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Review

Oligomers and macrocycles with *[m]*pyridine*[n]*pyrrole ($m + n \geq 3$) domains: Formation and applications of anion, guest molecule and metal ion complexes

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This article is dedicated to all the world's beer-quaffing, billionaire chemists; what inspiration.

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ABSTRACT

This review provides comprehensive coverage of larger *[m]*pyridine*[n]*pyrrole oligomeric ($m + n > 3$) chains or *[m]*pyridine*[n]*pyrrole ($m + n \geq 3$) macrocycles with at least three directly linked heterocyclic rings, their syntheses and the complexes they form with anions, guest molecules and metal cations. Their applications found to date are summarised and future prospects are considered.

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Abbreviations: CV, cyclic voltammetry; $Fc^{+/0}$, ferrocene/ferrocenium couple; K_a, association constant; Py, pyridine; Pyr, pyrrole/pyrrolide; SC-XRD, Single Crystal X-ray Diffraction; SCE, Standard Calomel Electrode; (TD)-DFT, (Time Dependent)-Density Functional Theory.

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1. Introduction

The focus of this review is linear *[m]*pyridine*[n]*pyrrole ($m + n > 3$) (H_n**L**) and *[m]*pyridine*[n]*pyrrole ring ($m + n \geq 3$) (H_n**M**)[1] systems, their syntheses and the complexes they form with anions, guest molecules and metal cations. The applications found to date are summarised and future prospects are considered.

We recently reviewed the coordination chemistry of tridentate pyridine-pyrrolide pincer ligands $\mathbf{B}^{-}$**–E**$^{2-}$, Fig. 1 [1]. These ligands can be thought of as being derived from the commonplace meridional-binding terpyridine ligand by replacement of one or two pyridyl donors by pyrrolide donors. The effects of substituting a pyrrolide for a pyridyl donor are: (*i*) the ligand becomes negatively charged, thus providing better charge compensation for higher oxidation state metal species; (*ii*) the pyrrolide donor is a weak-field donor, favouring high-spin species; (*iii*) coordination of the 5-membered pyrrolide ring leads to strain upon forming chelate ring(s) in a complex. Hence, the chemistry of complexes with ligands having cores **B–E** differ sharply from that displayed by metal-terpyridine complexes. We have identified new opportunities for metal ion coordination complexes of cores **B–E**.

Herein we consider systems of directly linked *[m]*pyridine*[n]*pyrrole rings in which one or more of cores **B**–**E** are incorporated into larger oligomeric chains ($m + n > 3$) or macrocycles ($m + n \geq 3$). The complexes of these systems with neutral molecules, anions and metal cations are comprehensively covered in this review. So-called porphyrinoid or expanded porphyrin systems exclusively with conjugated methinyl linkages between the pyrrole and pyridine rings or with pyridine rings only as substituents to a central oligo(pyrrole)-derived conjugated ring system are outside the scope of this review and are not considered. The reader is referred the many excellent articles already available that review these systems, a selection of which is given here [2–20].

A brief note on compound numbering and nomenclature. This is always a difficult, vexing issue. We have tried for simplicity. Throughout this review, linear *[m]*pyridine*[n]*pyrrole chains, where $m + n$ is the total number of heterocycle rings, are given the generic descriptor **L** for "linked", irrespective of whether they are formed from cores **B**–**E** and irrespective of subsequent aryl annulation of the heterocyclic rings, that is neither pyrrole (pyr) and indole nor pyridine (py) and quinoline are distinguished. Similarly, *[m]*pyridine*[n]*pyrrole rings are given the generic descriptor **M** for "macrocycle". Each *[m]*pyridine*[n]*pyrrole substance is numbered sequentially by a superscript on the right and with the acidic hydrogen atoms given to the left (*e.g.*, $H_2\mathbf{L}^5$ or $H_6\mathbf{M}^8$). We also include the following information in the name for macrocycles (**M**) in the Scheme caption and in the text at first mention: where π-conjugation around the macrocycle ring is complete, the prefix "cyclo" preceded by the number of π-electrons, X, in the shortest pathway in brackets [X] and, as a suffix, the Franck nomenclature for *meso*-bridges in parentheses (F1.F2.F3. . . where F1, F2, F3, *etc.* are the number of *meso*-C(sp^2) atoms proceeding from the longest bridge and ordered clockwise) [19,20]. We have omitted the Franck nomenclature [19,20] for macrocycles comprised only of directly linked heterocyclic rings as it is redundant; *i.e.* (0.0.0.0. . .). The prefix "calix" is employed to indicate macrocycles (**M**) where the π-conjugation around the macrocyclic ring is interrupted by methylene bridges, and macrocycles (**M**) that are cryptand-like cages are designated as a "cryptand". Dipyridinylpyrrole (H$\mathbf{B}^{a}$) or dipyrrolylpyridine ($H_2\mathbf{C}^{a}$) precursors are given exactly the same number code as appears in our recent review on tridentate pyridine-pyrrole systems [1]; we do this to assist the reader in looking further into the chemistry, *e.g.*, for details of the various routes to these synthons. Other reagents are given the generic descriptor **R** and numbered sequentially by a rightside superscript (*e.g.*, $\mathbf{R}^1$, $\mathbf{R}^2$. . .); the occasional non-pyridine-pyrrole host is generically labelled $H_X\mathbf{G}^{A}$, $H_y\mathbf{G}^{B}$, *etc.* Hopefully our nomenclature is straightforward and the reader can easily follow the text.

2. Linear *[m]*pyridine*[n]*pyrrole oligomers

2.1. Syntheses and properties

In the early 1990's, Thummel and co-workers disclosed extensions of the Fischer indole synthesis to obtain larger receptors [21,22]. Condensations of 8-quinolylhydrazone ($QnNHNH_2$) and the appropriate pyridyldiketone, followed by heating with polyphosphoric acid (PPA) afforded the cavity-shaped molecules $H_2\mathbf{L}^1$ – $H_2\mathbf{L}^4$, which have *linked* py-pyrH-py-pyrH-py chains (Scheme 1).

In 1998 Tollari et al. described several new indolyl-pyridines obtained from readily accessible *o*-nitrostyryl pyridine precursors in a Pd(II)-catalysed ring-closure under CO at 40 atm and high temperatures. Simple extension to an *o*-nitrostyryl 1,10-phenanthroline precursor afforded the phenanthroline-centred, linear *[2]*pyridine*[2]*indole $H_2\mathbf{L}^5$, Scheme 2 [23].

Setsune et al. employed the Suzuki coupling to access 6,6′-bis(3,4-diethyl-2-pyrrolyl)-2,2′-bipyridine ($H_2\mathbf{L}^6$) in 2006, starting from a 2-pyrrolylboronic ester and 6,6′-dibromo-2,2′-bipyridine, Scheme 3a [24,25]. Decarbonylation of $H_2\mathbf{L}^6$ in refluxing ethylene glycol afforded $H_2\mathbf{L}^7$, which was used as a synthon for the construction of extended macrocycles (see Section 3.1). Similarly in 2014, Sessler et al. used the Suzuki coupling between H$\mathbf{B}^9$ (4 equiv.) and $H_2\mathbf{C}^{11}$ using $Pd(OAc)_2/PPh_3$ as a catalyst and K_2CO_3 as a base to obtain the linear *[5]*pyridine*[4]*pyrrole $H_4\mathbf{L}^8$ in excellent yield (83%), ready for subsequent ring closing reactions to form macrocycles (Scheme 3b, and see Section 3.1) [26].

Dubreuil's group in 2010 constructed the larger alternating tripyridyl-dipyrrole molecular strands $H_2\mathbf{L}^9$ and $H_2\mathbf{L}^{10}$, with the optimal route to the pyridyl-pyridazine strands depicted in Scheme 4 [27]. The dipyridazinone was obtained in a 91% yield from a modified Coates procedure [28] by condensations of 2,6-diacetylpyridine with glyoxalate and then hydrazine in refluxing acetic acid. Treatment of the dipyridazinone with triflic anhydride and catalytic DMAP in pyridine at room temperature gave the corresponding triflate derivatives, which were used in the following Negishi coupling step [29] with a pyridyl zinc reagent that had, separately, been prepared by *in situ* metallation of the corresponding bromopyridine. The higher yields for the methylpyridyl- and dimethylpyridyl-pyrazine coupled products were attributed to improved solubilities. Stille cross-couplings were also attempted,

[1] Macrocycles incorporating *[m]*pyridine*[n]*pyrrole ($m + n = 3$) subunits are also included within the compass of this review as they were not considered in our forerunner, complementary, review on strictly tridentate *[m]*pyridine*[n]*pyrrole ($m + n = 3$) ligands and their complexes [1].