthesis and preliminary studies of the coordination behaviour of 4′-pentafluorophenyl-2,2′:6′,2″-terpyridine (**2**), a ligand that is activated towards attack by nucleophiles at the 4-position of the pentafluorophenyl substituent and attempts to utilise this enhanced reactivity in the attachment of sugars to the tpy metal-binding domain.

2. Experimental

2.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC300, AV300, Av400 or DRX500 spectrometers; ^{19}F NMR are referenced to external $CFCl_3$; electrospray (ESMS) and electron impact (EIMS) mass spectra were recorded on Kratos Profile, VG Prospect or Micromass LCT mass spectrometers. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer with a Golden Gate ATR sampler; electronic spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 system using platinum bead working and auxiliary electrodes with an Ag/AgCl electrode as reference. The experiments were conducted using purified acetonitrile as solvent and 0.1 M $[^{n}Bu_4N][BF_4]$ as supporting electrolyte; ferrocene was added at the end of each experiment as an internal reference. HPLC separations were made on a Luna 5 μ C18 column (dimensions 250×4.6 mm^2) with a mobile phase 1:4 H_2O–MeOH on a Dionex system using a UV detector at 225 nm. The compounds 6-tosyloxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose [7] and 1-(2-bromoethoxy)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside [8] were prepared by the literature methods.

2.2. 4′-Pentafluorophenyl-2,2′:6′,2″-terpyridine (2)

2-Acetylpyridine (2.2 cm^3, 20 mmol) was added to a solution of potassium *t*-butoxide (3.36 g, 30 mmol) in freshly distilled dry THF (160 cm^3) and the resultant creamy yellow suspension was treated with pentafluorobenzaldehyde (2.0 g, 10 mmol) and the mixture stirred overnight at room temperature under N_2. After this period, a solution of dry ammonium acetate (15.8 g) in 2:1 ethanol–acetic acid (190 cm^3) was added and the clear brown mixture so obtained heated to reflux for 5 h. The resulting reaction mixture was cooled to room temperature and treated with ice (126 g) and water (470 cm^3) to give a brown precipitate. The precipitate was collected by filtration and recrystallised from dichloromethane–acetonitrile to give 4′-pentafluorophenyl-2,2′:6′,2″-terpyridine (**2**) as an off-white solid (1.53 g, 38%). ^{1}H NMR ($CDCl_3$): δ 8.70 (d, 2H, H^6), 8.66 (d, 2H, H^3), 8.55 (s, 2H, $H^{3'}$), 7.90 (td, 2H, H^4), 7.37 (td, 2H, H^5). IR (KBr): ν 1582 s, 1555 m, 1520 s, 1493 m, 1393 s, 1265 w, 1080 s, 988 s, 795 s, 779 s, 660 s cm^{-1}. Mass spectrum (high resolution ESMS): *m*/*z* 422.0681 ($\{M+Na\}^+$ Calc. 422.0693).

2.3. 4′-(4-Methoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine (3)

4′-Pentafluorophenyl-2,2′:6′,2″-terpyridine (1.19 g, 2.97 mmol) was heated to reflux in methanol (150 cm^3) containing aqueous sodium hydroxide (40 cm^3, 2 M) for 3 h to give a cream suspension. The solvent was removed in vacuo to give an off-white powder that was recrystallised from dichloromethane-ether to give colourless needles of 4′-(4-methoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine (**3**) (0.79 g, 65%). Additional **3** could be obtained upon concentrating the aqueous ethanol solution after filtration of the solid product. ^{1}H NMR ($CDCl_3$): δ 8.70 (d, 2H, H^6), 8.66 (d, 2H, H^3), 8.55 (s, 2H, $H^{3'}$), 7.90 (td, 2H, H^4), 7.37 (td, 2H, H^5), 4.15 (t, 3H, OCH_3); ^{13}C NMR ($CDCl_3$): δ 155.9 (C^2), 155.6 ($C^{2'}$), 149.2 (C^6), 144.0 (d, C^o), 141.0 (d, C^m), 137.6 (C^p), 136.8 (C^4), 124.0 (C^5), 122.0 ($C^{3'}$), 121.2 (C^3), 62.1 (CH_3); ^{19}F NMR ($CDCl_3$): δ 157.6, 143.6. IR (KBr): ν 1651 w, 1543 m, 1489 s, 1396 s, 1273 w, 1088 s, 980 s, 895 m, 787 s, 741 s, 656 s cm^{-1}. Mass spectrum (high resolution ESMS): *m*/*z* 434.0896 ($\{M+Na\}^+$ Calc. 434.0892).

2.4. 4′-(4-Ethoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine (4)

4′-Pentafluorophenyl-2,2′:6′,2″-terpyridine (1.19 g, 2.97 mmol) was heated to reflux in ethanol (150 cm^3) containing aqueous sodium hydroxide (40 cm^3, 2 M) for 3 h to give a cream suspension. The solution was concentrated in vacuo to give two batches of cream needles of 4′-(4-ethoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine (**4**) (0.92 g, 73%). ^{1}H NMR ($CDCl_3$): δ 8.70 (d, 2H, H^6), 8.66 (d, 2H, H^3), 8.56 (s, 2H, $H^{3'}$), 7.89 (td, 2H, H^4), 7.36 (td, 2H, H^5), 4.39 (2H, q, CH_2), 1.47 (3H, t, CH_3). ^{13}C NMR ($CDCl_3$): δ 155.9 (C^2), 155.6 ($C^{2'}$), 149.2 (C^6), 144.5 (d, C^o), 141.5 (d, C^m), 137.5 (C^p), 136.9 (C^4), 124.0 (C^5), 122.0 ($C^{3'}$), 121.2 (C^3), 71.0 (CH_2), 15.4 (CH_3); ^{19}F NMR ($CDCl_3$): δ 156.8, 143.7.

IR (KBr): *v* 1651 s, 1582 m, 1543 m, 1489 w, 1447 m, 1389 m, 1265 w, 1184 w, 1084 m, 949 s, 795 s cm^{-1}. Mass spectrum (high resolution ESMS): *m/z* 426.12fw1 ($\{M\}^+$ Calc. 426.1230).

2.5. 4′-(Tetrafluoro-4-hydroxyphenyl-2,2′:6′,2″-terpyridine (5)

A mixture of pyridine (8.0 cm^3) and concentrated hydrochloric acid (9.0 cm^3) was heated to 210 °C for 3 h after which period no further water distilled out of the reaction mixture. The resultant pyridinium chloride was cooled to 130 °C and 4′-(4-ethoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine (0.100 g, 0.235 mmol) added and the mixture heated to 210 °C under N_2 for 3 h. Finally, the reaction mixture was cooled to 130 °C and treated with water to precipitate 4′-(tetrafluoro-4-hydroxyphenyl)-2,2′:6′,2″-terpyridine (**5**) as a pale brown solid (0.030 g, 31%). ^{1}H NMR (CD_3SOCD_3): δ 8.70 (br, 2H, H^6), 8.62 (d, 2H, H^3), 8.48 (s, 2H, $H^{3'}$), 8.01 (td, 2H, H^4), 7.51 (td, 2H, H^5). ^{19}F NMR ($CDCl_3$): −161.3 (F^m $^3J_{FF}$ 16.95 Hz), −146.6 (F^o) ^{13}C NMR ($CDCl_3$): δ 155.5 (C^2), 154.7 ($C^{2'}$), 149.6 (C^6), 144.3 (d, $^1J_{CF}$ 241.5 Hz, C^o), 139.8 (C^p), 139.0 (d, $^1J_{CF}$ 245.5, C^m), 138.5 ($C^{4'}$), 137.8 (C^4), 124.9 (C^5), 122.4 (C^{ipso}), 121.5 ($C^{3'}$), 121.1 (C^3). IR (KBr): *v* 1651 m, 1589 m, 1551 m, 1497 s, 1389 s, 1273 m, 1088 s, 972 m, 887 m, 787 s, 656 s cm^{-1}. Mass spectrum (FAB): *m/z* 398 $\{M+H\}^+$, 420 $\{M+Na\}^+$; exact mass: *m/z* 398.0906 (398.0917).

2.6. 4′-(Tetrafluoro-4-(2-hydroxyethoxy)phenyl)-2,2′:6′,2″-terpyridine (6)

A mixture of Cs_2CO_3 (2.24 g) and **5** (0.455 g, 1.15 mmol) was stirred in DMF (15 cm^3) for 1 h at 80 °C after which 2-chloroethanol (0.232 cm^3) was added and the heating continued overnight. A second portion of 2-chloroethanol (0.232 cm^3) was added and the reaction continued for a further 5 h, after which period solvent was removed in vacuo to give a brown oil containing solid caesium salts. This residue was treated with water (10 cm^3) and the resultant solution extracted with $CHCl_3$ (3×20 cm^3). The chloroform solution was dried over $MgSO_4$ and the solvent removed to give **6** as a colourless solid (82%). ^{1}H NMR ($CDCl_3$): δ 8.74 (d, 2H, H^6), 8.68 (d, 2H, H^3), 8.56 (s, 2H, $H^{3'}$), 8.07 (td, 2H, H^4), 7.53 (td, 2H, H^5), 4.36 (t, 2H, $HOCH_2CH_2O$), 3.76 (dt, 2H, $HOCH_2CH_2O$). Mass spectrum (FAB): *m/z* 464 $\{M+Na\}^+$

2.7. Attempted preparation of galactose-functionalised ligand 7

A mixture of NaH (60% dispersion in mineral oil, 0.018 g, 0.47 mmol) and **5** (0.164 g, 0.41 mmol) was refluxed in freshly distilled THF (10 cm^3) for 1 h after which 6-tosyloxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (0.171 g, 0.42 mmol) was added and the heating continued for 4 h. After this period, no new tpy species were detected by TLC analysis and the THF was removed in vacuo and DMF (5 cm^3) added. The mixture was heated to 80 °C overnight, but TLC analysis indicated only negligible amounts of new tpy species. A similar reaction at 130 °C was also unsuccessful and unreacted 6-tosyloxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose was recovered from the reaction mixture.

2.8. Preparation of $[Fe(2)_2][PF_6]_2$

A solution of **2** (0.020 g, 5×10^{-2} mmol) in CH_2Cl_2 (3 cm^3) and EtOH (3 cm^3) was added to a solution of $FeCl_2.4H_2O$ (0.005 g, 2.5×10^{-2} mmol) in ethanol (3 cm^3) to give a purple solution that was stirred for 1 h at room temperature. After this period, a solution of ammonium hexafluorophosphate in ethanol was added to precipitate a mixture of complexes containing **2** and **4**. Purification by chromatography over silica using MeCN–H_2O-saturated aqueous KNO_3 solution 7:0.5:1 as the mobile phase gave the pure complex $[Fe(\mathbf{2})_2][PF_6]_2$ as a purple solid (0.007 g, 24%). ^{1}H NMR (CD_3CN): δ 9.05 (s, 4H, $H^{3'}$), 8.49 (d, 4H, H^3), 7.91 (td, 4H, H^4), 7.14 (m, 8H, $H^{5,6}$). ^{19}F NMR (CD_3CN): δ −71.6 (d, J_{PF} 706 Hz, PF_6), −141.4 (d, 4F, $J = 14.4$ Hz, F^o), −151.4 (t, 2F, $J = 20.0$ Hz, F^p), −161.5 (d, 4F, $J = 20$, 14 Hz, F^m). Mass spectrum (ESMS): *m/z* 427 $\{M-2PF_6\}]^{2+}$, 873 $\{M-2PF_6+F\}^+$, 999 $\{M-PF_6\}^+$ and 1167 $\{M+Na\}^+$. UV–Vis (MeCN): λ (nm) (ε, $dm^3\ mol^{-1}\ cm^{-1}$)) 277 (83 000), 283 (96 000), 323 (61 000), 565 (31 000).

2.9. Preparation of $[Fe(4)_2][PF_6]_2$

A solution of **4** (0.030 g, 7×10^{-2} mmol) and $FeCl_2.4H_2O$ (0.007 g, 3.5×10^{-2} mmol) in ethanol (5 cm^3) was stirred for 1 h at room temperature, after which a solution of ammonium hexafluorophosphate in ethanol was added to precipitate $[Fe(\mathbf{4})_2][PF_6]_2$. Purification over silica using MeCN–H_2O-saturated aqueous KNO_3 solution 7:0.5:1 as the mobile phase gave the pure complex as a purple solid (0.027 g, 64%). ^{1}H NMR (CD_3CN): δ 9.05 (s, 4H, $H^{3'}$), 8.50 (d, 4H, H^3), 7.91 (t, 4H, H^4), 7.18 (d, 4H, H^6), 7.12 (t, 4H, H^5), 4.57 (q, 4H, CH_2), 1.52 (t, 6H, CH_3). ^{19}F NMR (CD_3CN): δ −71.7 (d, J_{PF} 708 Hz, PF_6), −143.6 (d, 4F, $J = 12.7$ Hz, F^o), −156.7 (d, 4F, F^m). Mass spectrum (ESMS): *m/z* 453 $\{M\}^{2+}$, 925 $\{M-2PF_6+F\}^+$, 1051 $\{M-PF_6\}^+$, 1219 $\{M+Na\}^+$. UV–Vis (MeCN): λ, (nm) (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 284 (93 000), 322 (63 000), 566 (29 000).

2.10. 1-(4-(2,2′:6′,2″-Terpyridine-4′-yl)-2,3,5,6-tetrafluorophenoxyoethyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (9)

A mixture of **5** (10 mg, 0.025 mmol) and K_2CO_3 (10 mg, 0.075 mmol) in MeCN (5 cm^3) was stirred for 5 min at 65 °C after which a solution of 1-(2-bromoethoxy)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (11 mg, 0.025 mmol) in MeCN (0.5 cm^3) was added dropwise. The MeCN was then removed in vacuo and the residue dissolved in DMF (5 cm^3), KI (5 mg, 0.025 mmol) added and the mixture stirred at 80 °C for 40 h. The orange–red solution that resulted was purified by HPLC (C18 column, 90% MeOH, 10% H_2O) to give a pale yellow solid (31%) that was recrystallised from methanol to give white crystals of 1-(4-(2,2′:6′,2″-terpyridine-4′-yl)-2,3,5,6-tetrafluorophenoxyoethyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside **9**. ^{1}H NMR ($CDCl_3$, tpy protons T, sugar protons S, linker protons L): δ 8.69 (d, 2H, H^{T6}), 8.65 (d, 2H, H^{T3}), 8.55 (s, 2H, $H^{T3'}$), 7.87 (t, 2H, H^{T4}), 7.34 (t, 2H, H^{T5}), 5.23 (t, 1H, H^{S3}), 5.10 (t, 1H, H^{S4}), 5.03 (dd, 1H, H^{S2}), 4.68 (d, 1H, H^{S1}), 4.45 (br t, 2H, H^{L1}), 4.27 (dd, 1H, $H^{S6a/b}$), 4.15 (dd, 1H, $H^{S6b/a}$), 4.12 (dt, 1H, $H^{L2a/b}$), 3.97 (m, 1H, $H^{L2b/a}$), 3.73 (ddd, 1H, H^{S5}), 2.09 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.99 (s, 3H, OAc). ^{19}F NMR ($CDCl_3$): δ −143.2 (dd, 2F, F^o), −156.6 (dd, 2F, F^m). ^{13}C NMR ($CDCl_3$): δ 170.6 (CH_3CO), 170.2 (CH_3CO), 169.4 (2 × CH_3CO), 156.0 (C^2), 155.6 ($C^{2'}$), 149.2 (C^6), 144.6 (d, $^1J_{CF}$ 248 Hz, C^o), 141.2 (d, $^1J_{CF}$ 248, C^m), 137.4 ($C^{4'}$), 136.8 (C^4), 124.0 (C^5), 122.0 ($C^{3'}$), 121.25 (C^3), 112.7, 112.5 (C^{ipso}), 100.8 (C^{S1}), 73.8 (C^{L1}), 72.8 (C^{S3}), 71.9 (C^{S5}), 71.1 (C^{S2}), 68.4 (C^{S4}), 67.0 (C^{L2}), 61.9 (C^{S6}), 20.6 (4 × CH_3CO) Mass spectrum (ESMS): *m/z* 494 $\{M+Na\}^+$; exact mass: *m/z* 794.1952 (794.1949 for $\{M+Na\}^+$). IR: $\nu = 1743$ s cm^{-1}.

2.11. Preparation of [Fe(9)$_2$][PF$_6$]$_2$

A solution of **9** (0.028 g, 0.036 mmol) in EtOH (5 cm^3) was added to a solution of $FeCl_2.4H_2O$ (0.0036 g, 0.018 mmol) in ethanol (0.5 cm^3) and the mixture stirred for 1 h at room temperature to give a purple solution. The solution was treated with ammonium hexafluorophosphate in ethanol, stirred for 10 min and the solvent removed in vacuo to give a residue that was recrystallised from aqueous acetonitrile to give $[Fe(\mathbf{9})_2][PF_6]_2$ as a purple solid (0.024 g, 71%). ^{1}H NMR (CD_3CN, tpy protons T, sugar protons S, linker protons L): δ 9.07 (s, 4H, $H^{T3'}$), 8.51 (d, 4H, H^{T3}), 7.91 (td, 4H, H^{T4}), 7.18 (dd, 4H, H^{T6}), 7.12 (td, 4H, H^{T5}), 5.27 (t, 1H, H^{S3}), 5.06 (t, 1H, H^{S4}), 4.91 (dd, 1H, H^{S2}), 4.78 (d, 1H, H^{S1}), 4.63 (br m, 2H, H^{L1}), 4.25 (dd, 1H, $H^{S6a/b}$), 4.18 (ddd, 1H, $H^{L2a/b}$), 4.11 (dd, 1H, $H^{S6b/a}$), 4.01 (m, 1H, $H^{L2b/a}$), 3.88 (ddd, 1H, H^{S5}), 2.16 (v br s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.99 (s, 3H, OAc). ^{19}F NMR ($CDCl_3$): δ −143.5 (dd, 2F, F^o), −156.0 (dd, 2F, F^m). Mass spectrum (ESMS): *m/z* 799.1, 799.5, 800.1 $\{M-2PF_6\}^{2+}$, 1743 $\{M-PF_6\}^+$. IR: $\nu = 1747$ s, 1740 s cm^{-1}. UV–Vis (MeCN): λ, (nm) (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 284 (23 000), 322 (16 000), 566 (8000).

2.12. Crystal structure determinations

The structures were solved and refined by direct methods using standard techniques as indicated in Table 1 using the programmes SHELXL-93 [9] and SHELXS-97 [10]. Data were collected on a Bruker AXS Smart 6000 CCD diffractometer. Diagrams and supplementary material were prepared using the above programmes together with ORTEP-3 for Windows [11], and PLATON [12].

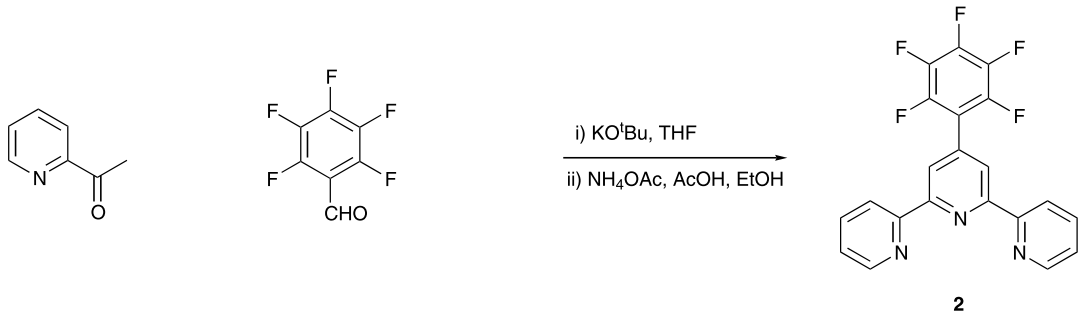
3. Results and discussion

3.1. Strategy

We planned a general and mild route for the preparation of sugars functionalised with tpy and 2,2′-bipyridine (bpy) metal-binding domains that could be extended to the preparation of oligosaccharide derivatives. We have previously shown that glucose and galactose derivatives can be linked to tpy metal-binding domains by the reaction of the nucleophilic anion of 2,2′:6′,2″-terpyridine-4′(1′*H*)-one with electrophilic sugars [6]. Although this approach was successful, the use of strongly basic reaction conditions limited the number

Table 1
Crystal data for **5** and **3**

Compound	**5**	**3**
Formula	$C_{21}H_{11}F_4N_3O$	$C_{22}H_{13}F_4N_3O$
M (g mol^{-1})	397.33	411.36
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
μ (mm^{-1})	1.116	1.049
Final *R* all (observed)	0.0951 (0.0612)	0.0777 (0.0681)
Final R_w all (observed)	0.1784 (0.1543)	0.1954 (0.1775)
a (Å)	7.4835(2)	14.1270(2)
b (Å)	11.2362(3)	7.4245(1)
c (Å)	20.1777(5)	18.4716(3)
α (°)	90	90
β (°)	95.755(2)	109.105(1)
γ (°)	90	90
V (Å^3)	1688.13(8)	1830.70(5)
T (K)	200	296
Z	4	4
F(0 0 0)	420	840
Number reflections	6410	6647
Number independent reflections	2964	3006
Number observed reflections	1960	2353
	$I > 2\sigma(I)$	$I > 2\sigma(I)$



Scheme 1.

of protecting groups that could be used and precluded reactions with the unprotected sugars. As a part of other studies investigating the use of substituents to fine tune the photophysical and redox properties of transition metal tpy complexes, we had recourse to prepare 4′-pentafluorophenyl-2,2′:6′,2″-terpyridine **2**, which has a strongly electron-withdrawing substituent. In the course of this work, we noted that the 4-fluoro substituent was relatively readily displaced by mild nucleophiles, a reactivity pattern that is well-established in other highly fluorinated systems [13,14]. In this paper we describe attempts to utilise this reactivity for the facile attachment of sugars or spacer groups to tpy metal-binding domains.

3.2. Synthesis of 4′-pentafluorophenyl-2,2′:6′,2″-terpyridine

As outlined above, our first approach to a new class of sugar-functionalised tpy ligands was based upon the introduction of an aromatic residue that could be functionalised readily through electrophilic or nucleophilic substitution. An attractive target was the novel ligand **2** in which the pentafluorophenyl substituent is strongly activated towards nucleophilic attack, in particular at the 4-position of the ring. Attempts to prepare the ligand **2** by a conventional Krohnke synthesis [15], in which the enolate equivalent 2-(1-oxo-2-pyridinioethyl)pyridine iodide and ammonium acetate were reacted with the enone obtained from the 1:1 condensation of 2-acetylpyridine with pentafluorobenzaldehyde were unsuccessful and gave only brown oily products. However, a one-pot synthetic method [16,17] in which the aromatic aldehdye is reacted with 2-acetylpyridine and potassium *t*-butoxide in THF followed by cyclisation with ammonium acetate in ethanolic acetic acid yielded the desired ligand as an off-white solid (Scheme 1 ^{1}H NMR spectroscopic analysis of the crude product revealed the presence of significant amounts of 4′-(4-ethoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine **4** which presumably arise from the attack of ethanol upon the ligand in the cyclisation step. This latter observation indicated that our synthetic strategy might be successful. Recrystallisation of the crude product from CH_2Cl_2–MeOH–diethyl ether gave the desired 4′-pentafluorophenyl-2,2′:6′,2″-terpyridine **2** as a white crystalline solid in 38% yield.

3.3. Reaction of 4′-pentafluorophenyl-2,2′:6′,2″-terpyridine with nucleophiles

The new ligand **2** was prepared with a view to displacement of the fluorine in the *para* position by oxygen nucleophiles which could either be subsequently structurally developed to bear sugar substituents or could derive from a sugar directly. The observation of 4′-(4-ethoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine **4** as a side-product in the preparation of **2** indicated that the compound was indeed activated towards nucleophilic attack and test reactions were performed with methanol and ethanol as nucleophiles.

In practice, we found that the *para* fluorine substituent in **2** could be displaced in exceptionally mild conditions. The reaction of **2** with methanol containing a small amount of aqueous sodium hydroxide solution gave the desired 4′-(tetrafluoro-4-methoxyphenyl)-2,2′:6′,2″-terpyridine **3** as a white crystalline solid in 65% yield. Similarly, reaction of **2** with ethanol containing a small amount of aqueous sodium hydroxide solution gave the desired 4′-(4-ethoxytetrafluorophenyl)-2,2′:6′,2″-terpyridine **4** as a white crystalline solid in 73% yield. These compounds were all characterised by standard methods.

In an attempt to introduce a spacer group, we investigated the reaction of **2** with diols. To our surprise, the reaction of **2** with an excess of ethane-1,2-diol in the presence of aqueous sodium hydroxide under a variety of reaction conditions did not result in any isolable amount of the desired spacer functionalised ligand 4′-(tetrafluoro-4-(2-hydroxyethoxy)phenyl)-2,2′:6′,2″-terpyridine (**6**). In the case of reaction in boiling ethane-1,2-diol for prolonged periods of time, some mass spectrometric evidence was found for the formation of multiply substituted derivatives in low yield but no clean products were isolated from these reactions.

In conclusion, the use of simple alcohol nucleophiles allows the preparation of 4′-(4-alkoxytetrafluorophenyl)-2,2′:6′,2″-terpyridines but extension of the method to the attachment of diols was unsuccessful (Scheme 2).

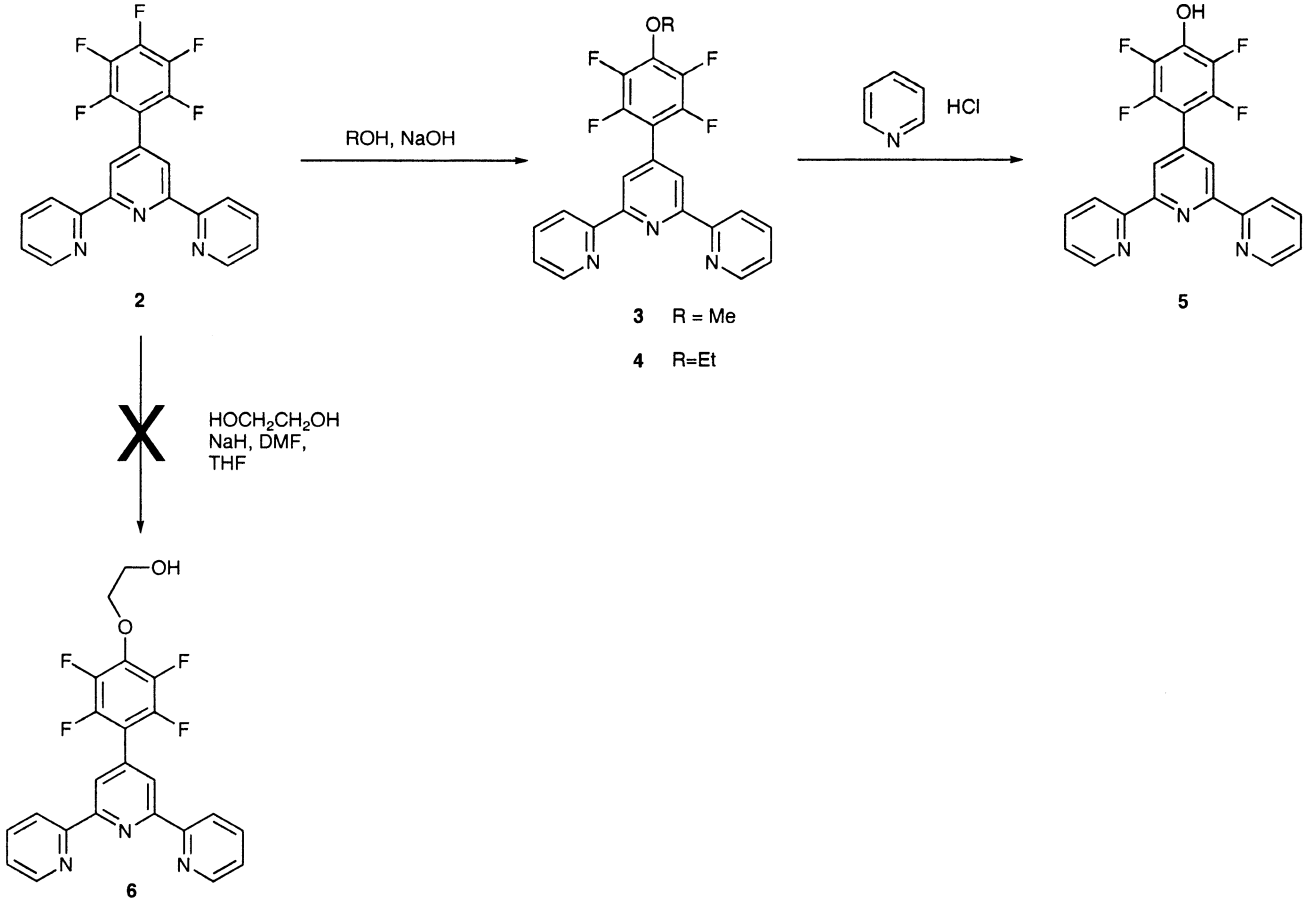
3.4. Synthesis of 4′-(tetrafluoro-4-hydroxyphenyl)-2,2′:6′,2″-terpyridine (5)

The derivatives **3** and **4** may be regarded as protected precursors for the nucleophilic ligand 4′-(tetrafluoro-4-hydroxyphenyl)-2,2′:6′,2″-terpyridine **5** and it has been demonstrated previously that methoxyphenyl compounds may be converted to hydroxyphenyl derivatives in high yield by reaction with molten pyridinium chloride [18–20]. This method has now been extended to the ethoxy derivative **4** which is converted into the hydroxy compound **5** in 31% isolated yield by reaction with molten pyridinium chloride (Scheme 2). A similar reaction with the methoxy compound **3** gave the phenol **5** in 47% yield. We also investigated the alternative deprotection route involving reaction with boron tribromide at low temperature (−78 °C) [18,20,21]. The reaction of **3** with BBr_3 in CH_2Cl_2 proceeded smoothly but after workup involving base the deprotected compound was obtained as a red sodium salt in 50% yield. For convenience and economy, we prefer the pyridinium chloride deprotection route for the preparation of **5**.

The new phenolic compound was fully characterised by the usual spectroscopic methods. The ^1H NMR spectrum of a dmso-d_6 solution was typical and exhibited a total of five resonances in the aromatic region. The ^{13}C NMR spectrum was also characteristic and was assigned by a ^1H-^{13}C correlation experiment. The carbon atoms of the fluorinated ring show coupling to the ^{19}F allowing facile assignment; the ^1J C–F couplings of the *ortho* and *meta* carbon atoms are typical and in the region of 245 Hz [22]. The FAB mass spectrum showed a parent ion for the compound and an exact mass experiment confirmed the formulation.

3.5. Solid state structure of 4′-(tetrafluoro-4-hydroxyphenyl)-2,2′:6′,2″-terpyridine 5

The solid state structure of 4′-(tetrafluoro-4-hydroxyphenyl)-2,2′:6′,2″-terpyridine is shown in Fig. 1 and exhibits a number of unique features. All bond lengths and angles within the molecule are normal and individual rings are near planar, but the compound exhibits an extremely rare *cis, trans* conformation of the tpy ring system. The rings containing N1 and N2 exhibit the



Scheme 2.

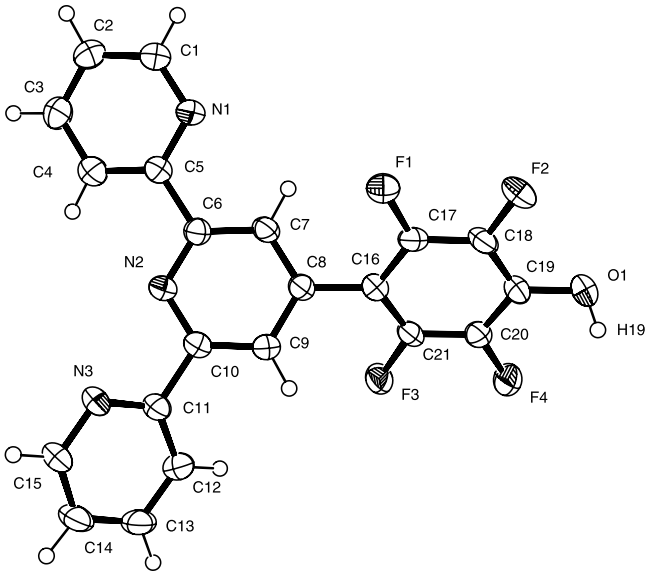


Fig. 1. Crystal and molecular structure of **5** showing the labelling scheme adopted. The *cis* arrangement of the rings containing N2 and N3 is notable. Selected bond lengths (Å) and angles (°):N1–C1 1.331(4), N1–C5 1.349(4), N2–C6 1.343(4), N2–C10 1.347(3), N3–C15 1.344(4), N3–C11 1.350(4), O1–C19 1.340(4), F1–C17 1.359(3), F2–C18 1.353(3), F3–C21 1.366(3), F4–C20 1.357(3), C1–N1–C5 117.0(3), C6–N2–C10 117.3(2), C15–N3–C11 117.3(3).

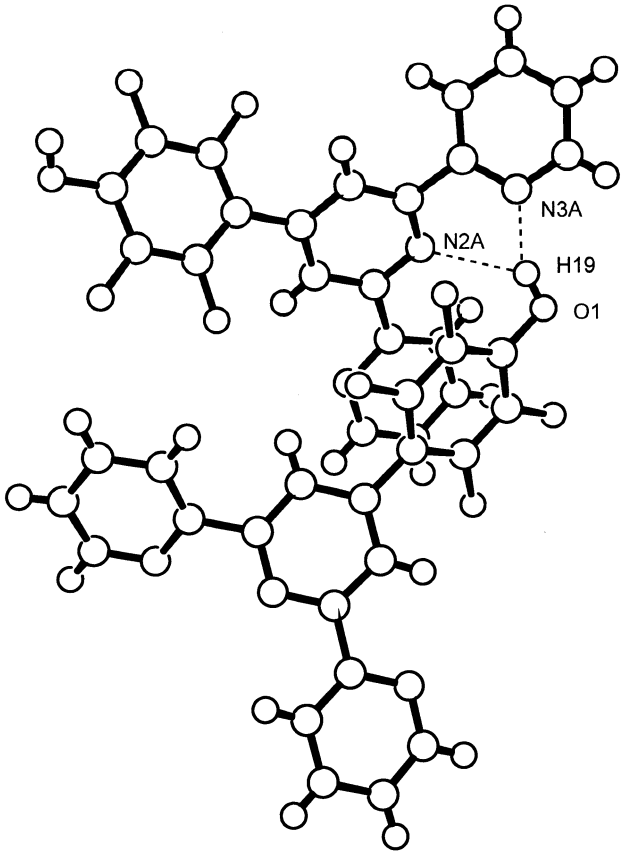


Fig. 2. The hydrogen-bonding between the phenolic hydroxy group and nitrogen atoms N2 and N3 accounts for the cis arrangement of the rings containing these two nitrogen atoms: H19–N3A 1.83 Å, H19–N2A 2.67 Å, O1–N3A 2.64 Å, O1–N2A 3.20 Å, N2A–H19–N3A 67.9°, O1–H19–N2A 166.4°.

expected *trans* conformation with a modest torsion angle N1–C5–C6–N2 of 17.5° typical for a free ligand 2,2′:6′,2″-terpyridine. However, the rings containing N2 and N3 are oriented with a *cis* conformation and are significantly distorted from coplanarity with a torsion angle N2–C10–C11–N3 of 32.9°. The phenyl ring is also significantly twisted with respect to the plane of the pyridine ring containing N2 with a torsion angle C9–C8–C16–C21 of 41.6°. The hydroxy group of the substituent is also twisted with respect to the phenyl ring giving a torsion angle C20–C19–O1–H19 of 31.4°. Although free ligand 2,2′:6′,2″-terpyridines show *trans, trans* conformations, monoprotonation results in the adoption *cis, trans* [23] and diprotonation of *cis, cis* conformations [24–28]. The only other cases in which the conformation is other than *trans, trans* arises when the ligand is constrained to this conformation or when intra- [29] or intermolecular hydrogen bonding to the nitrogen atoms results in a perturbation [30,31]. In the case of **5**, the *cis, trans* conformation arises from a hydrogen bonding interaction between the hydroxy substituent of one molecule and the *cis* bpy motif of another molecule as shown in Fig. 2. The twisting of the phenyl ring is necessary to bring the hydroxy group close to the bpy domain and the final hydrogen bond is strong with H19–N3A 1.83 Å, H19–N2A 2.67 Å, O1–N3A 2.64 Å and O1–N2A 3.20 Å. The N2A–H19–N3A angle is 67.9° and the O1–H19–N2A interaction is approximately linear with an angle of 166.4°. A consequence of the interaction is the construction of two dimensional units within the lattice in which the hydrogen bonding between the hydroxy group and the *cis* bpy domain leads to good π stacking between the tetrafluoro-4-hydroxyphenyl substituent and the terminal ring containing N1A of the hydrogen bond acceptor (Fig. 2(b)).

3.6. Solid state structure of 4′-(tetrafluoro-4-methoxyphenyl)-2,2′:6′,2″-terpyridine **3**

The unusual conformation of the phenol **5** led us to determine the solid state structure of the methoxy compound **3** which is structurally and electronically very similar but lacks the hydrogen-bonding capacity. The solid state structure of **3** is shown in Fig. 3; the expected *trans, trans* conformation of the tpy domain is adopted with all bond lengths and angles within the usual limits. The tpy domain is approximately planar with torsion angles between the terminal rings and the central ring of 5.26° and 6.22° and the tetrafluoro-methoxyphenyl substituent makes a torsion angle of

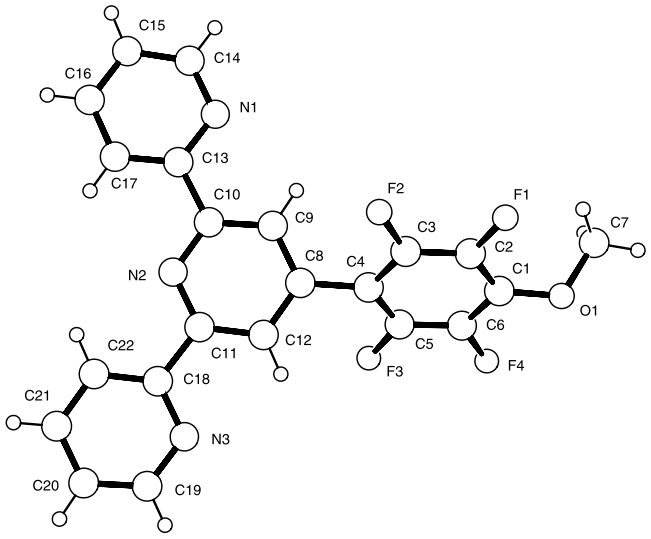


Fig. 3. Crystal and molecular structure of **3** showing the labelling scheme adopted. Selected bond lengths (Å) and angles (°):O1–C1 1.357(2), O1–C7 1.405(3), F1–C2 1.336(2), F2–C3 1.345(2), F3–C5 1.349(2), F4–C6 1.348(2), N1–C14 1.322(3), N1–C13 1.343(3), N2–C11 1.332(3), N2–C10 1.341(2), N3–C19 1.338(3), N3–C18 1.339(3), C1–O1–C7 117.5(2), C14–N1–C13 117.6(2), C11–N2–C10 118.5(2), C19–N3–C18 117.2(2).

48.28° with the central pyridine ring. There are extensive π-stacking interactions in the lattice involving terminal pyridine rings of one ligand with the central ring of the adjacent ligand.

3.7. Inverted strategy for the preparation of functionalised ligands

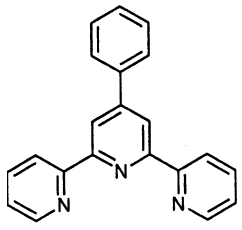
The lack of reaction of **2** with functionalised alcohols (and hence sugars) led us to reconsider the synthetic strategy. Instead of reacting the electrophilic pentafluorophenyl derivative **2** with a nucleophilic alcohol, we decided to use the nucleophilic tetrafluoro-4-hydroxyphenyl compound **5** in reactions with electrophilic sugars and spacers. As a first test reaction, we decided to attempt the preparation of the spacer functionalised compound **6** using this strategy. The reaction of the phenol **5** with 2-chloroethanol in the presence of caesium carbonate gave the desired hydroxyethoxy spacer functionalised species **6** as a white solid in 82% yield (Scheme 3). A similar reaction of **5** with $ClCH_2CH_2OCH_2CH_2OH$ gave the 2-(2-hydroxyethoxy)ethoxy functionalised ligand as a solid in 65% yield (Scheme 4).

Attempts to directly attach a sugar to the tetrafluorophenyl substituent using this approach were also unsuccessful. The reaction of **5** with the protected, electrophilic sugar 6-tosyloxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose [7] under these conditions gave none of the anticipated ligand **7**. Similarly, reaction using sodium hydride as the base, or using 6-mesyloxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose as electrophile gave none of the desired species **7**.

3.8. Representative coordination chemistry of the new ligands

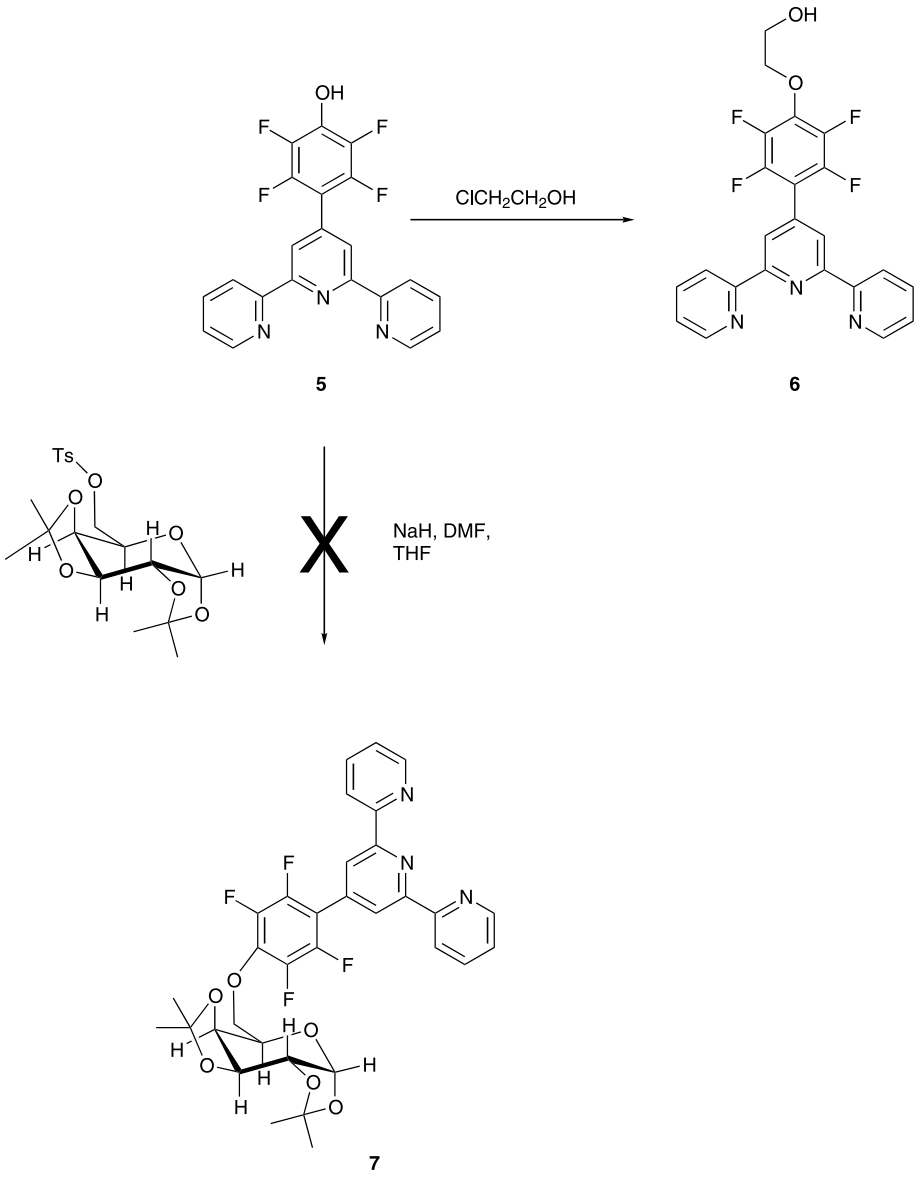
Compound **2** behaves as a typical tpy ligand and forms 2:1 complexes with octahedral transition metal centres. The reaction of **2** with iron(II) chloride in CH_2Cl_2–ethanol gave an intensely purple coloured solution from which the complex $[Fe(\mathbf{2})_2][PF_6]_2$ could be precipitated as a purple solid. ^1H NMR analysis of the isolated complex indicated that a mixed species containing both **2** and **4** had been formed, presumably as a result of nucleophilic attack by ethanol upon the activated complex. Purification by chromatography over silica using MeCN–H_2O-saturated aqueous KNO_3 solution as the mobile phase gave the pure complex $[Fe(\mathbf{2})_2][PF_6]_2$ as a purple solid in 24% yield. A similar reaction with **4** gave the authentic complex $[Fe(\mathbf{4})_2][PF_6]_2$ as a purple solid in 64% yield.

The ^1H NMR spectrum of $[Fe(\mathbf{2})_2][PF_6]_2$ is typical of a complex containing an $\{Fe(tpy)_2\}^{2+}$ motif and exhibits a low field singlet at δ 9.05 assigned to $H^{3'}$ of the central tpy ring. The ^{19}F NMR spectrum of the same complex exhibits four signals consisting of a doublet with $J_{PF} = 706$ Hz at $\delta -71.63$ (PF_6), a doublet at $\delta -141.4$ (2F, *ortho*), a triplet at $\delta -151.4$ (1F, *para*) and a doublet at $\delta -161.52$ (2F, *meta*). The ESMS shows peaks assigned to $[Fe(\mathbf{2})_2]^{2+}$, $\{[Fe(\mathbf{2})_2]F\}^+$, $\{[Fe(\mathbf{2})_2]-6)\}^+$ and $\{[Fe(\mathbf{2})_2](PF_6)_2Na\}^+$. The compound is intensely coloured and exhibits an MLCT absorption in the visible centred at 565 nm, typical for a $\{Fe(tpy)_2\}^{2+}$ chromophore. A comparison of $[Fe(\mathbf{2})_2][PF_6]_2$ with $[Fe(\mathbf{4})_2][PF_6]_2$ allows us to assess the influence of the remote substitution on the complex. The ^1H NMR spectrum and electronic spectra of $[Fe(\mathbf{2})_2][PF_6]_2$ with $[Fe(\mathbf{4})_2][PF_6]_2$ are almost identical; in particular, the chemical shift of $H^{3'}$ is the same, indicating that the electronic and magnetic environments of these protons in the two complexes are very similar.

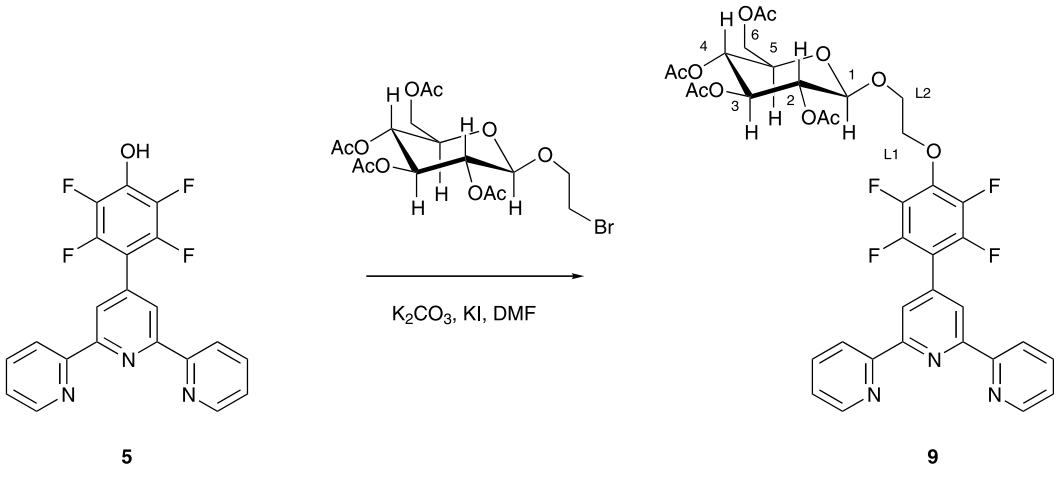


8

However, the electrochemical properties differ significantly and allow us to quantify the effect of the fluoro-substitutents. A comparison of cyclic voltammetry data for $[Fe(\mathbf{2})_2][PF_6]_2$ with those of $[Fe(\mathbf{8})_2][PF_6]_2$ containing



Scheme 3.



Scheme 4.

4′-phenyl-2,2′:6′,2″-terpyridine **8** confirms the electron-withdrawing nature of the substituent; the iron(II)/(III) processes are reversible in each case but shift from +0.69 V (versus Fc/Fc^+) for $[Fe(\mathbf{8})_2][PF_6]_2$ to +0.78 V for $[Fe(\mathbf{2})_2][PF_6]_2$. This is slightly less than the effect of formally positively charged protonated and quaternised pyridyl substituents [32] which show iron(II)/(III) processes with potentials greater than +0.8 V and confirms the electron-withdrawing character of the pentafluorophenyl substituent. The introduction of the electron-releasing ethoxy substituent in $[Fe(\mathbf{4})_2][PF_6]_2$ results in the iron(II)/(III) process being observed at a less positive potential of +0.76 V. The ligand reduction processes are similarly affected with those for $[Fe(\mathbf{4})_2][PF_6]_2$ (−1.65, −1.52 V) being about 20 mV more negative than those for $[Fe(\mathbf{2})_2][PF_6]_2$ (−1.63, −1.50 V). The differential pulse voltammogram of an acetonitrile solution of $[Fe(\mathbf{2})_2][PF_6]_2$ is presented in Fig. 4.

3.9. The glucose-functionalised ligand **9**

We finally prepared a sugar-functionalised ligand using the inverted approach of electrophilic attack upon **5**. Although **5** did not react with the electrophilic sugar derivative 2-bromoethyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside in acetonitrile or THF in the presence of K_2CO_3 and KI, reaction in DMF at 80 °C gave an orange–red solution. Purification by HPLC gave 1-(4-(2,2′:6′,2″-terpyridine-4′-yl)-2,3,5,6-tetrafluorophenoxyoethyl)-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside in 31% yield. This sugar was chosen because it has the spacer group already incorporated in a stereochemically unambiguous site and all of the hydroxy groups are protected as acetates. The new compound was fully characterised by conventional methods. The IR spectrum exhibited a strong absorption at 1743 cm^{-1} assigned to the acetyl protecting groups on the sugar and indicating that they are retained in the reaction. A parent ion in the ESMS at m/z 794 is assigned to $\{M+Na\}^+$. The ^1H NMR spectrum is most informative and confirms that the stereochemistry of the sugar is retained as are the acetyl protecting groups, which are observed as four singlets in the region of δ 2.0. The linker protons closest to the sugar L2a/b are diastereotopic and observed as complex pair of signals. The sugar CH_2 group is also observed as a pair of diastereotopic protons. Full assignments are given in the experimental section and are made on the basis of DEPT, ^1H–^1H COSY and ^1H-^{13}C HSQC spectra. The ^1H–^1H COSY spectrum of the region containing the sugar ring protons and the CH_2 groups of the linker and the sugar is presented in Fig. 5.

Finally, we prepared the iron(II) complex $[Fe(\mathbf{9})_2][PF_6]_2$ containing the protected sugar-functionalised ligand **9**. The purple compound was obtained from the reaction of iron(II) chloride with **9** in ethanol and exhibited a typical MLCT band at 566 nm. Mass spectrometry confirmed the identity of the product. The ^1H NMR spectrum of the complex was sharp and well resolved and was fully assigned (Section 2) by a ^1H–^1H COSY experiment. One of the methyl resonances of the acetyl protecting groups was broadened in the complex but not in the free ligand.

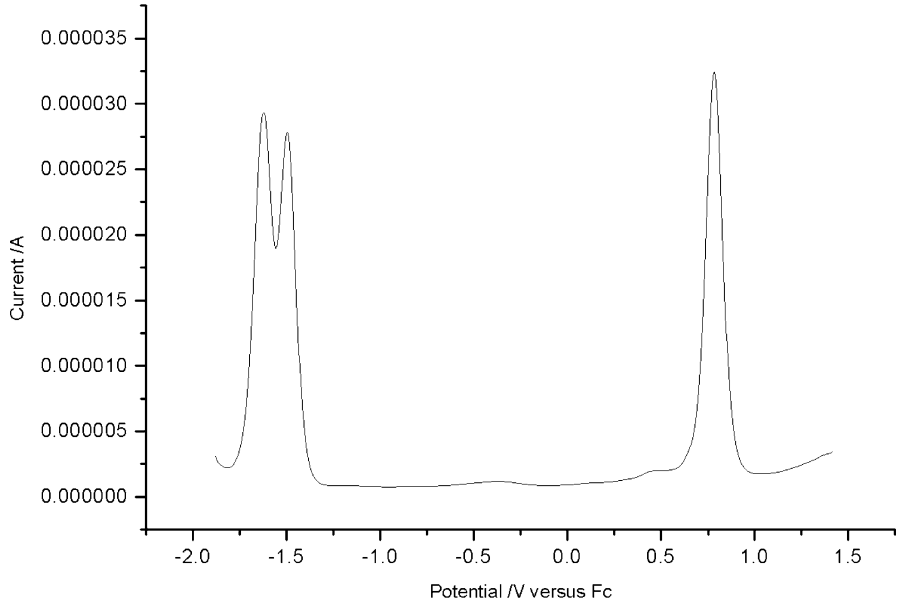


Fig. 4. Differential pulse voltammogram of $[Fe(\mathbf{2})_2][PF_6]_2$ (MeCN, $[^nBu_4N][PF_6]$ supporting electrolyte, conditioning potential 1 s at −1.8 V, modulation 0.04 s, interval 0.2 s, step potential 0.004 V, modulation amplitude 0.05).

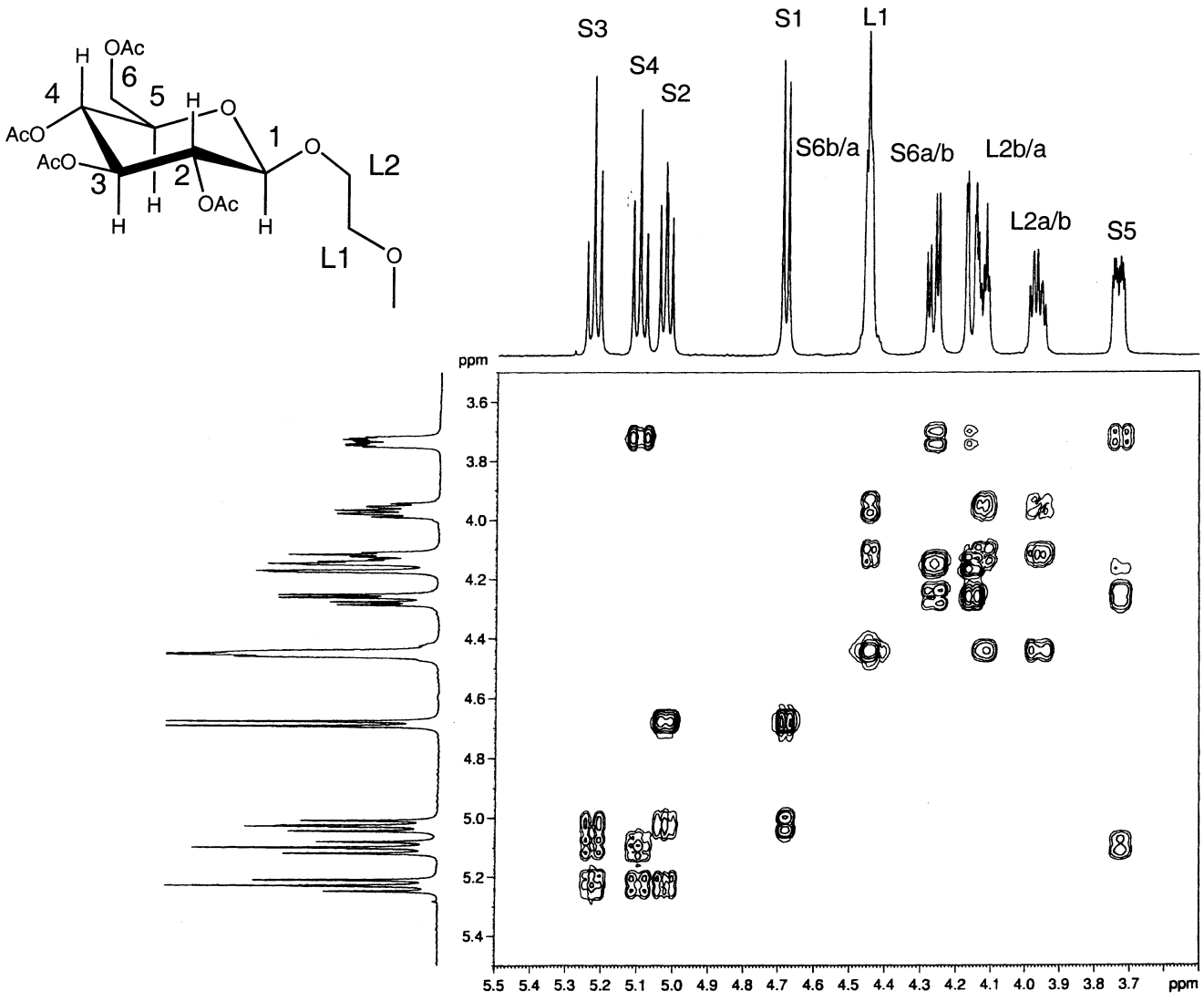


Fig. 5. 500 MHz $^{1}H-^{1}H$ gradient COSY of the aliphatic CH and CH_2 region glucose-functionalised ligand **9.**

We are currently investigating the properties of this complex and methods for the deprotection of both the complex and the free ligand.

4. Conclusions

We have shown the pentafluorophenyl derivatised tpy ligand **2** is activated towards attack by simple oxygen donor nucleophiles at the *para* position of the substituent. Structurally developed nucleophiles such as sugars could not be incorporated directly using this methodology but an alternative strategy involving attack of electrophiles upon the phenol **5** was successful in yielding the desired sugar-functionalised species. We do not feel that this approach has any significant advantages over more conventional synthetic pathways to functionalised tpy ligands.

5. Supplementary material

All crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 196026 (**3**) and 196027 (**5**) Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-366033; e-mail: deposit@ccdc.cam.ac.uk or http://www/ccdc.cam.ac.uk).

Acknowledgements

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References

[1] J.-P. Sauvage (Ed.), Transition Metals in Supramolecular Chemistry, Perspectives in Supramolecular Chemistry, Wiley, Chichester, 1999.
[2] G.F. Swiegers, T.J. Malefeste, Chem. Rev. 100 (2000) 2483.
[3] J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995.
[4] J.L. Atwood, J.E.D. Davies, D.D. McNicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, vol. 6, 7 and 9, Pergamon, Oxford, 1996.
[5] E.C. Constable, W. Meier, C. Nardin, S. Mundwiler, Chem. Commun. (1999) 1483.
[6] E.C. Constable, S. Mundwiler, Polyhedron 18 (1999) 2433.
[7] K. Freudenberg, R.M. Hixon, Chem. Ber. 56 (1923) 2119.
[8] J. Dahmen, T. Freid, G. Gronberg, T. Lave, G. Magnusson, G. Noori, Carbohydrate Res. 116 (1983) 303.
[9] G.M. Sheldrick, SHELXL-93. Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.
[10] G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.
[11] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
[12] (a) A.L. Spek, Acta Crystallogr., Sect. A A46 (1990) C34;
(b) L.J. Farrugia, PLATON for Windows, University of Glasgow, 1999.
[13] R.D. Chambers, D.J. Spring, Tetrahedron 27 (1971) 669.
[14] B. Baasner, H. Hagemann, J.C. Tatlow (Eds.), Methods of Organic Chemistry (Houben-Weyl), vol. E 10b/Part 2, Georg Thieme, Stuttgart, 2000.
[15] F. Krohnke, Synthesis (1976) 1.
[16] W. Spahni, G. Calzaferri, Helv. Chim. Acta 67 (1984) 450.
[17] S. Encinas, L. Flamigni, F. Barigelletti, E.C. Constable, C.E. Housecroft, E.R. Schofield, E. Figgemeier, D. Fenske, M. Neuburger, J.G. Vos, M. Zehnder, Chem. Eur.J. 8 (2002) 137.
[18] (a) C.O. Dietrich-Buchecker, J.-P. Sauvage, J.P. Kintzinger, P. Maltese, C. Pascard, J. Guilheim, New J. Chem. 16 (1992) 931;
(b) C.O. Dietrich-Buchecker, J.-P. Sauvage, New J. Chem. 46 (1990) 503.
[19] E.C. Constable, D.J. Morris, S. Carr, New J. Chem. 22 (1998) 287.
[20] E.C. Constable, C.E. Housecroft, M. Neuburger, I. Poleschak, M. Zehnder, Polyhedron, in press.
[21] G. Schill, C. Zuercher, E. Logemann, Chem. Ber. 108 (1975) 1570.
[22] E.R. Malinowski, J. Am. Chem. Soc. 83 (1961) 4479.
[23] A. Hergold-Brundic, Z. Popovic, D. Matkovic-Calogovic, Acta Crystallogr., Sect. C 52 (1996) 3154.
[24] K.N. Robertson, P.K. Bakshi, S.D. Lantos, T.S. Cameron, O. Knop, Can. J. Chem. 76 (1998) 583.
[25] M.G.B. Drew, M.J. Hudson, P.B. Iveson, M.L. Russell, J.-O. Liljenzin, M. Skalberg, L. Spjuth, C. Madic, J. Chem. Soc., Dalton Trans. (1998) 2973.
[26] M.G.B. Drew, P.B. Iveson, M.J. Hudson, J.O. Liljenzin, L. Spjuth, P.-Y. Cordier, A. Enarsson, C. Hill, C. Madic, J. Chem. Soc., Dalton Trans. (2000) 821.
[27] C.J. Kepert, B.W. Skelton, A.H. White, Aust. J. Chem. 47 (1994) 391.
[28] M.G.B. Drew, M.J. Hudson, P.B. Iveson, M.L. Russell, J.-O. Liljenzin, M. Skalberg, L. Spjuth, C. Madic, J. Chem. Soc., Dalton Trans. (1998) 2973.
[29] E. Murguly, T.B. Norsten, N. Branda, J. Chem. Soc. Perkin Trans. 2 (1999) 2789.
[30] L. Prasad, F.E. Smith, Acta Crystallogr., Sect. B 38 (1982) 1815.
[31] R. Keuper, N. Risch, U. Florke, H.-J. Haupt, Liebigs Ann. Chem. (1996) 705.
[32] E.C. Constable, A.M.W. Cargill Thompson, J. Chem. Soc., Dalton Trans. (1992) 2947.