Tetrahedron Letters xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Digest paper

Pyrrole, imidazole, and triazole derivatives as ion-pair recognition receptors

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ARTICLE INFO

Article history:
Received 18 April 2016
Revised 21 May 2016
Accepted 4 June 2016
Available online xxxx

Keywords:
Pyrrole
Imidazole
Triazole
Ion-pair receptor
Molecular recognition

ABSTRACT

This Digest traces the emergence of pyrrole-, imidazole-, and triazole-based receptors for ion-pairs recognition, and recent advances such as formation of ion-pair complexes in solid state, AND receptors, and multichannel detection of ion-pair complexes, are reviewed. The design of highly selective small molecules based on pyrrole, imidazole, and triazole core, as ion-pair receptors represents important advances in the field of the molecular recognition.

Contents

Introduction

The design and synthesis of heteroditopic receptors that contain two different binding sites for both the cation and anion guest species is a topical field of supramolecular chemistry and has been comprehensively reviewed.[1] A plethora of structural motifs have been designed for the construction of ion-pair recognition receptor to affect anion recognition, most ion pair receptors take advantage of hydrogen bonding donors, Lewis acidic sites, and positively charged groups. In contrast, the majority of ion pair receptors rely on lone pair-electron donors such as functionalized calixarenes for cation recognition.

Pyrrole-based receptors have emerged as useful anion-binding agents. These anion receptors have the advantage that they do not posses any hydrogen bond acceptor moieties, avoiding aggregation and competition for hydrogen bond donor sites, rendering pyrroles popular anion binding motives. The pyrrole ring can be incorporated into cyclic and acyclic structures, giving rise to pyrrole-based anion receptors that display a wealth in size, shape, structure, and electronic properties that are unmatched to other approaches to anion binding.[2]

The imidazole ring behaves as an excellent hydrogen bond donor moiety in synthetic anion receptor systems, and the acidity of the NH proton of the imidazole can be tuned by changing the electronic properties of the imidazole substituents. On the other hand, the presence of a donor pyridine-like nitrogen atom within the ring, capable of selectively binding cationic species also converts the imidazole derivatives into excellent metal ion sensors. In this sense, the binding properties of the imidazole core may

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http://dx.doi.org/10.1016/j.tetlet.2016.06.016

be modulated by linear or angular annulation to aza-heterocycles leading to expanded imidazole derivatives bearing several binding sites.[3] In addition the positively charged imidazolium derivatives have recently been widely used and comprehensively reviewed as selective anion receptors through charge-assisted C_2-H···anion interactions.[4]

The 1,2,3-triazole ring has proved to be a versatile ion recognition unit for both cations and anions. The nitrogen-rich triazole features a highly polarized carbon atom allowing the complexation of anions by hydrogen bond. On the other hand, the triazole ring offers several N-coordination modes including coordination via anionic and cationic nitrogen donors. After C–H deprotonation of the triazole ring a powerful carbanionic donor is available.[5]

Calix[4]pyrrole containing receptors

The vast majority of ion-pair pyrrole-based receptors reported to date are heteroditopic systems derived from the calix[4]pyrrole scaffold, bearing an additional cation binding site.

The calix[4]pyrroles are a class of macrocycles consisting of four pyrrole rings linked via fully substituted sp^3 hybridized *meso* or α (pyrrolic 2 and 5) carbon atoms. After being dormant in the literature for nearly a century, these macrocycles have been extensively studied by Sessler and co-workers since their discovery that the NH array, present in these species, had the ability to bind anionic and neutral species.[6] Calix[4]pyrroles are generally conformationally flexible and can adopt four different conformations, the 1,3-alternate conformation being the most stable in the absence of a suitable guest (Fig. 1).

However, it was demonstrated that formation of an anion-calix[4]pyrrole complex produces a dramatic conformational change in the cone conformation, so that while the four NH are acting as a binding site for the anion, an electron-rich aromatic cavity, that serves as a receptor for cations, is simultaneously created (Fig. 2).

Consequently, the presence within these species of two disparate binding sites, able to simultaneously bind both cationic and anionic guests, expanded the possibilities of such macrocycles for recognizing not only anionic species but also ion-pair salts. In this context, it should be highlighted that calix[4]pyrrole **1** can form ion pair complexes with halide anion salts containing charge diffuse cations, such as the cesium and imidazolium cations. Moreover, calix[4]pyrrole **1** (Fig. 3) is able to selectively transport the CsCl ion pair across phospholipid bilayers and can extract CsCl and CsBr from an aqueous phase into a nitrobenzene organic phase under two phase liquid–liquid extraction conditions.[7]

On the other hand, since calix[4]pyrroles are easy to synthesize and functionalize, they have become very attractive frameworks for the construction of multitopic ion pair receptors, used not only in recognition processes but also in ion transport and extraction. In this regard, it should be mentioned that the two most important

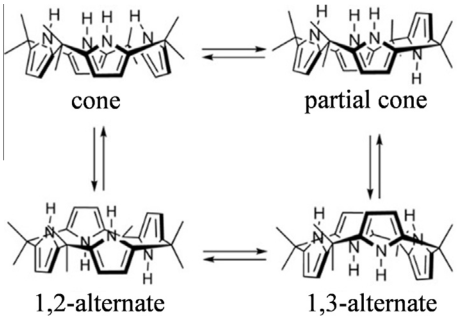

Figure 1. Representation of the four possible conformations that can adopt the calix[4]pyrroles.

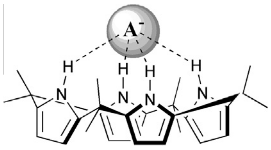

Figure 2. Schematic representation of the anion coordination by the calix[4] pyrroles, in the cone conformation.

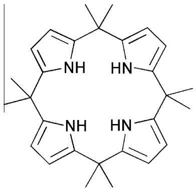

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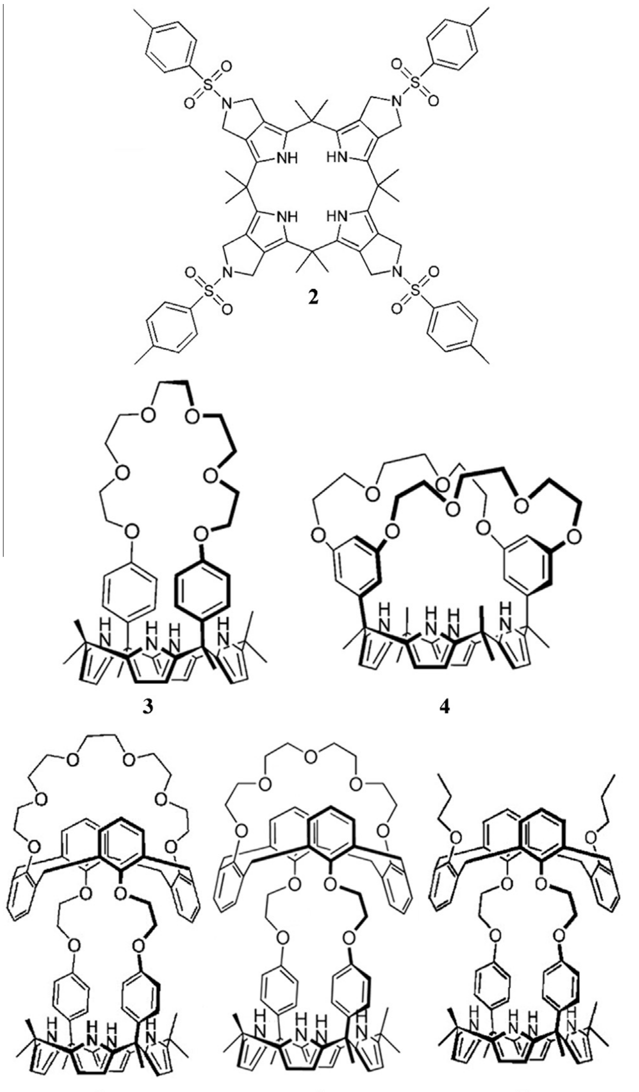
Figure 3. Structure of receptor **1**.



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3 4

5 6 7

Figure 4. Structure of receptors **2**–**7**.

Please cite this article in press as: Alfonso, M.; et al. *Tetrahedron Lett.* (2016), http://dx.doi.org/10.1016/j.tetlet.2016.06.016