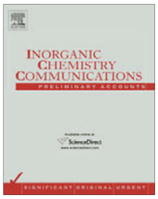
Inorganic Chemistry Communications 11 (2008) 1113–1116

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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



Synthesis and characterization of novel supercryptands-fused porphyrazines

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ARTICLE INFO

Article history:
Received 21 May 2008
Accepted 18 June 2008
Available online 25 June 2008

Keywords:
Tetraazaporphyrin
Porphyrazines
Cryptands
Magnesium
Zinc

ABSTRACT

Novel metal-free (**8**, **9**), magnesium and zinc porphyrazines (**6**, **7, 10, 11**) containing four peripheral tetraaza-dithiahexaoxa cyclindrical or spherical cryptand units have been prepared by tricyclotetramerization reactions using supercryptand **4** or **5**. All new products have been characterized by a combination of mass, elemental analyses, electronic absorption, FT-IR, ^1H and ^{13}C NMR spectroscopy.

In the recent years, the tetraazaporphyrins have aroused renewed research interest for a variety of reasons [1]. Unlike their more common tetrapyrrolic congeners, the porphyrins and phthalocyanines, they offer a much higher potential for creating structural diversity. With the inherent synthetic ease of including diverse peripheral substituents, they are seen as promising materials having potential applications in diverse areas [2]. The first synthesis of crowns-fused porphyrazines was reported independently by the groups of Hoffman and Nolte [3,4]. The coordination chemistry, aggregation and electrical properties of these compounds were investigated [5,6]. Such systems contain a metal center that is complexed by a porphyrazine ring, four macrocyclic binding and tridentate *meso*-pocket sites [3–6]. That is why such compounds, which are exemplified by $[(S_2,O_3 \text{ crown}]_4$pz, should show rich and varied coordination chemistry. In contrast to fused phthalocyanine-crown ether systems, metal ion coordination by the crown ether units in $[(S_2,O_3 \text{ crown}]_4$pz have profound effects on UV-vis spectra and other properties, since the key crown sulfur residues are in direct electronic contact with the macrocyclic central chromophore [7]. In addition, the attachment of oxacrown [8], azacrown or polyaza-polythia macrocycles to porphyrazine has received considerable attention since they allow for cation selectivity and complex stability to be enhanced through changing the numbers and types of macrocycle donors as well as the solubility of porphyrazines [9–14]. Lastly, being isoelectronic in terms of π electrons with the PcH_2 skeleton, these types of polynucleating macrocyclic compounds are promising new materials with potential applications in different fields such as electron transfer [15], magnetic interactions [16], optical phenomena [17], excited-state reactivity [18], mixed valency [19], and ionophoric activity [20].

Since the first cyclindrical [21,22] or spherical [23] macrotricylic ligands were reported by Lehn and co-workers, hundreds of macropolycyclic compounds with unusual shapes have been prepared and their properties have been investigated [24–26]. A very active current research activity in this area has led to the development of numerous procedures for effecting macrocyclization such as template effects and high dilution techniques, thus giving access to a great number of new macrocycles. Owing to their architectural and functional plasticity, supercryptand compounds are especially attractive for designing both biomimetic and abiotic receptor molecules for inorganic and organic substrates [27,28]. In addition, macropolycylic species continue to be an active field of research due to their use as models for metalprotein [29] and respiratory pigments [30].

Our previous papers have described a series of phthalocyanines with various functional groups. These phthalocyanines have N-, O- and S-containing functionalities such as diazadioxa [31], cryptand [26,32], crown ether fused diloop [33], diazadithia macrocyclic with tert-butyl [34], and tetrathiamonoaza macrocyclic [35]. The immediate consequences of these peripheral substituents are enhanced solubility in common organic solvents and additional donor sites for alkali or transition metal ions.

In this communication, the first examples of novel porphyrazines are reported, in which four peripheral supercryptands are bound (Scheme 1). Specifically, the magnesium and metal-free moieties of the porphyrazines substituted cyclindrical or spherical cryptands were synthesized starting from 5,8-dithiadodec-6-en-6,7-dicarbonitrile-1,2-di-*p*-toluenesulfonate **1** [36] including more

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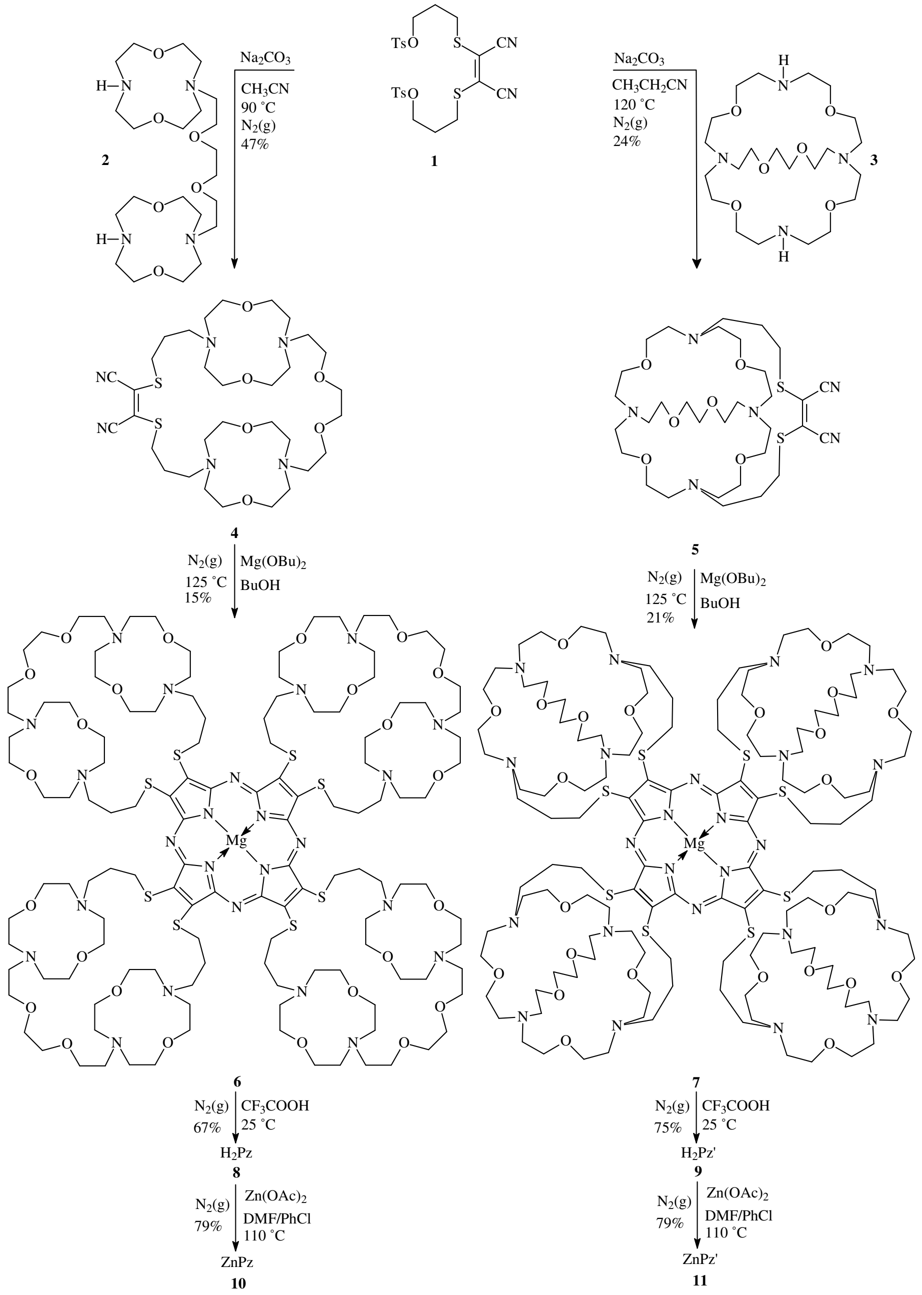
doi:10.1016/j.inoche.2008.06.012



Scheme 1. Synthesis of novel porphyrazines (**6**–**9**).

reactive ditosylate groups because of producing better yields in comparison to analogous dichloro systems for the synthesis of saturated polyazamacrocycles [37]. Reaction of the latter compound with 4,4′-[ethane-1,2-diyl-bis(oxyethane-2,1-diyl)]bis-1,7-dioxa-4,10-diazacyclododecane **2** [38] or 4,10,16,22,27,30-hexaoxa-1,7,13,19-tetrazabicyclo [11.11.8] dotriacontane **3** [39] in acetonitrile or propionitrile, in the presence of sodium carbonate, yielded supercryptands **4** [40] and **5** [40] (Scheme 1). The template effect of sodium cations and the effect of ditosylates account for the high yield obtained in the desired ring closure. Products **4** (47%) and **5** (24%) were isolated after purification by column chromatography on silica gel [eluent, $CHCl_3$–MeOH–NH_4OH, 98:1.5:0.5] or [eluent, $CHCl_3$–MeOH–NH_4OH, 98:1:1] (M.p. 218–219, 211–212 °C, respectively). The elemental analyses and ES mass spectrum data for **4** and **5** were satisfactory: 684.42 $[M]^+$ and 684.64 $[M]^+$, respectively.

The porphyrazines substituted supercryptands were prepared by the Mg(II) template cyclization of the appropriate supercryptand (**4** or **5**) as described (Scheme 1) [41]. The products were purified by column chromatography on silica gel. The cylindrical cryptand derivative MgPz **6** [42] and spherical cryptand derivative MgPz **7** [42] were obtained in 15% or in 21% yields, respectively, all as dark blue powders. MgPz **6** and MgPz **7** were finally demetalated with trifluoroacetic acid to give the metal-free derivatives H_2Pz **8** [43] in 67% yield and H_2Pz' **9** [43] in 71% yield as dark blue to purple powders. In the ^1H NMR spectra of **8** and **9**, the typical shielding of inner core protons was seen as broad signals at $\delta = -1.70$ (**8**) and -1.45 ppm (**9**), which could be attributed to the NH resonances as confirmed by deuterium exchange. The elemental analyses and ES mass spectrum data of all the porphyrazines (**6–9**) were satisfactory. The molecular ion peaks at $m/z = 2761.53$ $[M]^+$ **6**, 2761.42 $[M]^+$ **7**, 2739.52 $[M]^+$ **8** (see Fig. 1) and 2739.54 $[M]^+$ **9** were found