

# On the synthesis and properties of the Mg<sup>II</sup> complex of perfluorinated octaphenylporphyrazine<sup>☆</sup>



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## ARTICLE INFO

### Article history:

Received 22 July 2014

Received in revised form 28 August 2014

Accepted 2 September 2014

Available online 4 September 2014

### Keywords:

Perfluorinated octaphenylporphyrazine

Mg<sup>II</sup> complex

Free-base

Synthesis

## ABSTRACT

Reaction of *cis*-dicyanoperfluorostylbene (**1-cis**) with Mg<sup>II</sup> butoxide in *n*-butanol leads to the Mg<sup>II</sup> complex of octa-(pentafluorophenyl)porphyrazine (**2**), contaminated with by-products due to partial nucleophilic substitution of the fluorine atoms by butoxy groups. Treatment of the Mg<sup>II</sup> complex with CF<sub>3</sub>COOH gives the metal-free perfluorinated octaphenylporphyrazine (**3**). The UV–VIS spectral data obtained for the Mg<sup>II</sup> complex **2** and its behavior in CF<sub>3</sub>COOH solution differs from that reported for the “same” species obtained by cyclotetramerization in the presence of Mg<sup>II</sup> butoxide of the diiminopyrroline derived from dicyanoperfluorostylbene reported recently by S. Kayaköy and E. Gonca [Inorganic Chemistry Communications 21 (2012) 28–31].

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Recently we have reported the synthesis of perfluorinated octaphenylporphyrazine H<sub>2</sub>O<sub>2</sub>PhPAF<sub>40</sub> (**3**) [1] which was obtained by template cyclotetramerization of dicyanoperfluorostylbene (**1**) (mixture of *cis*- and *trans*-isomers, i.e. bis(perfluorophenyl) substituted maleo- and fumarodinitriles) in a melt with In<sup>III</sup> hydroxydiacetate followed by catalytic demetallation of the intermediate In<sup>III</sup> complex (HO)InOPhPAF<sub>40</sub> in the acidic medium containing chloride anions. This synthetic methodology (dinitrile → In<sup>III</sup> complex → free base) for metal free porphyrazines, which was elaborated by us for the non-fluorinated analogs [2], appears to be especially useful for the preparation of perfluorophenyl substituted porphyrazines, since it allows to avoid nucleophilic conditions of the Linstead's methodology (dinitrile → Mg<sup>II</sup> complex → free base) [3] more commonly used for preparation of various substituted porphyrazines [4]. We have supposed that the use of Mg<sup>II</sup> alkoxide (usually *n*-propoxide or *n*-butoxide) as template agent in the Linstead cyclotetramerization might cause a partial substitution of the fluorine atoms in perfluorinated phenyl rings by alkoxy groups. Indeed, it is known that the fluorine atom in pentafluorophenyl group, especially in the *para*-position, can be easily substituted by various nucleophiles [5,6] and this reaction was even used for the synthesis of polymers [7,8] and as a click approach in the functionalization of *meso*-pentafluorophenyl substituted porphyrins [9–11] and their analogs [12]. In the present communication we report the synthesis of the Mg<sup>II</sup> complex of perfluorinated octaphenylporphyrazine, MgOPhPAF<sub>40</sub> (**2**), by template cyclotetramerization of *cis*-dicyanoperfluorostylbene (**1**) in the presence of

magnesium(II) *n*-butoxide and, alternatively, by complexation of the metal free porphyrazine H<sub>2</sub>O<sub>2</sub>PhPAF<sub>40</sub> (**3**) with Mg(OAc)<sub>2</sub> in acetone or DMSO (Scheme 1). Our results and spectral data for the Mg<sup>II</sup> complex MgOPhPAF<sub>40</sub> (**2**) obtained by both approaches are in disagreement with the data recently reported by Kayaköy and Gonca [13] for the “same” compound prepared through diiminopyrroline derivative **6** (diiminoimide method, see Scheme 2 and discussion below).

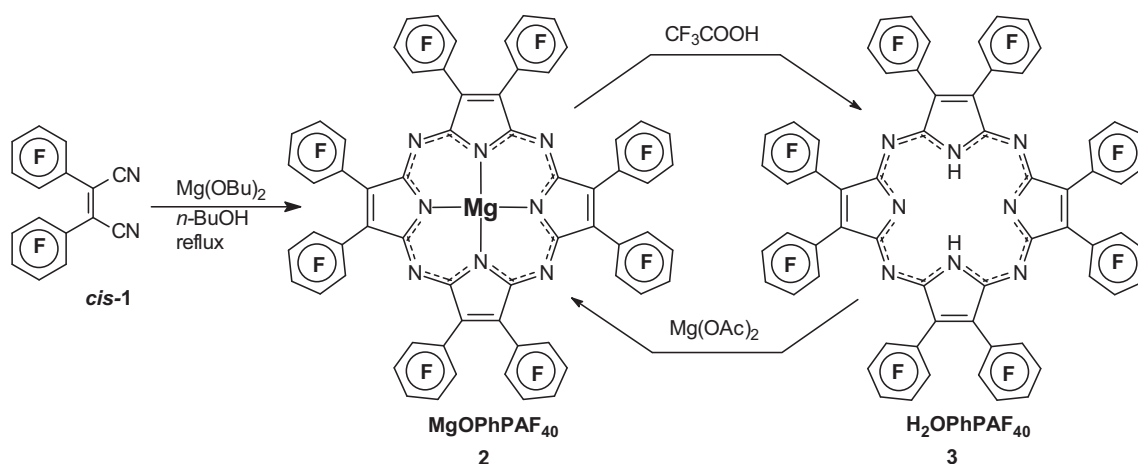
Bis(pentafluorophenyl)maleodinitrile (*cis*-dicyanoperfluorostylbene) (**1**) [1,14] (512 mg, 1.25 mmol) was refluxed with suspension of Mg<sup>II</sup> *n*-butoxide (1.25 mmol prepared from 30 mg of magnesium) in *n*-butanol (25 ml) until the reaction mixture became dark blue. The residue obtained after evaporation of solvent was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and purified by column chromatography on silica to remove non-macrocylic by-products. The UV–VIS spectrum of the main fraction contained the intense band at 628 nm and additional broad band at ca. 703 nm (Fig. 1, curve 1).

The MALDI-TOF spectrum of this fraction (Fig. 2) contains the negative molecular ion peak [M + H]<sup>−</sup> of the desired Mg<sup>II</sup> complex MgOPhPAF<sub>40</sub> (**2**) at *m/z* = 1665 and additional minor bands at *m/z* = 1719 and 1773 corresponding to the [M + H]<sup>−</sup> peaks of by-products in which butoxy group(s) are present instead of one or two fluorine atoms (MgOPhPAF<sub>40−*n*</sub>(OBU)<sub>*n*</sub>, *n* = 1 or 2). Possibility of partial substitution of the fluorine atoms in perfluorinated phenyl rings in the course of cyclotetramerization of the dinitrile occurring in the presence of Mg<sup>II</sup> butoxide was well expected (see above). The pure product MgOPhPAF<sub>40</sub> (**2**) with UV–VIS spectrum typical for symmetrical Mg<sup>II</sup> porphyrazines containing a single and narrow Q-band in the visible region at 628 nm and Soret band in the UV-region at 368 nm (Fig. 1, curve 2) was obtained after additional gradual chromatography using hexane–CH<sub>2</sub>Cl<sub>2</sub> mixture [15].

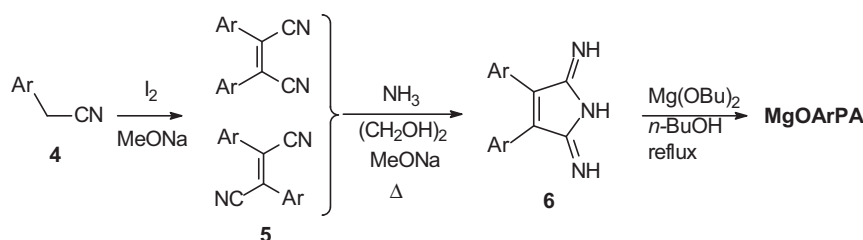
<sup>☆</sup> Perfluorinated porphyrazines. 2. Part 1 see Ref. [1].

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**Scheme 1.** Synthesis of perfluorinated octaphenylporphyrazines using Linstead's approach.



**Scheme 2.** Synthesis of Mg<sup>II</sup> octaarylporphyrazines (MgOArPA) by diiminoimide method.

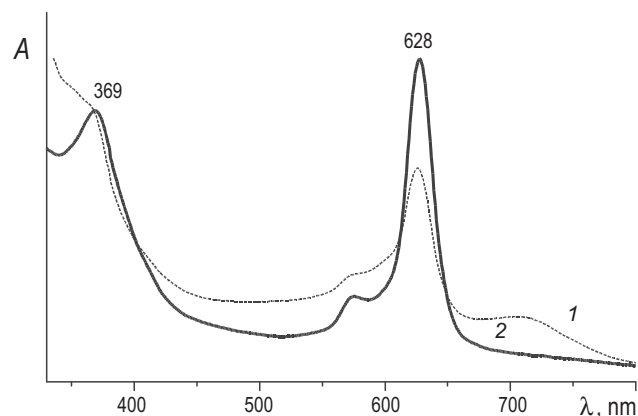
Acidification of the solution of Mg<sup>II</sup> complex **2** in CH<sub>2</sub>Cl<sub>2</sub> by CF<sub>3</sub>COOH leads to its smooth demetallation which can be followed spectrophotometrically (Fig. 3) by appearance of the split Q-band with maxima at 587 and 657 nm. The UV–VIS spectrum of the obtained product **3** is typical for metal free porphyrazines, and its spectral parameters [16] are identical to the data earlier reported for H<sub>2</sub>OPhPAF<sub>40</sub> prepared by demetallation of the In<sup>III</sup> complex (HO)InOPhPAF<sub>40</sub> [1]. The Mg<sup>II</sup> complex **2** can be also obtained from the metal free porphyrazine **3** in the presence of Mg<sup>II</sup> acetate in various solvents (acetone, DMSO, EtOH, THF, etc.) (Fig. 4).

The maxima of the Q bands in the UV–VIS spectra of perfluorinated Mg<sup>II</sup> complex **2** (628 nm) and metal free porphyrazine **3** (587 and 657 nm) are shifted hypsochromically as compared to the corresponding non-fluorinated octaphenylporphyrazines (637 nm for Mg<sup>II</sup> complex and 595 and 663 nm for the free base [17]). Interestingly, that introduction of CF<sub>3</sub> groups in the *m*-positions of phenyl rings leads to a lesser hypsochromic shift of the Q-band (631 nm for MgOPhPA(CF<sub>3</sub>)<sub>8</sub> and 589, 658 nm for H<sub>2</sub>OPhPA(CF<sub>3</sub>)<sub>8</sub> [18]), while introduction of *p*-*tert*-butyl groups results in the bathochromic shift (644 nm for MgOPhPA(<sup>t</sup>Bu)<sub>8</sub> and 614, 681 nm for H<sub>2</sub>OPhPA(<sup>t</sup>Bu)<sub>8</sub> [19]). The hypsochromic shift of the Q-bands in octaarylporphyrazines in the presence of electron-withdrawing groups in phenyl rings is due to stabilization of the highest occupied π-molecular orbital of the porphyrazine macrocycle, while electron-donating *p*-*tert*-butyl groups destabilize this orbital and lead to a bathochromic shift.

It should be noted that UV–VIS spectral data of the Mg<sup>II</sup> complex **2** obtained by us (368 and 628 nm in CH<sub>2</sub>Cl<sub>2</sub>) differ from the values reported by Kayaköy and Gonca [13] (356 and 668 nm in CHCl<sub>3</sub>) for the compound which they have assigned the same structure but prepared using diiminoimide approach through diiminopyrroline derivative **6** (Scheme 2). The strong bathochromic shift of the Q-band maximum in the Mg<sup>II</sup> complex reported by Kayaköy and Gonca [13] (668 nm) as compared to all known Mg<sup>II</sup> octaarylporphyrazines MgOArPA (Ar =

C<sub>6</sub>F<sub>5</sub> – 628 nm, *m*-CF<sub>3</sub>Ph – 631 nm, *p*-<sup>t</sup>BuPh – 644 nm, *p*-MeOPh – 648 nm) is a clear indication that substituents attached to the porphyrazine core in this species have strong electron-donating character. Indeed, such bathochromic position of the Q-band was observed only for Mg<sup>II</sup> porphyrazines bearing eight strongly electron-donating alkylsulfanyl or dialkylamino groups (MgPA(SMe)<sub>8</sub> – 672 nm [20], and MgPA(NMe<sub>2</sub>)<sub>8</sub> – 709 nm [21]).

The Mg<sup>II</sup> complex **2** prepared by us and the “same” species reported by Kayaköy and Gonca [13] exhibit also a quite different behavior in the acid medium. While we have observed a smooth demetallation of the Mg<sup>II</sup> complex **2** in the presence of CF<sub>3</sub>COOH with formation of the free base **3**, which even in 100% CF<sub>3</sub>COOH is non-protonated and stable in



**Fig. 1.** UV–VIS spectra recorded in CH<sub>2</sub>Cl<sub>2</sub> for the fractions obtained during chromatography of the cyclotetramerization products of *cis*-dicyanoperfluorostyrene in the presence of Mg<sup>II</sup> butoxide: 1 – after the 1st chromatography, 2 – pure MgOPhPAF<sub>40</sub> (**2**) after the 2nd chromatography.

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