Tetrahedron 71 (2015) 5238–5247

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

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

Clint P. Woodward [a], Campbell J. Coghlan [a], Thomas Rüther [a], Timothy W. Jones [b], Yanek Hebting [c], Richard L. Cordiner [c], Ryan E. Dawson [c], Diane E.J.E. Robinson [c], Gregory J. Wilson [b,*]

[a] CSIRO Energy Flagship, Clayton Laboratories, Bayview Ave, Clayton 3168, Australia
[b] CSIRO Energy Flagship, Energy Centre, 10 Murray Dwyer Cct, Mayfield West 2304, Australia
[c] Dyesol Australia Pty Ltd, 3 Dominion Place, Queanbeyan, NSW 2620, Australia

ARTICLE INFO

Article history:
Received 22 January 2015
Received in revised form 26 May 2015
Accepted 9 June 2015
Available online 14 June 2015

Keywords:
Oligopyridine
Dye anchoring
Krönhke synthesis
Krönhke synthesis
DSSC
Solar

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.

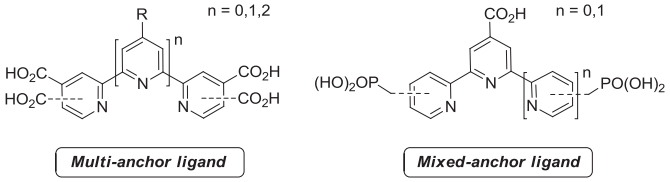


Fig. 1. Concept for improved ligand anchoring ability.

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

* Corresponding author. Tel.: +61 2 4960 6017; fax: +61 2 4960 6021; e-mail address: greg.wilson@csiro.au (G.J. Wilson).

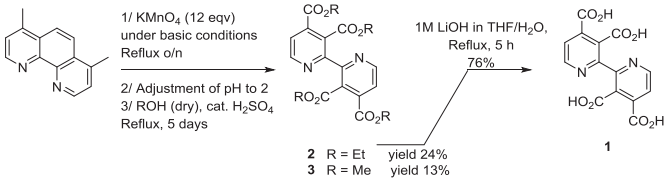
http://dx.doi.org/10.1016/j.tet.2015.06.029

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).

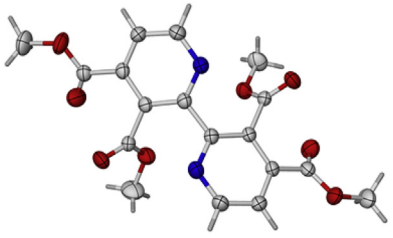
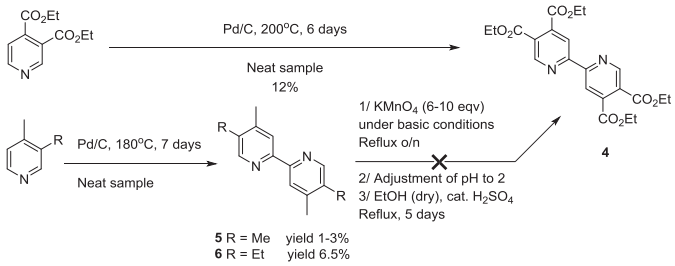


Fig. 2. Crystal structure of tetramethyl-2,2′-bipyridine-3,3′,4,4′-tetracarboxylate (**3**).

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