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Oligopyridine ligands possessing multiple or mixed anchoring functionality for dye-sensitized solar cells

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ABSTRACT

This paper describes the synthesis and characterisation of targeted 2,2′-bipyridine-3,3′,4,4′-tetracarboxylic acid and 2,2′-bipyridine-4,4′,5,5′-tetracarboxylic acid via succinct synthetic pathways. Further, we report methods for producing asymmetric bipyridines bearing both carboxylate and phosphonate anchoring groups in the ester protected form, and the first reported synthesis of a group of new polyoxo oligopyridine ligands based on terpyridine and quaterpyridine. A robust synthetic strategy using Krönhke conditions was developed and demonstrated for synthesising oligopyridine moieties targeted for application in the dye-sensitized solar cell (DSSC). This class of novel ligands was designed to provide alternative anchoring functionality and to improve the metal oxide surface binding properties of co-ordination complexes in DSSC applications.

1. Introduction

The use of d^6 ruthenium coordination complexes as surface adsorbed dyes namely *cis*-bis-diisothiocyanato bis(4,4′-dicarboxylato-2,2′-bipyridine) ruthenium(II) (N3), di-tetrabutylammonium *cis*-bis(diisothiocyanato) bis(4,4′-dicarboxylato-2,2′-bipyridine) ruthenium(II) (N719) and (triisothiocyanato)(4,4′,4″-tricarboxylato-2,2″6′,2″-terpyridine) ruthenium(II) (N749) in the dye-sensitized solar cell have remained a solid benchmark in terms of cell performance since their development. However, the long term durability of these complexes in photovoltaic devices may be improved through modification of the surface anchoring functionality of the dyes. Much work has been conducted to understand the relative strength and binding modes of linker groups for anchoring sensitisers to metal-oxide surfaces,[1,2] It is now well understood that increased surface adhesion can either be achieved through an increased electron-withdrawing ability of the functional group[2] (quantified by the Hammett parameter, σ) or by the use of multiple anchoring groups especially in tripodal binding configurations.[1]

In this work we considered that ligands bearing either more than one anchoring functional group per pyridine unit or a hybrid anchoring system could result in enhanced surface binding properties. With this in mind a series of ligands were designed to improve dye anchoring by introducing additional carboxylic acid groups at the ligand periphery, or by substituting for a stronger binding group at one site, as shown in Fig. 1. The proposed ligand structures retain at least one carboxylic acid functionality in the *para* position on one of the pyridine rings to ensure that effective electron injection to a metal oxide semiconductor can still be achieved.

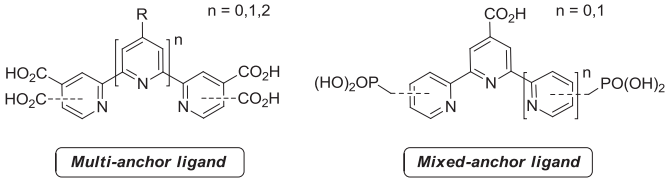

Fig. 1. Concept for improved ligand anchoring ability.

In this work we present succinct methodologies for preparation of polyoxo oligopyridines based on increased electron withdrawing

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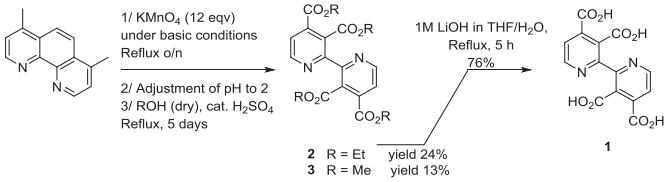
properties and substitutions for enhanced binding affinity. Preparation of ruthenium coordination complexes based on these compounds will be reported in a subsequent publication.

2. Results and discussion

2.1. Bipyridine synthesis

Synthesis of the 2,2′-bipyridine-3,3′,4,4′-tetracarboxylic acid (**1**) required oxidation of 1,10-dimethyl-2,7-phenanthroline at both methyl groups as well as at the phenanthroline backbone, analogous to a procedure detailed by Dawid et al.[3] Initial oxidation attempts (6 equiv of $KMnO_4$) failed to effect complete oxidation (Scheme 1), with preferential oxidation of the phenanthroline backbone. Using an excess of $KMnO_4$ (12 equiv) successfully oxidised the 4,7-dimethyl-1,10-phenanthroline to 3,3′,4,4′-tetracarboxylic acid 2,2′-bipyridine, indicated by the ^1H NMR spectrum (chemical shifts at 7.49 and 8.52 ppm) and LC-MS. Attempts to purify at this point by selective pH driven precipitation (after MnO_2 removal) proved difficult, as the product failed to precipitate upon adjusting the pH to 2. Conversion to the tetraethyl ester (refluxing EtOH, cat. H_2SO_4, 5 days) allowed for easier purification by selective precipitation from water after removal of the salt byproducts carried through from the oxidation step, giving the tetra-ethyl ester (**2**) in a modest yield of 24% after recrystallisation from H_2O/EtOH. Recrystallisation was deemed necessary to remove minor byproducts.



Scheme 1. Synthesis of 2,2′-bipyridine-3,3′,4,4′-tetracarboxylic acid (**1**).

The tetraethyl 2,2′-bipyridine-3,3′,4,4′-tetracarboxylate ligand was characterised by several analysis techniques (^1H NMR, ^{13}C NMR, IR, MS, EA), which were consistent with the expected structure. The oxidation/esterification process was modified using methanol in the esterification stage to produce a less sterically hindered ligand derivative, tetramethyl-2,2′-bipyridine-3,3′,4,4′-tetracarboxylate (**3**), as shown in Scheme 1. Although lower yields were encountered (~20%), the esterified product was recovered as a crystalline solid. The recovered product was characterised by ^1H NMR, ^{13}C NMR, IR, MS and EA without further recrystallisation. Crystals of the tetramethyl-2,2′-bipyridine-3,3′,4,4′-tetracarboxylate ligand (**3**) of suitable purity/quality for single-crystal X-ray diffraction were grown via slow diffusion of diethyl ether into a methanolic solution of the ligand. The two pyridine rings of the ligand displayed a *trans* configuration, minimising the steric interaction of the ester groups at the 3 and 3′ positions, as shown in Fig. 2 (see also CCDC 1056206).

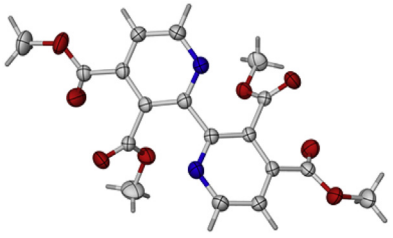
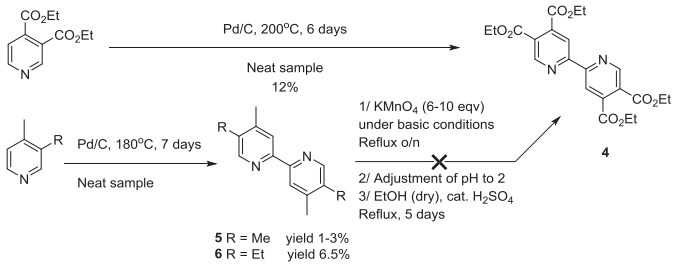


Fig. 2. Crystal structure of tetramethyl-2,2′-bipyridine-3,3′,4,4′-tetracarboxylate (**3**).

Access to the free acid ligand **1** was achieved under basic hydrolysis conditions (1 M LiOH in THF/water, 5 h reflux), yielding the deprotected product. After selective removal of the THF, the pH was adjusted to 2 and the solution was allowed to stand overnight resulting in the formation of the desired product as a white precipitate (~65–75%). Complimentary analytical structural characterisation (^1H NMR, ^{13}C NMR, IR, MS and EA) was performed, corresponding to the expected compound (**1**). The ^1H NMR spectrum showed only two doublet resonances at 7.78 and 8.67 ppm in deuterated methanol, whilst the ^{13}C NMR spectrum displayed seven carbon shifts including two distinct carboxylic acid resonances at 168.1 and 170.1 ppm.

For the synthesis of the target 2,2′-bipyridine-4,4′,5,5′-tetracarboxylic acid, several strategies were considered starting with pyridine dimerisation. The regioselective dimerisation of pyridines using Pd/C or Raney Ni have been reported previously.[4–7] Of particular interest is the procedure reported by Newkome et al. where ethyl isonicotinate is regioselectively dimerised at 200 °C over Pd/C under vacuum.[5] Investigating this reaction methodology on diethyl pyridine-3,4-dicarboxylate using conventional heating and no vacuum (Scheme 2) gave regioselective dimerisation to the desired tetraethyl-2,2′-bipyridine-4,4′,5,5′-tetracarboxylate (4) in ~10% conversion.

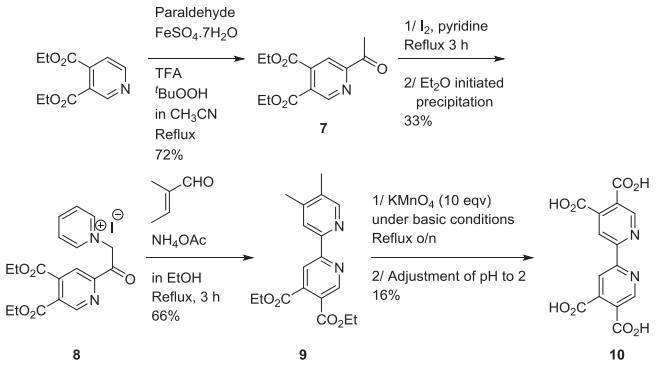


Scheme 2. Attempted synthesis routes to tetraethyl-2,2′-bipyridine-4,4′,5,5′-tetracarboxylate (**4**).

Our attempts to directly couple 3,4-pyridine dicarboxylic anhydride under similar conditions failed to yield any desired product. However, results of subsequent reactions varied with significantly lower conversion yields (<2%) observed. Due to the variability of this approach a more reliable procedure was developed. We envisaged a more reliable procedure by dimerising 3,4-alkyl substituted pyridines prior to conducting the oxidation and the esterification steps. The dimerisation of neat 3,4-lutidine over Pd/C (180 °C, 7 days) resulted in very low yields (1–3%) of the bipyridine product **5**, (Scheme 2). Switching the alkyl chain length at the 3-position from methyl to ethyl (3-ethyl-4-methyl pyridine) improved the dimerisation to ~7% conversion (5,5′-diethyl-4,4′-dimethyl-2,2′-bipyridine (**6**)) and an isolated yield of 6.5%, collected as colourless crystals, which formed upon standing. Oxidation of **5** was attempted using several methodologies (Scheme 2), however all gave unfavourable products. Oxidation with $KMnO_4$ and subsequent esterification yielded incomplete oxidation products, the main cause being poor solubility of starting reagent(s) (**5** or **6**). Further attempts with more polar solvent mixtures (water/^{t}BuOH (1:1)) were equally unsuccessful. Previous attempts by Kelly et al. who reported oxidation of 4,4′,5,5′-tetramethyl-2,2′-bipyridine using 4% aqueous HNO_3 resulted in decarboxylation at 5,5′positions.[8]

To circumvent the difficulties encountered in the generation of the 2,2′ bond an alternative synthesis pathway was considered using the Kröhnke pyridine synthesis to construct the second pyridine ring (Scheme 3).

The initial step, starting from diethyl-3,4-pyridine dicarboxylate, was a regioselective acetylation performed using an adapted



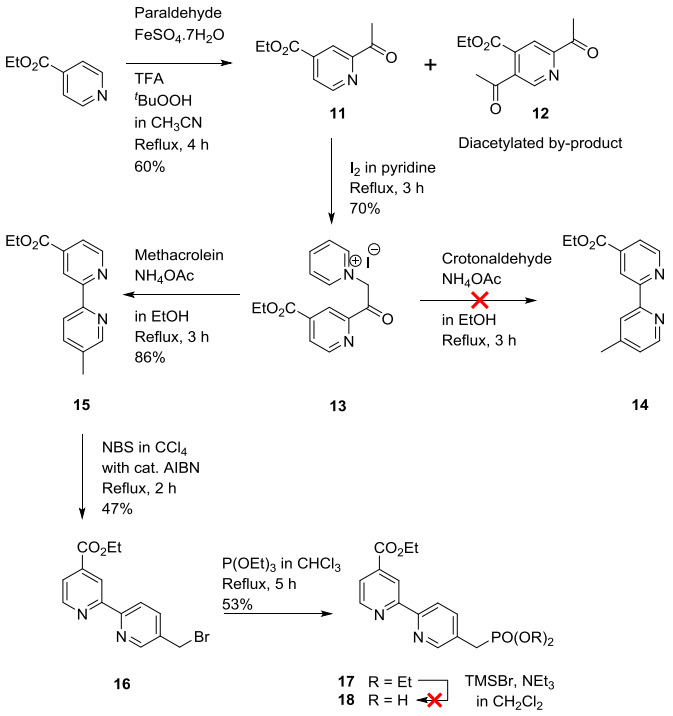
Scheme 3. Synthesis of 2,2′-bipyridine-4,4′,5,5′ tetracarboxylic acid (**10**).

literature method, giving the desired diethyl-6-acetylpyridine-3,4-dicarboxylate product (**7**) as the major product after chromatography (80% yield).[9] The acetylated pyridine **7** was then converted to the iodopyridinium salt **8** using the Ortoleva-King reaction,[10] a product precipitated upon addition of Et_2O to the reaction mixture. The iodopyridinium salt **8** was typically accompanied by pyridinium iodide (typically ~20–30%), so due to the difficulty of removing pyridinium iodide from the isolated material, the subsequent reaction was carried out without further purification. The reaction of the iodopyridinium salt **8** with 2-methyl-2-butenal and ammonium acetate yielded the desired diethyl-4′,5′-dimethyl-[2,2′-bipyridine]-4,5-dicarboxylate (**9**), which was purified by silica gel plug after aqueous reaction workup (39% yield). The purification process was simplified by performing a selective crystallisation after the ethanol had been removed, increasing the isolated yield to 66%. The oxidation of the bipyridine **9** was performed using $KMnO_4$ (10 equiv) under basic conditions in order to carry out the ester hydrolysis concurrently. After solvent concentration and pH adjustment using 4 M HCl, the desired product 2,2′-bipyridine-4,4′-5,5′-tetracarboxylic acid (**10**) flocculated out of solution as a white solid in an average yield of 16%. The ^{1}H NMR spectrum showed only two singlets in the aromatic region at 9.04 and 9.43 ppm. In a similar way to the 3,3′,4,4′ substituted ligand **1** the ^{13}C NMR spectrum displayed 7 resonances, with two distinct carbon environments of the carboxylic acid groups found at 169.5 and 171.2 ppm. The ESI accurate mass spectrum obtained show a signal at 331.0208 *m*/*z* in the negative mode corresponding to the value expected for $[MH]^-$.

2.2. Asymmetric bipyridine synthesis

Following our success with the Krönhke synthesis, a bipyridine bearing dual anchoring functionalities was also considered using an analogous strategy to the one detailed above. Firstly, ethyl 2-acetylisonicotinate (**11**) was synthesised by *ortho*-acetylation of ethyl isonicotinate using a literature procedure (Scheme 4).[9]

The reaction produced an undesirable diacetylated by-product **12**, not reported previously. The separation of the by-product was performed by column chromatography, giving the required mono *ortho*-acetylated product **11** in a 60% isolated yield. Ethyl-2-acetylisonicotinate (**11**) was further converted to the iodopyridinium salt **13** using Ortoleva-King conditions, with the desired compound simply filtered from the reaction mixture after a prolonged period of cooling at 4 °C, however the desired compound **13** was again accompanied by residual pyridinium iodide. The amount of pyridine used in the reaction could be reduced to 10 mL of pyridine per gram of starting material without significantly affecting the isolated yield. Reaction of the pyridinium salt **13** with crotonaldehyde under Krönhke conditions to produce ethyl-4′-methyl-



Scheme 4. Synthesis of ethyl 5′-methyl-[2,2′-bipyridine]-4-carboxylate (**14**) and ethyl 5′-((diethoxyphosphoryl)methyl)-[2,2′-bipyridine]-4-carboxylate (**17**).

4-carboxylate-[2,2′-bipyridine] (**14**) failed to yield the desired product effectively, and a complex mixture was generated. Replacing the crotonaldehyde with methacrolein and operating under the same reaction conditions resulted in the successful formation of ethyl-5′-methyl-[2,2′-bipyridine]-4-carboxylate (**15**). The compound was easily purified by passage through a silica gel plug (86% isolated yield). It was also found that the purity of the product could be improved by trituration using hexane/ethyl acetate to remove other reaction side products from the desired bipyridine.

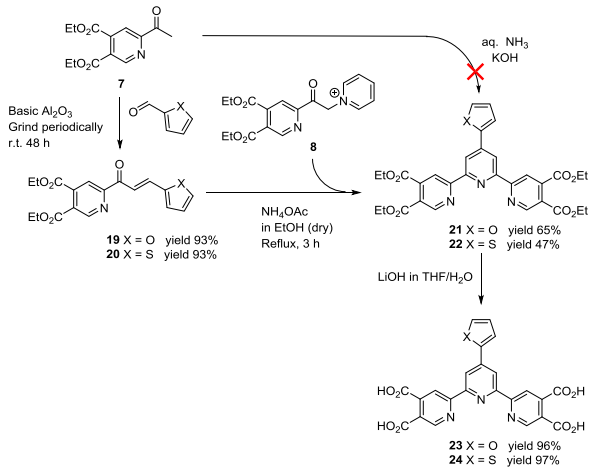
Using an adapted literature procedure,[11] the bromination of the ethyl-5-methyl-4′-carboxylate-[2,2′-bipyridine] (**15**) with NBS in CCl_4 and using AIBN as the radical initiator was successfully performed, resulting in the desired product in approximately 80% conversion. The mono brominated product **16** could be purified by column chromatography, with slight contamination by starting material (>90% pure).

The brominated bipyridine **16** was then reacted with a tenfold excess of triethyl phosphite in refluxing chloroform to install the phosphonate ester functionality. After removal of the solvent and excess triethyl phosphite by distillation, the ^{1}H NMR spectrum of the crude showed near complete conversion to the desired asymmetric ligand, ethyl 5′-((diethoxyphosphoryl)methyl)-[2,2′-bipyridine]-4-carboxylate (**17**). The mixture was then purified by column chromatography giving the desired asymmetric ligand precursor, **17**, in a 53% isolated yield. However, attempts to cleave the esters to form the required ligand **18** using acid (2 M HCl/THF reflux 5 h) or TMSBr (TMSBr 2 equiv in $CHCl_3$, NEt_3) were unsuccessful, yielding complex mixtures. Selectivity of the hydrolysis reaction in attempts to optimize reaction conditions proved difficult for isolating **18**. These were abandoned in favor of poly-carboxy analogues of the terpyridine ligand.

2.3. Terpyridine synthesis

Utilizing the method developed for the synthesis of **10** we considered that terpyridine and quaterpyridine derivatives possessing the 4,5-pyridyl ester substitution could also be accessed by

reacting a suitable chalcone with the previously prepared pyridinium iodide salt **8**. To investigate terpyridine preparation, (*E*)-diethyl-6-(3-(furan-2-yl)acryloyl)pyridine-3,4-dicarboxylate (**19**) was first synthesised by reaction of **7** with one equivalent of 2-furaldehyde over Al_2O_3 (basic) in a grind reaction, giving ~75% conversion after 48 h, with an isolated yield of 46% after column chromatography (Scheme 5).

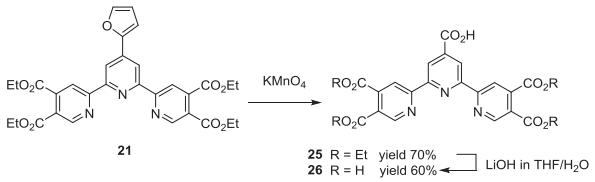


Scheme 5. Synthesis of heterocycle appended terpyridines.

As both of the reactants were liquids the grind mixing proceeded well, compared to mixing of solids under similar conditions.[12] It was later found that using additional furaldehyde (3 equiv) enhanced the conversion to near quantitative (~100%). This obviated the need for chromatographic separation of the unreacted starting materials (excess furaldehyde removed by high vacuum), yielding the desired chalcone, (*E*)-diethyl-6-(3-(furan-2-yl)acryloyl)pyridine-3,4-dicarboxylate (**19**) in a 75% isolated yield. (*Note*: Mass losses were attributed to the adsorption of organic material to the alumina surface). Improved electron withdrawing properties in the ligand can be installed through incorporation of a thiophene moiety to the heterocycle structure. Using this optimised grinding procedure, a thiophene analogue, (*E*)-diethyl-6-(3-(thien-2-yl)acryloyl)pyridine-3,4-dicarboxylate (**20**) was synthesised by reacting **7** with 3 equiv of thiophene-2-carboxaldehyde over Al_2O_3 (basic) in a grind reaction with an isolated yield of 93%. Reaction of chalcone **19** with the pyridinium salt **8** in the presence of ammonium acetate in refluxing ethanol produced the desired furan appended terpyridine, tetraethyl-4′-(furan-2-yl)-[2,2′:6′,2″-terpyridine]-4,4″,5,5″-tetracarboxylate (**21**) in ~80% conversion. After aqueous workup the terpyridine **21** was purified by column chromatography and isolated in a 69% yield. Purification was later simplified by trituration using ethanol. Reaction of the thiophene chalcone **20** with **8** under the same conditions used to prepare **19** resulted in the desired thiophene appended terpyridine, tetraethyl-4′-(thien-2-yl)-[2,2′:6′,2″-terpyridine]-4,4″,5,5″-tetracarboxylate (**22**) in 47% yield.

An attempt was made to directly construct the furan appended terpyridine **21** by reacting 2-furaldehyde with diethyl 6-acetyl-3,4-pyridine dicarboxylate **7** in an aqueous KOH solution containing ammonia (Scheme 5), as recently reported for the preparation of the N749 ligand. Unfortunately this was unsuccessful, most likely due to the basic conditions employed, resulting in ester hydrolysis. Both of the synthesised terpyridine esters (**21** and **22**) were subjected to the established LiOH hydrolysis conditions, resulting in the clean generation of tetra-acids, 4′-(furan-2-yl)-[2,2′:6′,2″-terpyridine]-4,4″,5,5″-tetracarboxylic acid (**23**) and 4′-(thiophen-2-yl)-[2,2′:6′,2″-terpyridine]-4.4″,5,5″-tetracarboxylic acid (**24**) after pH driven precipitation.

To allow for the ultimate carboxylic acid functionality installation, the furan ring system on terpyridine **21** was oxidised in the presence of $KMnO_4$ (Scheme 6).[13]

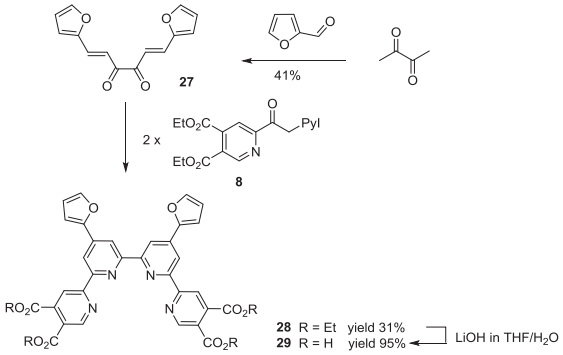


Scheme 6. Synthesis of pentacarboxy terpyridine **29**.

The reaction applied a modified literature method[14] using refluxing *t*-butanol:water (2:1) with $KMnO_4$ (10 equiv) in the absence of base for 14 h. This resulted in complete oxidation of the furan ring however the ester groups were partially hydrolysed, which lead to a poor mass recovery (~25%). Lowering the reaction temperature to 70 °C allowed for complete oxidation of the furan without ester group cleavage (60% isolated yield). Ester cleavage was then performed using LiOH·H_2O in refluxing THF:water (1:1) for 5 h. After removal of the THF, the solution was adjusted to pH 2 using 1 M H_2SO_4 to protonate the carboxylic acid groups although substantial gelation of the reaction mixture was encountered at this stage. Addition of water and gentle heating was required to disrupt the gel sufficiently to allow continued pH adjustment. Further disruption of the gel was performed through hot filtration allowing the collection of [2,2′:6′,2″-terpyridine]-4,4′,4″,5,5″-pentacarboxylic acid (**26**) as a white solid in isolated yields of 60–70%. The resultant pentacarboxy terpyridine **26** showed limited solubility and could only be dissolved in DMF, DMSO and basified aqueous media. The ^{1}H NMR spectrum of **26** displayed only three signals for the pyridine protons at 8.75, 8.96 and 9.14 ppm, whilst the ^{13}C NMR clearly displayed three different CO resonances at 165.7, 166.3, 167.7 ppm for the three different carboxylic acid carbon environments. HRMS was also obtained, giving a *m*/*z* value of 454.0516, which corresponded to the calculated *m*/*z* value of 454.0517 for the expected $[MH]^+$ peak (see Supplementary data). Elemental analysis of the ligand (post-drying) indicated the inclusion of one water molecule per ligand.

2.4. Quaterpyridine synthesis

Given the success of the terpyridine adducts, the preparation of a quaterpyridine was also undertaken (Scheme 7).



Scheme 7. Synthesis of furan appended quaterpyridine **29**.

First, a dichalcone (1*E*,5*E*)-1,6-difurylhexa-1,5-diene-3,4-dione (**27**) was prepared according to a literature method.[15] A double Krönhke reaction between **27** and two equivalents of **8** was then performed to give a difuran quaterpyridine, (tetraethyl-4′,4″-di(furan-2-yl)-[2,2′:6′,2″:6″,2‴-quaterpyridine]-4,4‴,5.5‴-tetracarboxylate (**28**), having four peripheral ester groups in a 31% isolated yield. The ester hydrolysis was accomplished using the same LiOH hydrolysis method used for the other oligopyridines aforementioned to produce 4′,4″-di(furan-2-yl)-[2,2′:6′,2″:6″,2‴-quaterpyridine]-4.4‴,5.5‴-tetracarboxylic acid (**29**) in 95% yield.

No attempt was made to synthesize an oxidised analogue of **29** as it was understood that the product would be extremely insoluble given the relatively low solubility of **26** even in highly basic media. Reduced solubility of a quaterpyridine analogue would prove impractical for a chelation ligand in DSSC applications.

3. Conclusion

A novel series of new oligopyridine ligands possessing novel anchoring group motifs have been synthesised for the preparation of further ruthenium complexes of increased surface stability. The synthesis of the respective complexes of these ligands and their evaluation of efficiency and stability in dye-sensitized solar cells will be the subject of future research articles from our laboratories.

4. Experimental section

4.1. General

Reagents were acquired from the CSIRO chemical store with the following exceptions: paraldehyde purchased from Merck and diethyl-pyridine-3,4-dicarboxylate purchased from Sigma Aldrich. All solvents used in the synthetic procedures were commercial high purity (HPLC or analytical grade) commercial products. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker BioSpin Av400 spectrometer operating at 400 MHz and 100 MHz respectively. Chemical shift values are reported relative to residual solvent signal (^{1}H, ^{13}C) as a reference. Infrared spectra were recorded on a Perkin Elmer Spectrum 400 FTIR spectrometer fitted with a Specac ATR crystal plate. Low resolution mass spectra were acquired on a Shimadzu Liquid Chromatography–Mass Spectrometer. High resolution mass spectra were acquired on Bruker Bioapex 47e Fourier Transform mass spectrometer. Elemental analyses were conducted at the microanalytical unit of the Research School of Chemistry Australian National University, Acton, ACT.

4.2. Tetraethyl 2,2′-bipyridine-3,3′,4,4′-tetracarboxylate (2)

A suspension of 4,7-dimethylphenathroline (5.00 g, 24.01 mmol) in sodium hydroxide (1.92 g, 48.02 mmol) dissolved in 100 mL of distilled water was treated with $KMnO_4$ (45.53 g, 288.10 mmol). The resulting mixture was heated to reflux and stirred for 18 h. The reaction mixture was cooled to room temperature and filtered. Activated charcoal pellets (10 g) were added to the filtrate and the resulting mixture was stirred and heated at 50 °C for 30 min then filtered through a Celite pad (2×20 mL). The filtrate solution was reduced to half the original volume, pH adjusted to 2 using 4 M HCl and the remaining water was removed under reduced pressure to give a solid mass. The solid was then suspended in ethanol (dry, 300 mL) and treated with 9 mL of conc. sulfuric acid. The resulting mixture was heated to reflux and stirred for 5 days. The white solid in the reaction mixture was collected via filtration, washed with ethanol (2×10 mL) and the filtrate solvent volume reduced by rotary evaporation down to 10–15 mL. The residue was then treated with ice/water slurry, resulting in precipitation of a white solid. Once the ice had melted the precipitate was collected by vacuum filtration, washed with water and dried in a desiccator to give a white solid (3.91 g). The solid was recrystallised with H_2O/EtOH (~2:1 ratio, 5–10 mL) filtered by suction filtration and dried to give the desired compound **2** as fine white crystals (2.60 g, 24%); mp: 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, 6H, J=7.1 Hz, CH_3), 1.38 (t, 6H, J=7.1 Hz, CH_3), 4.28 (q, 4H, J=7.1 Hz, OCH_2), 4.40 (q, 4H, J=7.1 Hz, OCH_2), 7.76 (d, 2H, J=4.9 Hz, ArH), 8.73 (d, 2H, J=4.9 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.1, 61.8, 62.5, 122.9, 129.2, 138.8, 149.4, 154.2, 164.9, 166.8. IR(ATR): 678(w), 737(w), 815(w), 853(w), 880(w), 1009(m), 1058(m), 1074(m), 1009(s), 1129(m), 1197(m), 1258(s), 1365(w), 1389(w), 1448(w), 1466(w), 1562(w), 1717(s), 2937, (w), 2976(m), 3082(w). MS (ESI): Calculated m/z $[MH]^+$ 445.2, Observed m/z $[MH]^+$ 445.1. Elemental Analysis for $C_{22}H_{24}N_2O_8$: C, 59.45; H, 5.44; N, 6.30. Found C, 59.42; H, 5.38; N, 6.27.

4.3. [2,2′-Bipyridine]-3,3′,4,4′-tetracarboxylic acid (1)

Tetraethyl 2,2′-bipyridine-3,3′-4,4′-tetracarboxylate (**2**) (2.60 g, 5.85 mmol) and lithium hydroxide monohydrate (2.45 g, 58.50 mmol) were combined in 40 mL of THF/water (1:1 ratio) and the resulting mixture was heated to reflux whilst stirring for 5 h. The reaction mixture was cooled to room temperature and THF was removed by rotary evaporation. The solution was adjusted to pH 1.5–2 with 4 M HCl then the solvent volume was reduced in volume by 1/3rd. The mixture was allowed to stand at room temperature, resulting in the precipitation of a solid. The solid was collected by filtration, washed with cold diethyl ether and dried to give a white solid (952 mg). The collected solid was found to be not completely soluble in methanol. The solid was taken up in methanol, filtered and solvent removed by rotary evaporation to give the desired compound **1** as a white solid, Crop 1 (559 mg). A second crop was obtained by taking the filtrate and removing the diethyl ether by rotary evaporation. Once the diethyl ether had been removed an additional 1/3rd volume of water was removed and the solution was then allowed to stand at room temperature, resulting again in the precipitation of a solid. The solid was collected by filtration, washed with cold diethyl ether and dried to give the desired compound **1** as a white solid, Crop 2 (921 mg), which was completely soluble in methanol. Characterisation data obtained was identical to previous preparations. Overall yield 76%; mp: >190 °C (decomp.); ^{1}H NMR (400 MHz, d_4-MeOD): δ7.78 (d, 2H, J=4.9 Hz, ArH), 8.67 (d, 2H, J=4.9 Hz, ArH).^{13}C NMR (100 MHz, d_4-MeOD): δ 123.9, 130.6, 141.3, 150.7, 155.9, 168.1, 170.1.MS (ESI): Selected IR bands (cm^{-1}): 3509 br m, 3384 br w, 3155 br m, 3098 br m, 1848 br m, 1777 m, 1705 m, 1674 m, 1620 m, 1602 m, 1407 m, 1273 m, 1246 m, 1120 w, 1103 w, 897 w, 849 w, 727 w, 667 w, 638 w, 568 w. Calculated m/z $[MH]^+$ 333.0, Observed m/z $[MH]^+$ 333.0. Calculated m/z $[MH]^-$ 331.0, Observed m/z $[MH]^-$ 330.9. Elemental Analysis for $C_{14}H_8N_2O_8$: C, 50.61; H, 2.43; N, 8.43. Found C, 47.60; H, 2.70; N, 7.7.

4.4. Tetramethyl 2,2′-bipyridine-3,3′,4,4′-tetracarboxylate (3)

A suspension of 4,7-dimethylphenathroline (5.00 g, 24.01 mmol) in sodium hydroxide (1.92 g, 48.02 mmol) dissolved in 100 mL of distilled water was treated with $KMnO_4$ (45.53 g, 288.10 mmol). The resulting mixture was heated to reflux and stirred for 18 h, cooled to room temperature and finally filtered. Activated charcoal pellets (10 g) were added to the filtrate and the resulting mixture was stirred and heated at 50 °C for 30 min then filtered through a Celite pad (2×20 mL). The filtrate solution was reduced to half the original volume, the pH was adjusted to 2 using 4 M HCl and the remaining water was removed under reduced pressure to give a solid mass. The solid was then suspended in methanol (dry, 250 mL) and treated with 9 mL of conc. sulfuric acid. The resulting mixture was heated to reflux and stirred for 5 days.

The white solid in the reaction mixture was removed by filtration, washed with methanol (2×20 mL) and the filtrate solvent volume reduced by rotary evaporation to 10–15 mL. The residue was then treated with ice/water slurry, resulting in precipitation of a white solid. Once the ice had melted the precipitate was collected by vacuum filtration, washed with water and dried in a desiccator to give a white solid (1.20 g, 13%); mp: 140–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 6H, 2×OCH_3), 3.93 (s, 6H, 2×OCH_3), 7.78 (d, 2H, J=5.0 Hz, ArH), 8.75 (d, 2H, J=5.0 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.8, 53.4, 123.2, 129.2, 138.5, 149.6, 153.8, 165.1, 167.5. Selected IR bands (cm^{-1}): 3009.9 br w, 2958.9 w, 2841.0 w, 1742.3 s, 1728.2, s, 1561.6 m, 1453.7 m, 1430.5 m, 1323.8 w, 1323.8 w, 1260.1 s, 1196.5 s, 1125.4 s, 1101.3 s, 1074.4 s, 1058.5 m, 956.4 s, 892.8 w, 862.6 m, 834.7 w, 810.4 s, 767.6 m, 750.5 m, 709.8 w, 680.4 m. High resolution MS (+ve mode ESI): Calculated m/z $[M+Na]^+$ 411.0799, Observed m/z 411.0806. Elemental Analysis for $C_{18}H_{16}N_2O_8$: C, 55.67; H, 4.15; N, 7.21. Found C, 55.63; H, 4.24; N, 7.25; X-ray Crystallographic Data: $C_{18}H_{16}N_2O_8$, M=388.33 Triclinic, space group P-1. Unit Cell Dimensions: a=7.699(3), b=8.123(3), c=16.632(6) Å, α=99.928(11)°, β=90.596(11)°, γ=117.481(9)° Å, V=904.1(5) Å^3, Z=2, D_c=1.426 g cm^{-3}, μ=0.114 mm^{-1}, F_{000}=404, T=199 K, $2\theta_{max}$=50.1°, 3150 reflections collected, 2542 unique (R_{int}=0.0343). R1=0.0390, wR2=0.1201 for 2542 data with I>2σI; Largest diff. peak and hole 0.946 and −0.984 e.A^{-3}.

4.5. Tetraethyl 2,2′-bipyridine-4,4′,5,5′-tetracarboxylate (4)

Diethyl pyridine-3,4-dicarboxylate (1.00 g, 4.48 mmol) was treated with palladium on carbon (200 mg, Pd/C with 50% H_2O) and heated to 200 °C under an argon atmosphere and left to stir for 7 days. The mixture was hot filtered through a Celite pad and washed with portions of $CHCl_3$ (3×50 mL). The $CHCl_3$ was removed by distillation and the collected residue purified by column chromatography (EtOAc), giving the desired product as a colourless crystalline solid **4** (120 mg, 12%). Note: Procedure could not be consistently repeated. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36–1.43 (m, 12H, CH_3), 4.37–4.47 (m, 8H, OCH_2), 8.66 (s, 2H, ArH), 9.12 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 14.2, 62.2, 62.5, 120.0, 125.8, 142.3, 150.6, 157.4, 165.1, 166.5. Selected IR bands (cm^{-1}): 3453 br w, 3082 w, 2976 w, 2937 w, 1717 s, 1562 w, 1466 w, 1448 w, 1389 w, 1365 w, 1258 s, 1197 m, 1129 w, 1099 m, 1074 m, 1058 m, 1009 m, 880 w, 853 w, 815 w, 771 w, 750 w, 737 w, 678 w. MS (ESI): Calculated m/z $[MH]^+$ 445.1605, Observed m/z $[MH]^+$ 445.1592.

4.6. 4,4′,5,5′-Tetramethyl-2,2′-bipyridine (5)

Bipyridine prepared according to a literature procedure by Mines et al.[4]

4.7. 5,5′-Diethyl-4,4′-dimethyl-2,2′-bipyridine (6)

3-Ethyl-4-methylpyridine (50.0 g, 412.61 mmol) was treated with palladium on carbon (10 g, Pd/C with 50% H_2O) and heated to 180 °C under an argon atmosphere and left to stir for 7 days. The mixture was hot filtered through a Celite pad and washed with portions of $CHCl_3$ (3×50 mL). The $CHCl_3$ was removed by distillation and the remaining mixture left to cool to room temperature, which resulted in the formation of colourless crystals. The crystals were collected by suction filtration and washed with heptanes until the washings were clear, giving the desired product as a colourless crystalline solid **6** (3.20 g, 6.5%); mp: 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, 6H, J=7.6 Hz, CH_3), 2.38 (s, 6H, $ArCH_3$), 2.68 (q, 4H, J=7.6 Hz, OCH_2), 8.12 (s, 2H, ArH), 8.38 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 18.9, 23.7, 122.2, 137.9, 146.0, 148.8, 154.2. MS (ESI): Calculated m/z $[MH]^+$ 241.2, Observed m/z $[MH]^+$ 241.1.

4.8. Diethyl 6-acetyl-3,4-pyridine dicarboxylate (7)

Synthesis conducted following a modified literature method.[9]

Diethyl pyridine-3,4-dicarboxylate (10.00 g, 44.8 mmol) was added to a solution of paraldehyde (29.6 g, 672 mmol) in CH_3CN (140 mL) at room temperature. Addition of $FeSO_4$·$7H_2O$ (0.6 g), TFA (6.8 g) and 70% ^{t}BuOOH (20 g) was then performed and the resulting mixture was heated to reflux for 18 h. Once cooled to room temperature the acetonitrile was removed in vacuo and the residue was taken up in water (150 mL) and extracted with toluene (4×100 mL). The combined organic fractions were dried over $MgSO_4$, filtered and solvent remove by rotary evaporation. The brown residue was purified by passage through multiple silica gel plugs (SiO_2, heptane/ethyl acetate, 3:1, ~5 g of crude material per column) with the desired compound eluting first, collected as a pale yellow oil **7** (8.51 g, 72% yield) after solvent removal. NB: Able to recover additional amounts by conducting further chromatography on impure fractions. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27–1.41 (m, 6H, CH_3×2), 2.74 (s, 3H, CH_3), 4.39–4.45 (m, 4H, OCH_2×2), 8.20 (d, 1H, J=0.6 Hz, ArH), 9.05 (d, 1H, J=0.6 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 26.0, 62.6, 62.7, 120.1, 128.6, 141.5, 150.0, 155.6, 165.0, 165.7, 198.7. MS (ESI): Calculated m/z $[MH]^+$ 266.1, Observed m/z $[MH]^+$ 266.0. Calculated m/z $[M+Na]^+$ 288.1, Observed m/z $[M+Na]^+$ 288.0.

4.9. Pyridinium iodide salt of diethyl 6-acetyl-3,4-pyridine dicarboxylate (8)

Synthesis conducted following a modified literature method.[9]

A solution of diethyl 6-acetyl-3,4-pyridine dicarboxylate (**7**) (4.00 g, 15.08 mmol), and iodine (4.21 g, 16.59 mmol), in dry pyridine (40 mL) was heated to reflux for 3 h under an argon atmosphere. After this time the reaction mixture was cooled, treated with diethyl ether (40 mL), and then stored at 4 °C overnight whilst remaining under argon. The precipitate formed was filtered by suction filtration, washed with diethyl ether (3×40 mL) then dried in a vacuum desiccator, giving the desired product (**8**) as a brown solid (8.12 g, 29% purity by NMR, 33% Yield). Product used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.29–1.35 (m, 6H, CH_3), 4.35–4.42 (m, 4H, OCH_2), 6.51 (s, 2H, CH_2), 8.25 (s, 1H, Py-H), 8.30 (t, 2H, J=7.0 Hz, Py-H), 8.75 (t, 1H, J=7.8 Hz, Py-H), 9.00 (d, 2H, J=6.0 Hz, Py-H), 9.26 (s, 1H, Py-H). LR-MS (ESI): Calculated m/z $[MH]^+$ 343.1, Observed m/z $[MH]^+$ 343.

4.10. Diethyl-4′,5′-dimethyl-[2,2′-bipyridine]-4,5-dicarboxylate (9)

Procedure adapted from a literature method.[9]

A mixture of pyridiumium salt (**8**) (6.06 g, 7.48 mmol), 2-methyl-2-butenal (629.18 mg, 7.48 mmol) and ammonium acetate (5.69 g, 74.80 mol) was dissolved in ethanol (90 mL) and heated to reflux for 3 h. The ethanol was then removed by rotary evaporation and the oil was stored at 4 °C overnight. The mixture was then filtered and washed with cold ethanol (3×20 mL) giving the desired product **9** as a yellow solid (1.62 g, 66%); mp: 264 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29–1.40 (m, 6H, CH_3×2), 2.32 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.31–4.44 (m, 4H, OCH_2×2), 8.22 (d, 1H, J=0.6 Hz, ArH), 8.41 (d, 1H, J=0.6 Hz, ArH), 8.53 (d, 1H, J=0.6 Hz, ArH), 9.10 (d, 1H, J=0.6 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 14.1, 16.4, 19.3, 61.9, 62.2, 118.7, 122.6, 123.9, 133.9, 142.1, 146.7, 149.9, 150.2, 152.1, 159.6, 165.2, 166.8. Low Resolution MS (ESI): Calculated m/z $[MH]^+$ 329.1, Observed m/z $[MH]^+$ 329.0.

4.11. 2,2′-Bipyridine-4,4′,5,5′-tetracarboxylate (10)

Diethyl 4′,5′-dimethyl-[2,2′-bipyridine]-4,5-dicarboxylate (**9**) (2.50 g, 7.61 mmol) and sodium hydroxide (609 mg, 15.23 mmol)

was added to water (100 mL) then potassium permanganate (12.03 g, 76.14 mmol) was added in small portions over a 10 min period. The resulting mixture was heated to reflux and stirred for 18 h. The reaction mixture was cooled to room temperature, filtered through a Celite pad and washed with water (3×20 mL). The solution was concentrated to approximately half its original volume. The pH of the solution was adjusted to pH 2 using 4 M HCl and the solution left at room temperature to precipitate. The mixture was filtered and washed with copious amounts of water to remove any traces of salt. The precipitate was dried in a desiccator overnight giving the product **10** as a white precipitate (400 mg, 16%); mp: 282 °C (decomp.); ^{1}H NMR (400 MHz, d$_4$-MeOH): δ 9.04 (s, 2H, ArH), 9.43 (s, 2H, ArH). ^{13}C NMR (100 MHz, d$_4$-MeOH): δ 122.1, 129.0, 145.8, 159.8, 169.5, 171.2. MS (ESI, -ve mode): Calculated *m*/*z* [M]$^-$ 331.0208, Observed 331.0208 [MH]$^-$. Elemental Analysis for $C_{14}H_8N_2O_8$: C, 50.61; H, 2.43; N, 8.43. Found C, 50.50; H, 2.38; N, 8.74.

4.12. Ethyl 2-acetyl-isonicotinate (11)

Synthesis conducted following a previously reported method.[9]

Methyl isonicotinate (9.07 g, 60.0 mmol) was added to a solution of paraldehyde (45.0 g, 1.50 mol) in CH_3CN (150 mL) at room temperature. Addition of $FeSO_4 \cdot 7H_2O$ (300 mg, 1.08 mmol), TFA (7.0 g) and 70% ^{t}BuOOH (16.0 g) was then performed and the resulting mixture was heated to reflux for 4 h. Once cooled to room temperature the acetonitrile was removed in vacuo and the residue was taken up in water (100 mL) and extracted with toluene (3×75 mL). The combined organic fractions were dried over $MgSO_4$, filtered and solvent removed by rotary evaporation. The brown residue was purified by passage through a silica gel plug (SiO_2, heptane/ethyl acetate, 4:1) with the desired compound **11** eluting first (R_f=0.26), collected as a yellow solid (6.90 g, 60% yield) after solvent removal; mp: 48–49 °C (lit. 56 °C);[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, *J*=7.1 Hz, CH_3), 2.74 (s, 3H, $COCH_3$), 4.43 (q, 2H, *J*=7.1 Hz, OCH_2), 8.02 (dd, 1H, *J*=4.9 and 1.6 Hz, ArH), 8.54 (dd, 1H, *J*=1.6 and 0.8 Hz, ArH), 8.82 (dd, 1H, *J*=4.9 and 0.8 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 26.1, 62.6, 121.1, 126.3, 139.1, 150.0, 154.7, 164.7, 199.5. Characterisation data for the byproduct ethyl 2,5-diacetylisonicotinate (**12**) Eluted second, 4:1 heptane/ethyl acetate (R_f=0.13). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, 3H, *J*=7.2 Hz, CH_3), 2.61 (s, 3H, $COCH_3$), 2.73 (s, 3H, $COCH_3$), 4.41 (q, 2H, *J*=7.2 Hz, OCH_2), 8.34 (d, 1H, *J*=0.8 Hz, ArH), 8.77 (d, 1H, *J*=0.8 Hz, ArH).

4.13. Pyridinium iodide salt of ethyl 2-acetyl-isonicotinate (13)

Synthesis conducted following a modified literature method.[9]

A solution of ethyl 2-acetyl isonicotinate (**11**) (4.00 g, 20.70 mmol), and iodine (5.25 g, 20.70 mmol), in dry pyridine (40 mL) was heated to reflux for 3 h under an argon atmosphere. After this time the reaction mixture was cooled and then stored at 4 °C overnight whilst remaining under argon. The precipitate formed in the cooled mixture was filtered by suction filtration, washed with $CHCl_3$ (1×10 mL) and diethyl ether (3×20 mL) then dried in a vacuum desiccator, giving the desired product **13** as a beige crystalline solid (5.75 g, 70%). Product used without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.35 (t, 3H, *J*=7.1 Hz, CH_3), 4.41 (q, 2H, *J*=7.1 Hz, OCH_2), 6.55 (s, 2H, CH_2), 8.24 (d, 1H, *J*=4.9 Hz, Py-H), 8.30 (t, 2H, *J*=7.0 Hz, Py-H), 8.35 (s, 1H, Py-H), 8.75 (t, 1H, *J*=7.8 Hz, Py-H), 9.03 (d, 2H, *J*=5.9 Hz, Py-H), 9.09 (d, 1H, *J*=4.9 Hz, Py-H). ^{13}C NMR (100 MHz, DMSO-d_6): 14.4, 62.6, 67.1, 120.7, 124.5, 128.2, 139.4, 146.8, 149.7, 151.5, 152.0, 164.2, 191.3. MS (ESI): Calculated *m*/*z* [MH]$^+$ 271.1, Observed *m*/*z* [MH]$^+$ 271.0.

4.14. Ethyl 5′-methyl-[2,2′-bipyridine]-4-carboxylate (15)

Synthesis conducted following a modified literature method.[17]

A mixture of pyridinium salt (**13**) (5.75 g, 14.44 mmol), methacrolein (3.04 g, 43.32 mmol) and ammonium acetate (10.99 g, 144.40 mmol) dissolved in dry ethanol (40 mL) was heated to reflux for 3 h. The ethanol was then removed by rotary evaporation, water (100 mL) was added and the crude mixture was extracted with ethyl acetate (3×100 mL). The combined organic fractions were dried over $MgSO_4$, filtered and solvent removed in vacuo to give a crystalline orange solid, which was further purified by column chromatography (SiO_2, heptane/ethyl acetate, 2:1, R_f=0.22) to give the desired product **15** as a light yellow solid (3.04 g, 86% yield); mp: 69–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, *J*=7.1 Hz, CH_3), 2.39 (s, 3H, CH_3), 4.43 (q, 2H, *J*=7.1 Hz, OCH_2), 7.62 (ddd, 1H, *J*=8.1, 2.2 and 0.7 Hz, ArH), 7.82 (dd, 1H, *J*=5.0 and 1.5 Hz, ArH), 8.28 (d, 1H, *J*=8.1 Hz, ArH), 8.52 (d, 1H, *J*=1.5 and 0.7 Hz, ArH), 8.78 (dd, 1H, *J*=5.0 and 0.8 Hz, ArH), 8.87 (dd, 1H, *J*=1.5 and 0.8 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 18.6, 61.9, 120.1, 120.2, 121.0, 122.6, 134.1, 137.7, 139.0, 150.0, 153.1, 157.6, 165.5. Selected IR bands (cm^{-1}): 3425 br w, 2976 w, 2937 w, 1726 s, 1719, s, 1552 m, 1414 m, 1369 m, 1279 m, 1243 s, 1224 s, 1102 m, 1017 s, 837 s, 770 m, 751 s, 727 s, 680 m, 647 w, 579 w. MS (ESI): Calculated *m*/*z* [MH]$^+$ 243.1, Observed *m*/*z* [MH]$^+$ 243.0. Anal. calcd for $C_{14}H_{14}N_2O_2$; C, 69.41; H, 5.82; N, 11.56. Found C, 68.67; H, 6.46; N, 11.20.

4.15. Ethyl 5′-(bromomethyl)-[2,2′-bipyridine]-4-carboxylate (16)

Procedure adapted from a literature method.[11]

A mixture of bipyridine (0.50 g, 2.06 mmol), NBS (404 mg, 2.27 mmol) and AIBN (40 mg) was dissolved in carbon tetrachloride (10 mL) was heated to reflux for 2 h. The reaction mixture was filtered and the solvent was then removed by distillation. The crude mixture was purified further by column chromatography (SiO_2, $CHCl_3$/ethyl acetate, 4:1) to give the desired product **16** as a colourless solid (310 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (t, 3H, *J*=7.1 Hz, CH_3), 4.45 (q, 2H, *J*=7.1 Hz, OCH_2), 4.55 (s, 2H, CH_2Br), 7.85–7.89 (m, 2H, ArH), 8.42 (d, 1H, *J*=8.2 Hz, ArH), 8.72 (d, 1H, *J*=2.0 Hz, ArH), 8.82 (dd, 1H, *J*=4.9 and 0.6 Hz, ArH), 8.93 (d, 1H, *J*=0.6 Hz, ArH). MS (LR-ESI): Calculated *m*/*z* [MH]$^+$ 331, Observed *m*/*z* [MH]$^+$ 331.

4.16. Ethyl 5′-((diethoxyphosphoryl)methyl)-[2,2′-bipyridine]-4-carboxylate (17)

Synthesis conducted following a modified literature method.[18]

Ethyl 5′-(bromomethyl)-[2,2′-bipyridine]-4-carboxylate (**16**) (200 mg, 0.62 mmol) was added to a solution of $CHCl_3$ (10 mL) containing triethylphosphite (1.0 g, 6.23 mmol) and the resulting mixture was heated to reflux for 5 h under an argon atmosphere. Once cooled to room temperature the $CHCl_3$ and triethylphosphite were removed by vacuum distillation and the residue was purified by column chromatography (SiO_2, ethyl acetate: acetone, 3:1) with the desired compound **17**, eluting (R_f=0.35), collected as a colourless oil (124 mg, 53% yield) after solvent removal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (t, 6H, *J*=7.1 Hz, CH_3), 1.34 (t, 3H, *J*=7.1 Hz, CH_3), 3.12 (d, 2H, *J*=21.8 Hz, $CH_2PO(OEt)_2$), 4.01–3.96 (m, 4H, OCH_2), 4.36 (q, 2H, *J*=7.1 Hz, OCH_2), 7.72 (dt, 1H, *J*=8.2 and 2.4 Hz, ArH), 7.77 (dd, 1H, *J*=5.0 and 1.6 Hz, ArH), 8.29 (d, 1H, *J*=8.2 Hz, ArH), 8.53 (t, 1H, *J*=2.4 Hz, ArH), 8.71 (dd, 1H, *J*=5.0 and 0.8 Hz, ArH), 8.81 (d, 1H, *J*=1.6 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 14.3, 16.4, 16.5, 61.8, 62.3, 62.4, 120.3, 120.9, 122.8, 138.1, 138.2, 150.0, 150.1, 154.1, 157.0, 165.2. MS (LR-ESI): Calculated *m*/*z* [MH]$^+$ 379.1, Observed *m*/*z* [MH]$^+$ 379.0. Elemental Analysis for $C_{18}H_{23}N_2O_5P$: C, 56.99; H, 6.38;

N, 7.38. Found (Run 1) C, 56.82; H, 6.30; N, 7.21. (Run 2) C, 56.81; H, 6.43; N, 7.24.

4.17. (*E*)-Diethyl-6-(3-(furan-2-yl)acryloyl)pyridine-3,4-dicarboxylate (19)

Synthesis conducted following a modified literature method.[12]

A mixture of diethyl 6-acetylpyridine-3,4-dicarboxylate (**7**) (5.00 g, 18.85 mmol) and 2-furaldehyde (5.43 g, 56.55 mmol) was added to 10 g of basic alumina and the resulting mixture was ground together in a mortar and pestle for 20 min then left to stand for 48 h with occasional grinding of the solid mixture. The mixture then transferred onto a sinter and the organics were extracted by continual washing with $CHCl_3$ until the washings ran clear. The combined organic were taken to dryness by heating under vacuum. The solid was then placed under high vacuum to remove the excess 2-furaldehyde to give the desired product as crystalline yellow solid (6.02 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, 6H, J=7.1 Hz, $CH_3\times2$), 4.42 (q, 4H, J=7.1 Hz, $OCH_2\times2$), 6.51 (dd, 1H, J=3.4 and 1.8 Hz, Furan-H), 6.79 (d, 1H, J=3.4 Hz, Furan-H), 7.55 (d, 1H, J=1.8 Hz, Furan-H), 7.71 (d, 1H, J=15.7 Hz, Alkene-H), 8.06 (d, 1H, J=15.7 Hz, Alkene-H), 8.32 (d, 1H, J=0.7 Hz, ArH), 9.10 (d, 1H, J=0.7 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 62.5, 62.7, 113.0, 117.3, 118.2, 121.2, 128.1, 131.8, 141.6, 145.7, 149.9, 152.1, 156.5, 165.1, 165.9, 187.8. Selected IR bands (cm^{-1}): 3147 w, 2984 w, 1731 m, 1715 s, 1660 m, 1598 m, 1580 s, 1548 s, 1473 w, 1443 w, 1391 w, 1382 w, 1372 w, 1361 w, 1287 s, 1264 s, 1235 s, 1205 s, 1182 s, 1144 s, 1110 m, 1082 s, 1075 s, 1030 m, 974 s, 775 s, 749 s, 683 m, 673 m, 592 m. MS (ESI): Calculated m/z $[MH]^+$ 344.1, Observed m/z $[MH]^+$ 344. Anal. calcd for $C_{18}H_{17}NO_6$; C, 62.97; H, 4.99; N, 4.08. Found C, 62.54; H, 5.30; N, 4.04.

4.18. (*E*)-Diethyl-6-(3-(thien-2-yl)acryloyl)pyridine-3,4-dicarboxylate (20)

Synthesis conducted following the same procedure as for **19** using **7** (5.00 g, 18.85 mmol) and 2-thenaldehyde (6.34 g, 56.55 mmol) to give the desired product as yellow solid (1.25 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (t, 6H, J=7.1 Hz, $CH_3\times2$), 4.44 (q, 4H, J=7.1 Hz, $OCH_2\times2$), 7.11 (dd, 1H, J=5.0 and 3.5 Hz, Thienyl-H), 7.45 (d, 1H, J=3.5 Hz, Thienyl-H), 7.48 (d, 1H, J=5.0 Hz, Thienyl-H), 8.01 (d, 1H, J=15.8 Hz, Alkene-H), 8.11 (d, 1H, J=15.8 Hz, Alkene-H), 8.35 (s, 1H, ArH), 9.13 (s, 1H, ArH).

4.19. Tetraethyl-4′-(furan-2-yl)-[2,2′:6′,2″-terpyridine]-4,4″,5,5″-tetracarboxylate (21)

Synthesis conducted following a modified literature method.[9]

A mixture of pyridinium salt (**8**) (4.50 g, 9.57 mmol), (*E*)-diethyl 6-(3-(furan-2-yl)acryloyl)pyridine-3,4-dicarboxylate (**19**) (13.28 g, 9.57 mmol) and ammonium acetate (7.28 g, 95.67 mmol) dissolved in absolute ethanol (80 mL) was heated to reflux for 3 h under argon. The ethanol was then removed by rotary evaporation, water (100 mL) was added and the crude mixture was extracted with ethyl acetate (4×75 mL). The combined organic fractions were dried over $MgSO_4$, filtered and solvent removed in vacuo to give a crystalline dark brown solid. The solid was dissolved in a minimal amount of hot ethanol then stored at 4 °C for 3 h. The solid was filtered and washed with cold ethanol (4×20 mL) to give the desired product as a beige/yellow solid (3.67 g, 65% yield); mp: 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39–1.43 (m, 12H, $CH_3\times4$), 4.41 (q, 4H, J=7.2 Hz, $OCH_2\times2$), 4.47 (q, 4H, J=7.2 Hz, $OCH_2\times2$), 6.53 (dd, 1H, J=3.4 and 1.5 Hz, Furan-H), 7.08 (d, 1H, J=3.4 Hz, Furan-H), 7.57 (d, 1H, J=1.5 Hz, Furan-H), 8.68 (d, 2H, J=0.6 Hz, ArH), 8.73 (s, 2H, ArH), 9.14 (d, 2H, J=0.6 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 14.2, 14.3, 62.1, 62.5, 110.0, 112.4, 116.9, 119.2, 124.6, 139.9, 142.4, 144.3, 150.5, 151.3, 154.6, 158.8, 165.1, 167.1. MS (ESI): Calculated m/z $[MH]^+$ 588.2, Observed m/z $[MH]^+$ 588. Selected IR bands (cm^{-1}): 3110 w, 2981,w, 2934 w, 1716 versus, 1611 m, 1591 s, 1549 s, 1469 m, 1366 s, 1235 versus, 1219 s, 1169 m, 1139 s, 1112 s, 1068 m, 1016 versus 990 m, 894 m, 852 m, 795 m, 749 s, 713 s, 681 m. Anal. calcd for $C_{31}H_{29}N_3O_9$; C, 63.37; H, 4.97; N, 7.15. Found C, 62.34; H, 5.06; N, 6.92.

4.20. Tetraethyl-4′-(thien-2-yl)-[2,2′:6′,2″-terpyridine]-4,4″,5,5″-tetracarboxylate (22)

Synthesis conducted following the same procedure as for **21** using **20** as the chalcone to give the desired product as a beige solid (860 mg, 47% yield); mp: 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (t, 6H, J=7.2 Hz, $CH_3\times2$), 1.46 (t, J=7.2 Hz, 6H, $CH_3\times2$), 4.45 (q, 4H, J=7.2 Hz, $OCH_2\times2$), 4.50 (q, 4H, J=7.2 Hz, $OCH_2\times2$), 7.20 (dd, 1H, J=5.0 and 3.4 Hz, Thienyl-H), 7.50 (dd, 1H, J=5.0 and 1.2 Hz, Thienyl-H), 7.80 (dd, 1H, J=3.4 and 1.2 Hz, Thienyl-H), 8.74 (d, 2H, J=0.78 Hz, ArH), 8.80 (s, 2H, ArH), 9.20 (d, 2H, J=0.7 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 14.2, 14.4, 62.3, 62.6, 119.1, 119.4, 124.7, 126.5, 128.0, 128.7, 141.3, 142.6, 144.1, 150.6, 154.9, 158.9, 165.2, 167.2. Selected IR bands (cm^{-1}): 3116 w, 2982 w, 1729 s, 1711 s, 1584 s, 1547 m, 1462 m, 1441 m, 1396 m, 1367 m, 1270 s, 1266 s, 1226 s, 1172 m, 1124 s, 1089 s, 1066 s, 1009 s, 889 m, 851 m, 835 m, 794 m, 773 m, 712 s, 682 m, 625 w. MS (ESI): Calculated m/z 604.17 $[MH]^+$, Observed m/z 604.2. Anal. calcd for $C_{31}H_{29}N_3O_8S$; C, 61.68; H, 4.84; N, 6.96. Found C, 61.20; H, 4.79; N, 6.64.

4.21. 4′-(Furan-2-yl)-[2,2′:6′,2″-terpyridine]-4,4″,5,5″-tetracarboxylic acid (23)

Terpyridine **21** (2.00 g, 3.40 mmol) and lithium hydroxide monohydrate (1.43 g, 34.04 mmol) were combined in 80 mL of THF/water (1:1 ratio) and the resulting mixture was heated to reflux whilst stirring for 6 h. The reaction mixture was cooled to room temperature and THF was removed by rotary evaporation. The solution was adjusted to pH 2 with 1 M H_2SO_4 resulting the formation of a yellow solid. The solid was collected by filtration, washed with cold water (3×20 mL) and dried under high vacuum to give the desired product as a yellow solid (1.56 g, 96% yield); mp: >250 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.74–6.78 (m, 1H, ArH), 7.54–7.60 (m, 1H, ArH), 7.99 (s, 1H, ArH), 8.71 (s, 2H, ArH), 8.79 (s, 2H, ArH), 9.12 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 112.9, 115.8, 118.6, 139.5, 143.0, 145.1, 150.1, 150.2, 154.5, 157.3, 166.3, 167.7. Selected IR bands (cm^{-1}): 3364 br m, 3073 br m, 2641 br w, 2508 br m, 1980 br w, 1721 s, 1585 s, 1531 s, 1435 m, 1402 m, 1365 m, 1307 s, 1262 s, 1144 m, 1019 m, 988 m, 917 s, 896 s, 838 m, 777 s, 746 s, 625 m, 561 m. Accurate Mass (ESI): $C_{23}H_9N_3O_7$ (dianhydride form) – Calculated m/z $[MH]^+$ 439.0440, Observed m/z $[MH]^+$ 439.0437.

4.22. 4′-(Thiophen-2-yl)-[2,2′:6′,2″-terpyridine]-4.4″,5,5″-tetracarboxylic acid (24)

Terpyridine **22** (400 mg, 0.66 mmol) and lithium hydroxide monohydrate (278 mg, 6.63 mmol) were combined in 30 mL of THF/water (1:1 ratio) and the resulting mixture was heated to reflux whilst stirring for 6 h. The reaction mixture was cooled to room temperature and THF was removed by rotary evaporation. The solution was adjusted to pH 2 with 1 M H_2SO_4 resulting the formation of a yellow solid. The solid was collected by filtration, washed with cold water (3×10 mL) and dried under high vacuum to give the desired product as a yellow solid (316 mg, 97% yield); mp: >225 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.30 (dd, J=5.1 and 3.8 Hz, 1H, ArH), 7.85 (dd, J=5.1 and 1.1 Hz, 1H, ArH), 8.05 (dd, J=3.8 and 1.1 Hz, 1H, ArH), 8.75 (m, 4H, ArH), 8.79 (s, 2H, ArH), 9.16 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 117.7, 118.7, 126.0, 127.5,

129.2, 129.4, 139.9, 143.1, 143.4, 150.1, 154.7, 157.3, 166.4, 167.8. Accurate Mass (ESI): $C_{23}H_{13}N_3O_8S$ (dianhydride form)—Calculated m/z 455.0207 $[MH]^+$, Observed 455.0208 m/z $[MH]^+$.

4.23. 4,4″,5,5″-Tetrakis(ethoxycarbonyl)-[2,2′:6′,2″-terpyridine]-4′-carboxylic acid (25)

Tetraethyl-4′-(furan-2-yl)-[2,2′:6′,2″-terpyridine]-4.4″,5,5″-tetracarboxylate (**21**) (4.00 g, 6.81 mmol) was added to a 2:1 mixture of ^{t}BuOH/water (90 mL) then potassium permanganate (10.76 g, 68.08 mmol) was added in portions over a 10 min period. The resulting mixture was left to stir at 70 °C overnight. The reaction mixture was treated with a saturated solution of sodium metabisulphite until all residual purple coloration had been removed then the mixture was filtered through a Celite pad to remove the spent MnO_2 and was washed with water (2×50 mL) and warm acetone (2×50 mL). The solution was concentrated to half of the original volume then pH adjusted to 2 using 1 M H_2SO_4 and the resulting precipitate was collected by suction filtration, giving the desired compound **25** as a white solid (2.70 g, 70% yield); mp: 323 °C (melt-decomp.); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.35 (m, 12H, CH_3×4), 4.35–4.43 (m, 8H, OCH_2×4), 8.76 (s, 2H, ArH), 8.92 (s, 2H, ArH), 9.14 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 13.7, 13.9, 62.0, 62.2, 118.8, 121.6, 125.2, 141.4, 150.1, 154.4, 157.1, 164.5, 165.5, 165.6. Accurate Mass (ESI): $C_{28}H_{28}N_3O_{10}$—Calculated m/z for $[MH]^+$ 566.1769, Observed m/z $[MH]^+$ 566.1764. Selected IR bands (cm^{-1}): 3148 w, 2986 w, 2938 w, 2905 w, 1723 versus, 1591 s, 1549 s, 1466 m, 1444 w, 1386 w, 1367 s, 1266 versus, 1229 s, 1204 s, 1173 m, 1128 s, 1116 versus, 1088 m, 908 m, 882 s, 773 s, 690 versus, 677 m. Anal. calcd for $C_{28}H_{27}N_3O_{10}$: C, 59.47; H, 4.81; N, 7.43. Found C, 58.47; H, 4.65; N, 7.07.

4.24. [2,2′:6′,2″-Terpyridine]-4,4′,4″,5,5″-pentacarboxylic acid (26)

4,4″,5,5″-Tetrakis(ethoxycarbonyl)-[2,2′:6′,2″-terpyridine]-4′-carboxylic acid (**25**) (5.5 g, 9.73 mmol) and lithium hydroxide monohydrate (4.08 g, 97.25 mmol) were combined in 160 mL of THF/water (1:1 ratio) and the resulting mixture was heated to reflux whilst stirring for 6 h. The reaction mixture was cooled to room temperature and THF was removed by rotary evaporation. The solution was adjusted to pH 2 with 1 M H_2SO_4 resulting the formation of a gel. Additional amounts of water were added (100 mL) and the resulting mixture was stirred and heated to 70–80 °C on a rotary evaporator for 20 min then immediately hot filtered collect the precipitated solid. The solid was collected by filtration, washed with cold water (3×20 mL) and dried under high vacuum to give **26** as a white solid (2.66 mg, 60% yield); mp: 325 °C (melt-decomp.); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.75 (s, 2H, ArH), 8.96 (s, 2H, ArH), 9.14 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 118.67, 121.5, 126.2, 141.3, 143.2, 150.2, 155.0, 156.9, 165.7, 166.3, 167.7. Accurate Mass (ESI): $C_{20}H_{12}N_3O_{10}$ – Calculated m/z $[MH]^+$ 454.0517, Observed m/z $[MH]^+$ 454.0516. Selected IR bands (cm^{-1}): 2965 br m, 2662 br w, 2526 br m, 1700 versus, 1593 s, 1553 s, 1483 w, 1420 s, 1374 m, 1340 m, 1279 m, 1260 s, 1180 m, 1128 m, 1092 s, 961 m, 926 m, 908 s, 773, 804 m, 777 m, 725 m, 688 m, 660 s. Anal. calcd for $C_{20}H_{13}N_3O_{11}$ (ligand + $1H_2O$): C, 50.97; H, 2.78; N, 8.92. Found C, 51.59; H, 2.96; N, 8.57.

4.25. (1*E*,5*E*)-1,6-Difurylhexa-1,5-diene-3,4-dione (27)

To a solution of furfural (8.93 g, 92.93 mmol) and 2,3-butanedione (2.00 g, 23.23 mmol) in MeOH (25 mL), piperidine (395 mg, 4.65 mmol) and glacial acetic acid (279.02 mg, 2.65 mmol) were added sequentially. The mixture was then sto reflux for 6.5 h. Once cooled to room temperature the MeOH was removed in vacuo and the mixture was placed at 4 °C for 4 h. The mixture was then filtered and washed with cold MeOH then dried in a vacuum desiccator, giving the desired product as an orange solid (2.31 g, 41%); mp: 153 °C (mp: 156.8–158.9 °C);[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46–6.56 (2H, m, Fur-H), 6.80, (2H, d, Fur-H), 7.31 (2H, d, Fur-H), 7.58 (2H, d, CH), 7.63 (2H, d, CH). LR-MS 243.0 m/z $[MH]^+$.

4.26. (Tetraethyl-4′,4″-di(furan-2-yl)-[2,2′:6′,2″:6″,2‴-quaterpyridine]-4,4‴,5.5‴-tetracarboxylate (28)

A mixture of pyridinium salt **8** (2.00 g (45% purity), 1.91 mmol), (1*E*,5*E*)-1,6-difurylhexa-1,5-diene-3,4-dione (231.8 mg, 0.96 mmol) and ammonium acetate (1.48 g, 19.14 mmol) dissolved in dry ethanol (10 mL) was heated to reflux for 3 h under argon. After being left to standing at room temperature overnight the mixture was filtered and washed with ethanol to give a gray solid. The collected solid was then dissolved in $CHCl_3$ and triturated with heptane, with the resultant solid collected by suction filtration then dried in a vacuum desiccator, giving the desired product **28** as a brown solid (220 mg, 31%); mp: 211 °C (melt-decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36–1.54 (12H, m, CH_3), 4.40–4.60 (8H, m, CH_2), 6.54–6.64 (2H, m, Fur-H), 7.17 (2H, d, Fur-H), 7.66 (2H, s, Fur-H), 8.87 (6H, t, Py-H), 9.09 (2H, s, Py-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.3, 62.2, 62.5, 109.7, 112.4, 116.4, 116.5, 119.5, 124.9, 139.8, 142.0, 144.2, 150.4, 151.8, 154.3, 156.1, 159.2, 165.4, 167.0. MS (ESI): Calculated m/z for $C_{40}H_{34}N_4O_{10}$ $[M]^+$ 730.2, observed m/z $[M]^+$ 730.1.

4.27. 4′,4″-Di(furan-2-yl)-[2,2′:6′,2″:6″,2‴-quaterpyridine]-4.4‴,5.5‴-tetracarboxylic acid (29)

Tetraethyl 4′,4″-di(furan-2-yl)-[2,2′:6′,2″:6″,2‴-quaterpyridine]-4.4‴,5.5‴-tetracarboxylate (115 mg, 0.27 mmol) and lithium hydroxide monohydrate (225 mg, 5.38 mmol) were combined in 10 mL of THF/water (1:1 ratio) and the resulting mixture was heated to reflux whilst stirring for 6 h. The reaction mixture was cooled to room temperature and THF was removed by rotary evaporation. The solution was adjusted to pH 2 with 1 M H_2SO_4 resulting the formation of a gel. Additional amounts of water were added (20 mL) and the resulting mixture was stirred with a plastic spatula (*not nickel metal*) to break up the gel. The mixture was heated to 60–70 °C on a rotary evaporator then hot filtered to remove the precipitated solid. The solid was collected by filtration, washed with cold water (3×20 mL, pH 2) and dried to give **29** as a brown solid (95 mg, 95%); mp: >240 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (2H, q, Fur-H), 7.60 (2H, d, Fur-H), 8.03 (2H, s, Fur-H), 8.82 (2H, d, Py-H) 8.87 (2H, s, Py-H) 8.89 (2H, d, Py-H), 9.2 (2H, s, Py-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 110.9, 112.8, 115.4, 115.5, 118.5, 125.7, 139.3, 143.0, 145.3, 149.9, 150.5, 154.2, 155.4, 157.4, 166.4, 167.8. Accurate Mass (ESI): $C_{32}H_{18}N_4NaO_{10}$ – Calculated m/z $[M+Na]^+$ 641.0915, Observed m/z $[M+Na]^+$ 641.0918.

5. Crystallographic data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1056206. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.06.029. These data include MOL files and InChiKeys of the most important compounds described in this article.

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