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Synthesis and characterization of new soluble polyfluorinated *seco*-porphyrazines

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ABSTRACT

The synthesis of new polyfluorinated magnesium porphyrazine bearing pentafluorophenyl moieties was achieved by cyclotetramerization of 3,4-bis(pentafluorophenyl)pyrroline-2,5-diimine in the presence of $Mg(BuO)_2$. Acid-mediated demetallation of the magnesium porphyrazine resulted in peripheral oxidation of one pyrrole ring to reveal the *seco*-porphyrazine, [2,3,7,8,12,13,17,18-octakis(pentafluorophenyl)-2-*seco*-2,3-dioxoporphyrazine]. Further reaction of that product with copper (II) acetate, zinc (II) acetate and cobalt (II) acetate has led to the metallated *seco*-derivatives, [2,3,7,8,12,13,17,18-octakis(pentafluorophenyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) [M = Cu(II), Zn(II), Co(II)]. The spectroscopic and aggregation behavior of all the target porphyrazines were investigated in different solvents and at different concentrations in chloroform. The compounds were characterized by using many spectroscopic techniques such as FT-IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, UV–vis, mass and elemental analysis. The porphyrazines were soluble in various organic solvents such as chloroform, dichloromethane, pyridine, and THF.

Porphyrins (P) and their structural derivatives –phthalocyanines (Pc) and porphyrazines (Pz)– constitute a distinct class of macrocyclic tetrapyrrole systems with unique physical and chemical properties. Phthalocyanines have received a great deal of interest owing to their extensive use in a number of applications involving chemical sensors, electrochromic devices, batteries, semiconductors, catalysts, and liquid crystals [1,2]. Metallated phthalocyanines (MPcs) are also currently undergoing clinical trials for use in the photodynamic therapy (PDT) of cancer [3–8]. Because of their chemical diversity, these compounds, and in particular porphyrins and phthalocyanines, have been at the focus of multidisciplinary interest for many years. However, although the molecular structures of all three types of macrocycles are very similar, benzo- and especially aza-substitution have a strong impact on the overall chemical behavior of the corresponding tetrapyrrole ligands [9–11].

The porphyrazines have specific optical properties because they have symmetrical rich 18 π-electron aromatic macrocycle, which can play as a host to different metal ions in its central cavity. Therefore, they have been extensively used in optical recording media, photosensors, optical filters and copy preventing inks. A *seco*-porphyrazine is defined as a porphyrazine in which one of the pyrrole rings has been effectively cut and replaced by two acyclic substituents attached to the macrocyclic core.

Fluorinated metallated tetrapyrrole compounds currently receive a great deal of attention because of their interesting electron transfer, photosensitizing properties, along with magnetic and thermal characteristics [12–17]. The presence of pentafluorophenyl groups on the macrocycle ring can increase the catalytic activity and stability [18]. Fluoro-substituted tetrapyrrole compounds are known for their high solubility, even in polar, aprotic solvents. The increased solubility may be due to fluorine, which has the highest electronegativity of all elements [19].

Our group has been heavily interested in the preparation of new soluble porphyrazine derivatives. Among these, Pzs with peripheral functional groups such as 3,5-bis(trifluoromethyl)benzylthio [20] and 3-thiopropylpentafluorobenzoate [21] can be cited. Recently, we have synthesized novel *seco*-porphyrazines substituted with 1-naphthyl [22], *o*-tolyl and *p*-tolyl [23], 4-tert-butylphenyl [24], 4-biphenyl [25], and 3,5-bis(trifluoromethyl)phenyl [26] groups on the peripheral positions as encountered by Barrett, Hoffman and coworkers, with peripheral amino derivatives [27–30].

In the present paper, octasubstituted symmetric magnesium porphyrazine (**3**), unsymmetrical metal-free *seco*-porphyrazine (**4**), and metallated *seco*-porphyrazines (**5**–**7**) containing polyfluorophenyl groups on the periphery were synthesized. Magnesium porphyrazine was prepared by a direct cyclotetramerization of 3,4-bis(pentafluorophenyl)pyrroline-2,5-diimine (**2**) in the presence of $Mg(BuO)_2$. Even though the first step of this process to obtain **3** has been actualized in the requested direction, demetallation to metal-free compound leads to an oxidized **4** as encountered by Nie et al. [31] with peripheral amino derivatives. Together with further metallated products (**5**–**7**), these new soluble complexes were characterized by elemental analysis, together with FT-IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, UV–vis, and mass spectral data.

3, **4** and **5**–**7** with eight pentafluorophenyl groups bound to the periphery are 2,3-bis(pentafluorophenyl)dinitrile derivative (**1**) [32] which was obtained by oxidative coupling of pentafluorophenylacetonitrile in the presence of I_2. The solid product

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(**1**) was obtained in a yield of 64% (Scheme 1). It was a mixture of maleo and fumaronitriles and the latter was present in higher ratio as expected from the presence of pentafluorophenyl substituents. The product was brown colored and was very soluble in chloroform, dichloromethane and acetone, but insoluble in *n*-hexane. Its reluctance to turn into porphyrazine under the usual conditions (i.e. $Mg(OR)_2$ in refluxing *n*-propanol or *n*-butanol) points out the lower ratio of the maleonitrile component. This problem was solved by activation of the fumaronitrile derivative to the corresponding diiminopyrroline derivative (**2**) [33] which cyclizes quite easily to porphyrazine at reflux temperature of *n*-propanol or *n*-butanol [34]. In order to convert the diiminopyrroline derivative (**2**) into porphyrazine, we have made use of its template reaction in the presence of magnesium butanolate, which is the typical method generally applied in cyclotetramerization of these tetrapyrrole derivatives [35–37]. The dark blue octakis(pentafluorophenyl)porphyrazinatomagnesium (**3**) [38] was soluble in chloroform, dichloromethane, acetone, THF and pyridine (Fig. 1). The conversion of **3** to metal-free *seco*-porphyrazine derivative (**4**) [39] was achieved by treatment with trifluoroacetic acid followed by neutralization with ammonia and aqueous precipitation. The purity of the product could be raised by dissolving the crude substance in minimum amount of chloroform and then reprecipitating it by dropwise addition of the solution to *n*-hexane. Further reaction of **4** with copper (II) acetate, zinc (II) acetate and cobalt (II) acetate has led to the metallated *seco*-derivatives, [2,3,7,8,12,13,17,18-octakis(pentafluorophenyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) [M = Cu(II), Zn(II), Co(II)] (**5**–**7**) [40–42] (Scheme 1) (Fig. 2).

The newly synthesized compounds were characterized by using standard spectral methods (FT-IR, UV–vis, mass, ^{1}H, ^{13}C and ^{19}F NMR) in addition to elemental analysis. Spectral investigations for all new products were consistent with the assigned structures.

Elemental analysis results correspond closely with the calculated values for (**1**–**7**) (Table 1).

In the FT-IR spectrum of 2,3-bis(pentafluorophenyl)dinitrile derivative (**1**), the characteristic stretching vibration of C≡N is observed at 2218 cm^{-1}, the aromatic C=C peak is at 1610 cm^{-1} and the stretching vibrations of C–F are at 1346, 1166 and 1125 cm^{-1}. In the FT-IR spectrum of 3,4-bis(pentafluorophenyl)pyrroline-2,5-diimine (**2**), stretching vibration of N–H is observed at 3330 cm^{-1}, the aromatic C=C peak is at 1610 cm^{-1} and the characteristic C–F peaks are at 1344, 1184, 1123 cm^{-1} [20,21,26,43,44]. In the FT-IR spectrum of **3** the N–H groups in the inner core show absorption at 3335 cm^{-1}.

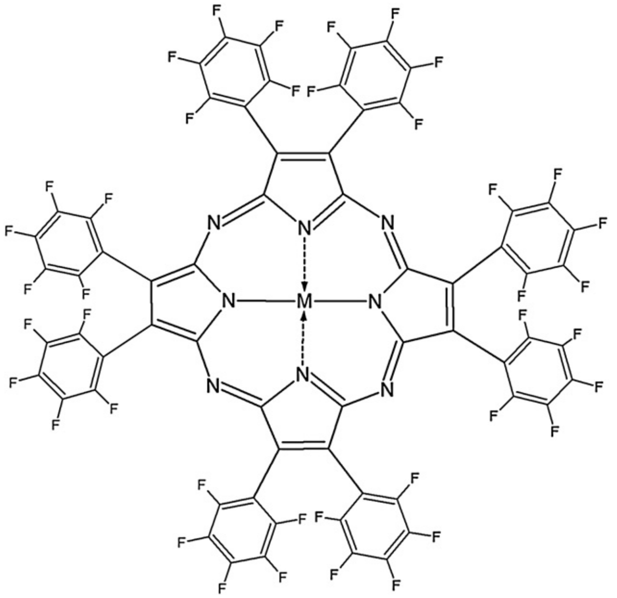
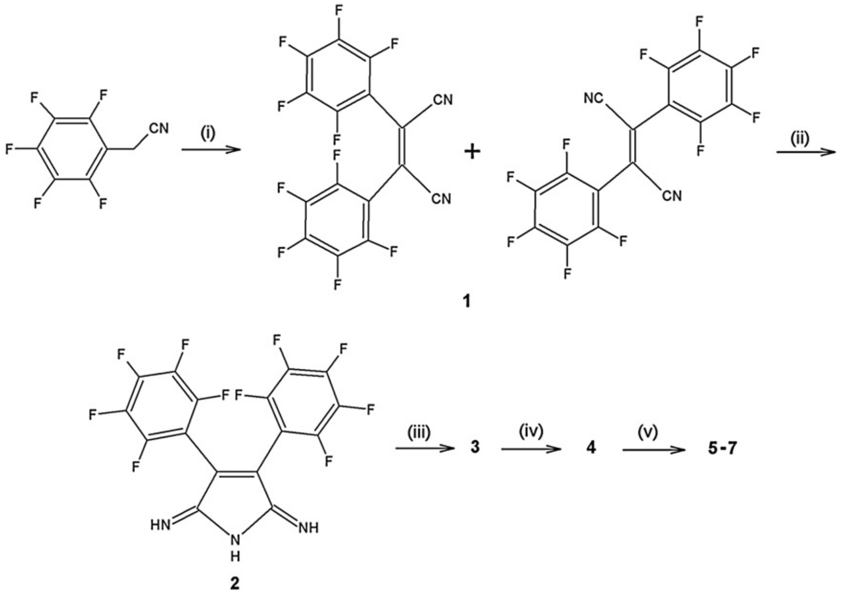


Fig. 1. [2,3,7,8,12,13,17,18-octakis(pentafluorophenyl)porphyrazinato]Mg(II) (**3**).

^{1}H NMR investigations of **2** and **4** provide the characteristic chemical shifts for the structures as expected. The N–H protons of **2** were also identified in the ^{1}H NMR spectrum with a broad singlet peak at $\delta = 4.80$ ppm, presenting the diiminopyrroline derivative. ^{1}H NMR spectrum of **4** showed chemical shift belonging to metal-free porphyrazine ring protons (broad singlet) at −1.35 ppm [45,46].

In the ^{13}C NMR spectra of diamagnetic porphyrazines **3**, **4** and **6**, six different single chemical shifts for carbon atoms were clearly seen.

^{19}F NMR spectroscopy has been a very useful technique for investigating the fluorinated compound. ^{19}F NMR spectrum of **6** showed three different peaks at −142.8 ppm, −152.3 ppm and −161.9 ppm, respectively, relative to the fluorine atoms in the *ortho*, *para* and *meta* positions of the phenyl substituents and the spectrum showed the expected signals of the five fluorine atoms attached to the aromatic ring [47,48]. Integration of the peaks gave a 2:1:2 ratio as expected.



Scheme 1. (i) NaOMe, MeOH, I_2; (ii) NH_3, *cat* Na, Ethylene glycol; (iii) Mg turnings, I_2, n-BuOH; (iv) CF_3CO_2H; (v) EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.