



Review

Synthesis and uses of fluorous and highly fluorinated macrocyclic and spherical molecules



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ABSTRACT

Fluorous and highly fluorinated molecules have special physical, chemical, and biological properties. The development of fluorous technologies has generated a significant impact on the chemistry of macrocyclic and spherical compounds. This paper highlights the synthesis of such compounds and their applications in the fields including catalysis, molecular recognition, surface chemistry, molecular probing, molecular imaging, photomaterials, and nanomaterials.

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1. Introduction

The birth and definition of the fluorous biphasic concept by Horvath and Rabai have led to the rapid development of fluorous chemistry in last two decades [1]. Fluorous and highly fluorinated

molecules have distinct properties such as low surface tension, good biocompatibility, sensitive temperature-dependent miscibility with organic solvents, and hydrophobic property [2,3]. Organic molecules can be rendered fluorous by perfluorination to disclose all introduced fluorines as sp^3 C–F bonds or by the attachment of perfluorinated groups which can be derived from perfluoroalkanes, perfluoroalkylethers and/or perfluorotrialkyl-amines [1]. Applications of fluorous phase tags to facilitate separation [4] have been well accomplished for biphasic catalysis [1,5], small compound library synthesis [6], and separation of biomolecules including

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peptides [7], oligosaccharides [8], glycopeptides [9], and oligonucleotides [10]. Fluorous chemistry has also been applied to biocatalysis [11], organocatalysis [12], flow chemistry [13], green chemistry [14], proteomics [15], radiolabeling [16], bioimaging [17], microarray and screening [18], drug delivery [19], ionic liquids [20], nanomaterial [21], and biomaterial [22]. This review article highlights some selected examples on synthesis and application of fluorous macrocyclic and spherical molecules. Some perfluoroaryl compounds, which are not considered as fluorous, are also covered in this article.

Macrocyclic [23] and spherical molecules [24] have broad applications in phase-transfer catalysis (PTC), self-aggregation and assembly, molecular recognition, photomaterial, molecular probing, molecular imaging, and nanomaterial chemistry. Fluorous chemistry has been successfully integrated into the design and synthesis of macrocyclic and spherical molecules. This review consists of the following four sections: (1) non-conjugated fluorous macrocycles including crown ethers and other heteromacrocycles; (2) conjugated fluorous and fluorinated macrocycles including porphyrins and thiophene-containing analogs; (3) fluorous and fluorinated calix[4]arenes including resorcin[4]arenes and calix[4]pyrroles; and (4) fluorous spherical molecules such as fullerenes.

2. Non-conjugated fluorous macrocycles

2.1. Crown ethers and aza-crown ethers

The synthesis of perfluorocrown ethers was first described by Lagow's group back in 1985 [25a]. Perfluorocrown ethers such as perfluoro-15-crown-5 **1a** and perfluorodicyclohexano-24-crown-8 **1b** were prepared by the Lagow group through direct fluorination of corresponding ethers (Scheme 1) [25b]. The reactions were conducted in the cryogenic fluorination reactor using the La Mar process, a well-established technique for controlling the reaction of elemental fluorine. These stable fluorous crown ethers have been used for the studies as host-guest complexes in gas phase.

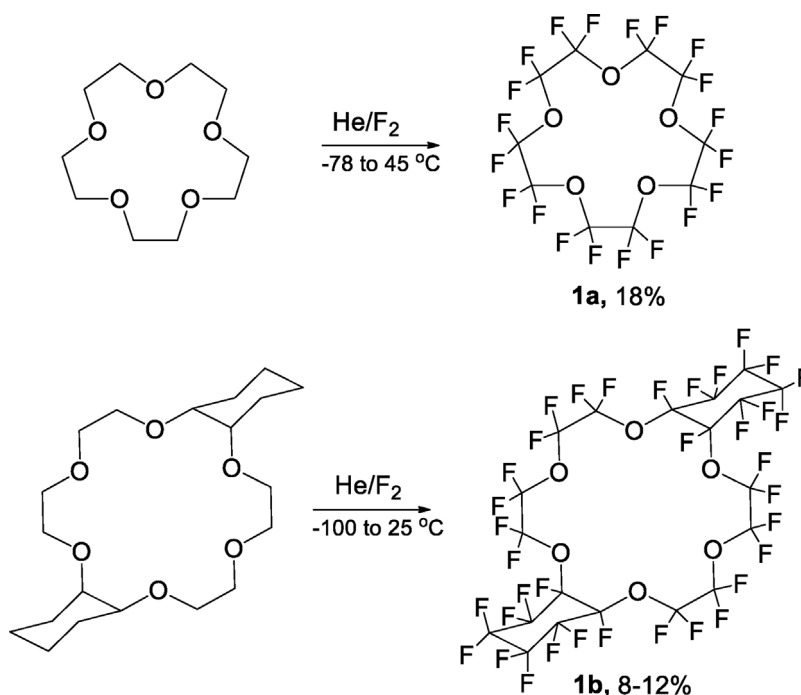
They were found having unique properties to coordinate ionic species such as F^- and CH_3O^- [25c].

The Kirchmeier group reported the synthesis of monosubstituted 18-crown-6 **2a** by the reaction of 1:1 ratio of 18-crown-6 and perfluoroalkene and also for the disubstituted 18-crown-6 **2b** with 1:2 molar ratio of the substrates (Scheme 2) [26]. The studies of fluorous crown ethers expanded the scope of coordination chemistry. The monosubstituted crown ether was able to form an 1:1 complex with $La(OTf)_3$ to increase the extraction efficiency of rare earth element.

The Pozzi and Fish groups reported the synthesis of fluorous dibenzo-18-crown-6 ethers such as **3** by metal-catalyzed cross-coupling reactions (Scheme 3) [27,28]. Polysubstituted fluorous crown ethers were found to be almost insoluble in common organic solvents at room temperature, but well-soluble in fluorous solvents. Catalyst **3** was found effective for the Finkelstein reaction of 1-bromooctane with KI to give the product in quantitative yield (Scheme 3). For the challenging nucleophilic aromatic substitutions such as the reaction of 4-nitrochlorobenzene with KOMe, catalyst **3** was able to promote the reaction to give 4-nitroanisole product in moderate yields. The fluorous catalyst could also prompt the aerobic oxidation of fluorene to form fluorenone.

The Stuart group reported the synthesis of a series of dibenzo-18-crown-6 lariat ethers bearing two fluorous side arms **4a-d** (Scheme 4) [29]. These light fluorous PTCs have good catalytic performance and recycled efficiently by fluorous solid-phase extraction (F-SPE). For example, fluorous dibenzo-18-crown-6 lariat ethers **4c** was recycled four times in the iodide displacement reaction of 1-bromooctane and four times in the fluoride displacement reaction of 2,4-dinitrochlorobenzene by fluorous solid-phase extraction by F-SPE without loss of activity.

The Stuart group synthesized a series of *N,N*-dialkyl-4,13-diaza-18-crown-6 lariat ethers possessing two C_8H_{17} , $(CH_2)_3C_8F_{17}$, $(CH_2)_3C_{10}F_{21}$, or $(CH_2)_2C_8F_{17}$ side chains by *N*-alkylation of 4,13-diaza-18-crown-6 (Scheme 5) [30]. All the fluorous macrocycles were able to extract potassium picrate from an aqueous solution into an organic phase and evaluated as recyclable phase-transfer



Scheme 1. Synthesis of fluorous crown ethers.

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