



**Repositorio Institucional de la Universidad Autónoma de Madrid**

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:

This is an **author produced version** of a paper published in:

JOURNAL OF PORPHYRINS AND PHTHALOCYANINES 21.12 (2018): 782-789

**DOI:** <https://doi.org/10.1142/S1088424617500882>

**Copyright:** © 2018 WILEY

El acceso a la versión del editor puede requerir la suscripción del recurso  
Access to the published version may require subscription

# Metallo-organic ensembles of tritopic subphthalocyanine ligands

M. A. Revuelta-Maza,<sup>a</sup> E. Fazio,<sup>a</sup> G. de la Torre,<sup>\* a,b</sup> T. Torres<sup>\*a,b,c</sup>

<sup>a</sup> Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain

<sup>b</sup> Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain

<sup>c</sup> IMDEA Nanociencia, C/Faraday, 9, Cantoblanco, 28049 Madrid, Spain

Received date (to be automatically inserted after your manuscript is submitted)

Accepted date (to be automatically inserted after your manuscript is accepted)

**ABSTRACT:** Organic building blocks containing amines and aldehydes can be used for the preparation of complex metallo-organic structures, such as  $M_2L_3$  triple helicates or face-capped  $M_4L_4$  tetrahedral cages, through the formation of both dynamic covalent and coordinative linkages during the self-assembly process. Herein we describe how the subcomponent self-assembly method can be successfully applied over a triamine-functionalized subphthalocyanine (SubPc) ligand to build metallo-supramolecular helicates. Two isomeric SubPcs (**C<sub>1</sub>-SubPc1** and **C<sub>3</sub>-SubPc1**) have been prepared from the corresponding **C<sub>1</sub>-SubPcI<sub>3</sub>** and **C<sub>3</sub>-SubPcI<sub>3</sub>** precursors under optimized Suzuki conditions. We selected the tritopic **C<sub>3</sub>-SubPc1** derivative as ligand for the subcomponent self-assembly experiments, which involved the reaction with 2-formylpyridine and different Fe(II) salts. The self-assembly process was mainly studied by mass spectrometry (ESI direct injection techniques), and in all the conditions applied, we could observe the formation of helicate-type  $Fe_2SubPc_3$  structures and/or  $Fe_2SubPc_4$  species, which can be considered as open precursor of  $Fe_4SubPc_4$  tetrahedral cages.

**KEYWORDS:** subphthalocyanines, metallo-organic complexes, subcomponent self-assembly

\*Correspondence to: Tomás Torres; e-mail: [tomas.torres@uam.es](mailto:tomas.torres@uam.es)

## INTRODUCTION

Subcomponent self-assembly is a powerful tool for the construction of increasingly complex metallo-supramolecular architectures [1]. Thus, organic building blocks containing amines and aldehydes can be used for the preparation of complex structures through the formation of both dynamic coordinative ( $N \rightarrow \text{metal}$ ) and covalent ( $N=C$ ) bonds during self-assembly processes [2]. Following this strategy, a wide variety of metallo-supramolecular ensembles have been reported in the last decade [3]. In particular, using  $C_3$ -tritopic ligands and octahedral metal centers, either  $M_2L_3$  triple helicates or face-capped  $M_4L_4$  tetrahedral capsules can be formed, depending on the stoichiometry of the reactants and on the chemical structure of the ligand [4,5]. Although most synthetic hosts are transparent to visible light and are redox

inactive, some fascinating example of photo- and electro-active metallo-supramolecular architectures exist. In this regard, appropriately functionalized, bidentate perylenebisimide [6], porphyrin [7,8] and bodipy [9] ditopic ligands have been used to build tetrahedral  $M_4L_6$  cages showing outstanding photophysical and electrochemical properties.

Here, we describe for the first time the application of the M(II)-templated subcomponent self-assembly protocol using a tritopic subphthalocyanine (SubPc) as ligand, aiming at building optically and electronically active, metallo-supramolecular cages. SubPcs [10] are 14  $\pi$ -electron aromatic macrocycles containing three 1,3-diiminoisoindole units N-fused around a central boron atom. These chromophores unveil remarkable electrochemical and photophysical properties that render them interesting probes for studying light-induced processes [11,12]. Interestingly, their particular concave  $\pi$ -extended structure sets them as potential receptors for complementary convex-shaped molecules, such as fullerenes [13], widely used in the field of molecular materials [14]. In this regard, supramolecular SubPc-based capsules have been previously synthesized in our group by Pd(II)-directed self-assembly of tritopic SubPcs endowed with three 3-pyridyl units into heterochiral  $C_{3h}$  symmetric  $M_3L_2$  cages [15,16]. These supramolecular conjugates have demonstrated their ability to encapsulate fullerenes, forming host-guest complexes able to undergo, upon photoexcitation, a transduction of the SubPc singlet excited-state energy to the fullerene inside the cavity.

Therefore, we have prepared a triamine-functionalized subphthalocyanine (**SubPc1**) with a  $C_3$  symmetry to test it as ligand for the preparation of  $Fe_2L_3$  triple helicates or face-capped  $M_4L_4$  tetrahedral capsules. The self-assembly process was mainly studied by mass spectrometry (ESI direct injection techniques). Under the different conditions applied, only  $M_2L_3$  triple helicates were detected, although open  $M_2L_4$  species were also observed in some cases, which can be considered as non-closed precursor of  $M_4L_6$  tetrahedron.

## EXPERIMENTAL

### General

Chemicals were purchased from commercial suppliers and used without further purification unless stated otherwise. The monitoring of the reactions has been carried out by thin layer chromatography (TLC), employing aluminum sheets coated with silica gel type 60 F254 (0.2 mm thick, E. Merck). Purification and separation of the synthesized products was performed by column chromatography, using silica gel (230-400 mesh, 0.040-0.063 mm, Merck). Infrared (IR) spectra were recorded on a Perkin Elmer Spotlight 200 (macro IR) spectrophotometer, employing in all cases solid samples in KBr pellets (transmission measurements). High Resolution Mass Spectrometry (HRMS) spectra were recorded employing ESI Positive Q-TOF using a Bruker Maxis II, and Matrix Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) using a Bruker Ultraflex III spectrometer, with a Nd-YAG laser. The different matrixes employed are indicated for each spectrum. Mass spectrometry data are expressed in  $m/z$  units. NMR spectra ( $^1H$ -NMR,  $^{13}C$ -NMR) were recorded on a Bruker AC-300 (300 MHz). UV-Vis spectra were recorded on a JASCO-V660 UV-Vis spectrophotometer using spectroscopic grade solvents.

### Synthesis

**4-tert-butylphenoxy(2,9,16(17)-tri(4-aminophenyl)subphthalocyaninato)boron(III) (SubPc1) ( $C_1$  and  $C_3$  isomers).** The corresponding SubPcI<sub>3</sub> isomer (0.0217 mmol, 20 mg), previously dried overnight in a vacuum oven, 4-aminophenylboronic acid pinacol ester (0.156 mmol, 34 mg), CsF (0.195 mmol, 30 mg), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.0032 mmol, 3.8 mg) were dissolved in dry THF (2.2 ml), and the mixture refluxed for 15 h under argon atmosphere. After that time, additional 4-aminophenylboronic acid pinacol ester (0.078 mmol, 17 mg) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.0016 mmol, 1.9 mg) were added, and the mixture refluxed for additional 25 h. Then the mixture was diluted with chloroform, washed with water

(2 x 20 mL) and brine (20 mL). After that, the organic phase was dried with MgSO<sub>4</sub>, filtered and the solvent removed under vacuum. The product was purified by column chromatography on SiO<sub>2</sub> in EtOAc. The product was dissolved in DCM and precipitated with heptane, collected by filtration and dried overnight in a vacuum oven. Yield: 10 mg, (56%). IR(ATR)  $\nu^{-1}$  (cm<sup>-1</sup>): 3450 (NH<sub>2</sub>), 3391 (NH<sub>2</sub>), 3213, 2957, 2929, 2858, 1605, 1466, 1261, 1056 (B-O), 819.; HR-MS (MALDI, matrix DCTB + PPGNa 790):  $m/z$  817.3474 [M<sup>+</sup>] (calculated: 817.3452); UV-Vis (CHCl<sub>3</sub>),  $\lambda_{\max}$  (log  $\epsilon$ ): 590 (5.2), 541 (sh), 423 (sh), 380 (4.8) nm.

**NMR data for SubPc1-C<sub>1</sub>** (see Supporting Information for numerical order of the atoms)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.01 (br s, 3H; H-1, H-8, H-18), 8.88-8.75 (m, 3H; H-3/4, H-10/11, H-15/16), 8.15-8.01 (m, 3H; H-3/4, H-10/11, H-15/16), 7.75-7.57 (m, 6H, H-23/24), 6.89-6.79 (m, 6H, H-23/24), 6.79-6.71 (m, 2H, H-28), 5.46-5.31 (m, 2H, H-27), 3.83 (br s, 6H, NH<sub>2</sub>), 1.08 (s, 9H, H-31); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 152.0, 151.9, 151.7, 151.6, 151.3, 151.2 (6C; C-2, C-9, C-17, C-22), 150.4 (1C; C-26), 146.8 (6C; C-5, C-12, C-14 / C-7, C-19, C-21), 143.6 (1C; C-29), 143.2, 143.1 (6C; C-5, C-12, C-14 / C-7, C-19, C-21), 132.1 (C-4a, C-7a, C-11a / C-14a, C-18a, C-21a), 130.8, 130.7 (3C; C-25), 128.9 (3C; C-4a, C-7a, C-11a / C-14a, C-18a, C-21a), 128.8 (6C; C-23/24), 128.3, 128.2 (3C; C-3/4, C-10/11, C-15/16), 125.8 (2C, C-27/28), 122.5, 122.4 (3C; C-3/4, C-10/11, C-15/16), 119.5, 119.4 (3C; C-1, C-8, C-18), 118.0 (2C; C-27/28), 115.7 (6C; C-23/24), 34.0 (1C; C-30), 31.5 (3C; C-31).

**NMR data for SubPc1-C<sub>3</sub>** (see Supporting Information for numerical order of the atoms)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.01 (d,  $J$  = 0.88 Hz, 3H; H-1, H-8, H-15), 8.82 (d,  $J$  = 8.34 Hz, 3H; H-3/4, H-10/11, H-17/18), 8.08 (dd,  $J$  = 8.34 Hz,  $J$  = 1.60 Hz, 3H; H-3/4, H-10/11, H-17/18), 7.69 (d,  $J$  = 8.54, 6H; H-23/24), 6.84 (d,  $J$  = 8.54, 6H; H-23/24), 6.80-6.74 (m, 2H; H-27/28), 5.41-5.33 (m, 2H; H-27/28), 3.84 (br s, 6H, NH<sub>2</sub>), 1.08 (s, 9H, H-31); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 151.8, 151.5 (6C; C-2, C-9, C-16, C-22), 150.4 (1C; C-26), 146.8 (6C; C-5, C-12, C-14 / C-7, C-19, C-21), 143.6 (1C; C-29), 143.2 (6C; C-5, C-12, C-14 / C-7, C-19, C-21), 132.1 (C-4a, C-11a, C-18a / C-7a, C-14a, C-21a), 130.8 (3C; C-25), 129.0 (C-4a, C-11a, C-18a / C-7a, C-14a, C-21a), 128.8 (6C; C-23/24), 128.3 (3C; C-3/4, C-10/11, C-17/18), 125.8 (2C, C-27/28), 122.5 (3C; C-3/4, C-10/11, C-17/18), 119.4 (3C; C-1, C-8, C-15), 118.0 (2C; C-27/28), 115.7 (6C; C-23/24), 34.0 (1C; C-30), 31.5 (3C; C-31).

### Self-assembly experiments

**C<sub>3</sub>-SubPc1** (2.0 mg, 2.45  $\mu$ mol), Fe(II) salt (Fe(OTf)<sub>2</sub> or Fe(NTf<sub>2</sub>)<sub>2</sub>), (2.45  $\mu$ mol) and 2-formylpyridine (73.4  $\mu$ L of a stock solution 0.1 M in CD<sub>3</sub>CN or DMF-d<sub>7</sub>, 7.34  $\mu$ mol) were dissolved in the corresponding deuterated solvent (MeCN or DMF-d<sub>7</sub>) (0.6 mL) in a J-Young NMR tube. The solution was degassed by three evacuation/argon fill cycles and, then, sonicated for 30 minutes. The resultant solution was heated at 45°C for 24 h and analyzed by ESI MS spectroscopy. After analysis, it was heated to 80°C for 24 h and analyzed again by ESI MS spectroscopy, taking the samples directly from the NMR tube and diluting them in acetonitrile before injection in the equipment. **Self-assembly experiment 1:** CD<sub>3</sub>CN, Fe(OTf)<sub>2</sub>; **experiment 2:** DMF-d<sub>7</sub>, Fe(OTf)<sub>2</sub>; **experiment 3:** CD<sub>3</sub>CN, Fe(NTf<sub>2</sub>)<sub>2</sub>; **experiment 4:** DMF-d<sub>7</sub>, Fe(NTf<sub>2</sub>)<sub>2</sub>.

**NMR data for SubPc1-C<sub>3</sub>** in the solvents used for the self-assembly experiments (see Supporting Information for numerical order of the atoms)

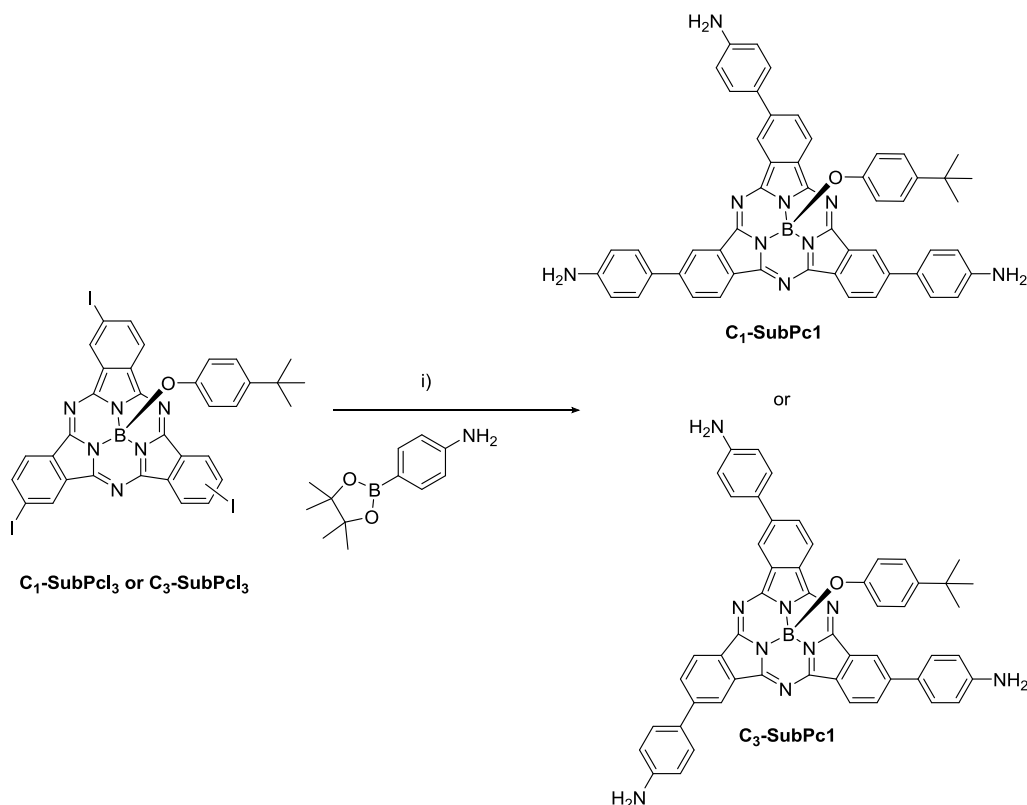
<sup>1</sup>H-NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) 8.90 (s, 3H; H-1, H-8, H-15), 8.72 (d,  $J$  = 8.30 Hz, 3H; H-3/4, H-10/11, H-17/18), 8.14 (d,  $J$  = 8.30 Hz, 3H; H-3/4, H-10/11, H-17/18), 7.70 (d,  $J$  = 8.49, 6H; H-23/24), 6.83 (d,  $J$  = 8.49, 6H; H-23/24), 6.80 (d,  $J$  = 8.78 Hz, 2H; H-27/28), 5.40 (d,  $J$  = 8.78 Hz, 2H; H-27/28), 4.42 (br s, 6H, NH<sub>2</sub>), 1.08 (s, 9H, H-31). <sup>1</sup>H-NMR (300 MHz, DMF-d<sub>7</sub>):  $\delta$  (ppm) 9.00 (s, 3H; H-1, H-8, H-15), 8.84 (d,  $J$  = 8.33 Hz, 3H; H-3/4, H-10/11, H-17/18), 8.26 (d,  $J$  = 8.33 Hz, 3H; H-3/4, H-10/11, H-17/18), 7.78 (d,  $J$  = 8.44, 6H; H-23/24), 6.92 (d,  $J$  = 8.44, 6H; H-

23/24), 6.84 (d,  $J = 8.67$  Hz, 2H; H-27/28), 5.59 (br s, 6H, NH<sub>2</sub>), 5.42 (d,  $J = 8.67$  Hz, 2H; H-27/28), 1.06 (s, 9H, H-31).

## RESULTS AND DISCUSSION

### Synthesis of SubPc1 ligands

The first step towards the preparation of SubPc tritopic ligands is the synthesis of 4-*tert*-butylphenoxy(2,9,16(17)-triiodosubphthalocyaninato)boron(III) (**SubPcI<sub>3</sub>**), which was performed following described procedures [17]. Importantly, the constitutional isomers (**C<sub>1</sub>-SubPcI<sub>3</sub>** and **C<sub>3</sub>-SubPcI<sub>3</sub>**) were separated at this stage by column chromatography on silica gel, thus allowing us to independently prepare the tritopic **C<sub>1</sub>-SubPc1** and **C<sub>3</sub>-SubPc1** ligands [18]. Then, substitution of the peripheral iodine atoms of each of the **SubPcI<sub>3</sub>** isomers by 4-phenylamine groups was performed by a triple Suzuki cross-coupling reaction with 4-aminophenylboronic acid pinacol ester in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst (Scheme 1), affording the desired **C<sub>1</sub>-SubPc1** and **C<sub>3</sub>-SubPc1**. For this purpose, we first applied general conditions for reactions with phenylboronic reagents, using Pd(PPh<sub>3</sub>)<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub> as base in dry DMF, but in our case (Table 1, entry 1), the reaction of **C<sub>1</sub>-SubPcI<sub>3</sub>** and **C<sub>3</sub>-SubPcI<sub>3</sub>** with 4-aminophenylboronic acid pinacol ester proceeded in very low yield. For that reason, we tried to optimize this conversion changing different parameters, as depicted in Table 1. This subset of experiments were performed over **C<sub>1</sub>-SubPcI<sub>3</sub>**. First, changing to CsF as base in dry THF as solvent, **C<sub>1</sub>-SubPc1** was isolated in 17% yield (entry 2). Better conversions were achieved when increasing the relative amount of pinacol ester (entry 3), but we did not observe further improvement when more CsF was added (entry 4). In the last experiment (entry 5), after 15 h of reaction under the conditions of entry 3, a second addition of catalyst (i.e., 0.075 eq) and pinacol ester (i.e., 3.6 eq) was done, affording **C<sub>1</sub>-SubPc1** in 56% yield. This optimized conditions were applied to the **C<sub>3</sub>-SubPcI<sub>3</sub>** with a similar outcome.



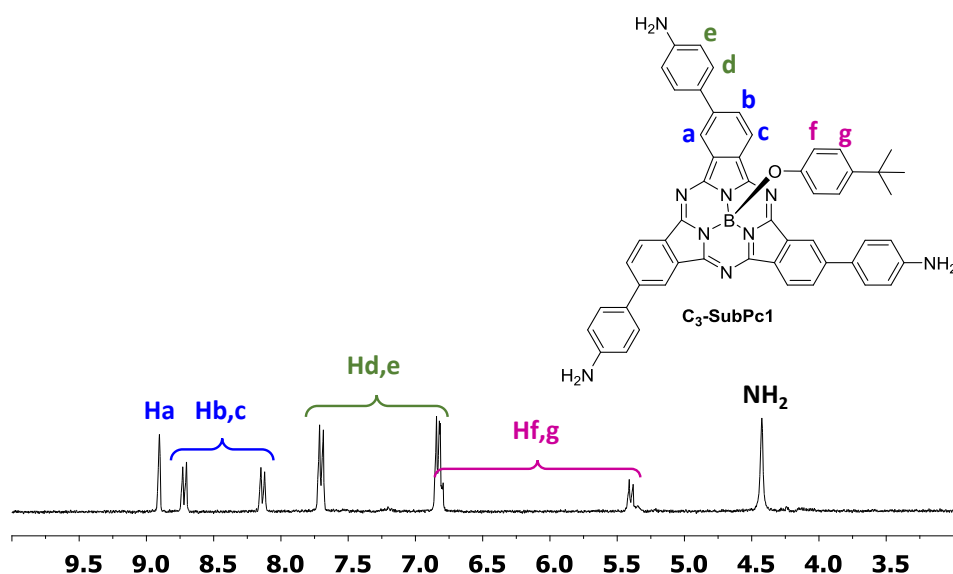
**Scheme 1.** Synthesis of **C<sub>1</sub>-SubPc1** and **C<sub>3</sub>-SubPc1**. i) Reflux, 40h, dry THF, Pd(PPh<sub>3</sub>)<sub>4</sub>, CsF (see Table 1).

**Table 1.** Investigation of conditions for the Suzuki cross-coupling reaction of **C<sub>1</sub>-SubPcI<sub>3</sub>** with 4-aminophenylboronic acid pinacol ester to obtain **C<sub>1</sub>-SubPc1** (Scheme 1).

entry	eq pinacol ester <sup>a</sup>	eq Pd(PPh <sub>3</sub> ) <sub>4</sub> <sup>a</sup>	base (eq) <sup>a</sup>	time <sup>b</sup>	solvent <sup>c</sup>	yield
1	6	0.15	K <sub>2</sub> CO <sub>3</sub> (3.9)	15 h	dry DMF	11 %
2	3.6	0.15	CsF (9)	15 h	dry THF	17 %
3	7.2	0.15	CsF (9)	15 h	dry THF	29 %
4	7.2	0.15	CsF (12)	15 h	dry THF	29 %
5	10.8 <sup>d</sup>	0.225 <sup>d</sup>	CsF (9)	40 h	dry THF	56 %

<sup>a</sup>For 1 eq of **C<sub>1</sub>-SubPcI<sub>3</sub>**. <sup>b</sup>Reaction at reflux temperature. <sup>c</sup>[SubPc] = 0.01 M. <sup>d</sup>Two consecutive additions, first 0.15 eq Pd(PPh<sub>3</sub>)<sub>4</sub> and 7.2 eq pinacol ester, followed by 0.075 eq Pd(PPh<sub>3</sub>)<sub>4</sub> and 3.8 eq pinacol ester after 15 h.

The structures of **C<sub>1</sub>-SubPc1** and **C<sub>3</sub>-SubPc1** were unequivocally confirmed by MALDI mass spectrometry, UV-vis, and NMR (see SI). In Figure 1, the <sup>1</sup>H NMR spectrum of **C<sub>3</sub>-SubPc1** shows a well-defined pattern of signals for the SubPc, protons, the aminophenyl ring and the *tert*-butylphenoxy axial substituent, the latter signals appearing upfielded (i.e., 6.77 and 5.37 ppm for the AA'XX' system) due to the shielding of the aromatic ring current of the SubPc (Figure 1). The <sup>1</sup>H-NMR of **C<sub>1</sub>-SubPc1** shows identical pattern and shifts of the signals, but broadened and more poorly resolved.



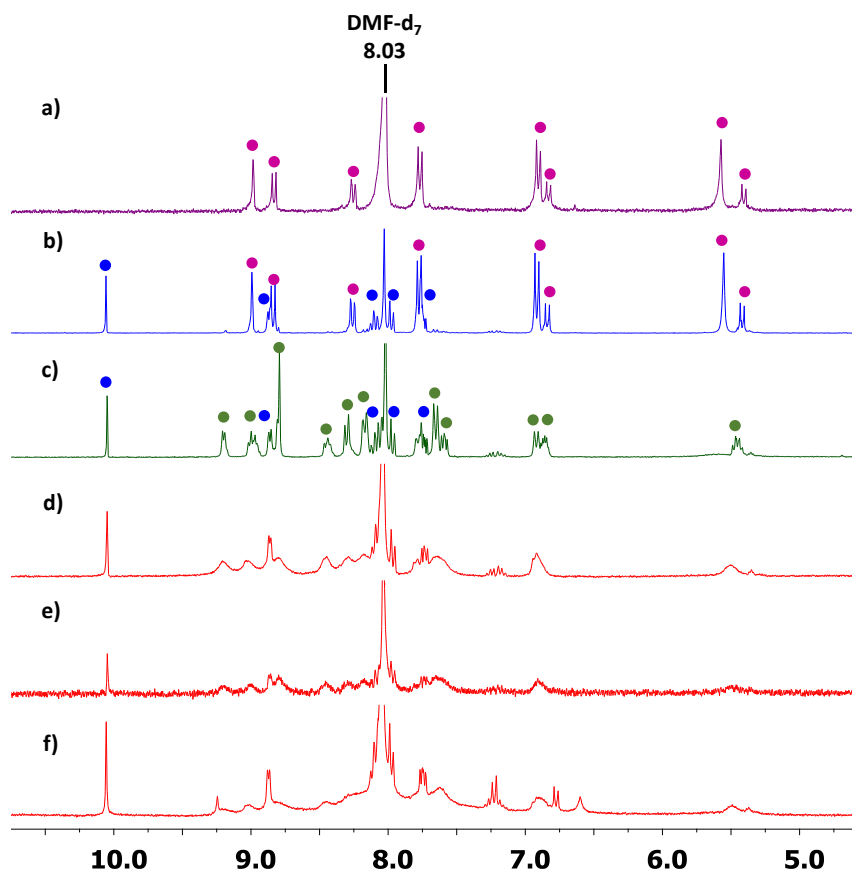
**Figure 1.** <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN of **C<sub>3</sub>-SubPc1**

### Self-assembly experiments

We selected **C<sub>3</sub>-SubPc1** to perform self-assembly experiments since this isomer presents a well-defined binding geometry that is appropriate for shifting the dynamic equilibrium towards the formation of discrete metallo-supramolecular species.

We started our experiments using Fe(OTf)<sub>2</sub> as metal source, since Fe(II) is the more broadly used octahedral metal for building metallo-supramolecular architectures [19], and, in particular, it has afforded excellent results in previous

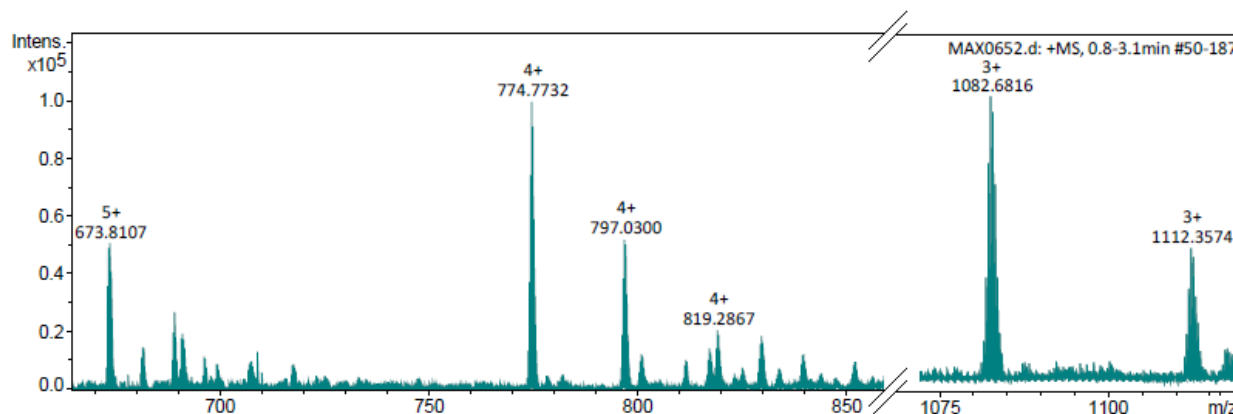
work of our group on metallo-organic helicates constructed with ditopic Pc ligands [20]. Therefore, we dissolved equimolar amounts of **C<sub>3</sub>-SubPc1**, Fe(OTf)<sub>2</sub> and a three-fold excess of 2-formylpyridine in CD<sub>3</sub>CN, in a J-Young NMR tube, (**self-assembly experiment 1**) in order to follow the reaction by <sup>1</sup>H NMR. After 24 hours at room temperature, a precipitate appeared that did not allow us to analyze the conversion by NMR. Then, we turned to DMF-d<sub>7</sub> as solvent for the reaction (**self-assembly experiment 2**). The reaction mixture was heated to 45°C for 24 h, and then for another 24 h at 80°C, searching for a shifting of the equilibrium towards a thermodynamic minimum. <sup>1</sup>H-NMR measurements on freshly prepared samples, and after heating cycles show broadening and shifting of some of the signals, together with the development of new ones as the formation of the iminopyridine moieties, in a first step, and the octahedral Fe(II) complex, in a second step, progresses (Figure 2).



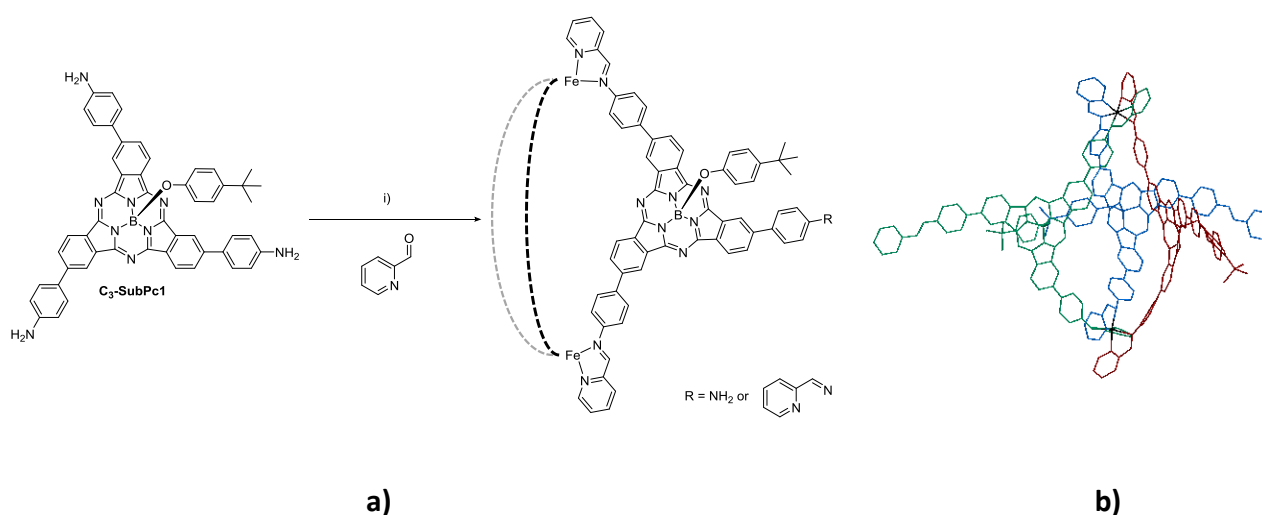
**Figure 2.** <sup>1</sup>H NMR spectra at room temperature of the **self-assembly experiment 2** in DMF-d<sub>7</sub> at different stages: a) **C<sub>3</sub>-SubPc1**; b) **C<sub>3</sub>-SubPc1** (pink spots) + 2-formylpyridine (blue spots), t = 0, r.t.; c) **C<sub>3</sub>-SubPc1** + 2-formylpyridine, t = 15 min, r.t. (green spots are related to the evolution of the reaction); d) **C<sub>3</sub>-SubPc1** + 2-formylpyridine + Fe(II), t = 0, r.t.; e) **C<sub>3</sub>-SubPc1** + 2-formylpyridine + Fe(II), t = 24 h, 45°C; f) **C<sub>3</sub>-SubPc1** + 2-formylpyridine + Fe(II), t = 48 h, 80°C.

The mixtures were also analyzed by ESI MS spectroscopy (Figure 3), and, in all the stages, we observed peaks corresponding to tetra-charged [Fe<sub>2</sub>SubPc<sub>3</sub>]<sup>4+</sup> helicates. Specifically, peaks at *m/z* 774.7712, 797.0279, 819.2848 match with a [Fe<sub>2</sub>SubPc<sub>3</sub>]<sup>4+</sup> structure, all these species being present in the dynamic equilibrium because only two of the three amino groups (Figure 4) attached at each **C<sub>3</sub>-SubPc1** ligand are involved in the formation of the metallo-organic complex, and the remaining ones can be, or not, derivatized as iminopyridine moieties. In fact, the above mentioned peaks correspond to [Fe<sub>2</sub>SubPc<sub>3</sub>]<sup>4+</sup> with three, two or one free amino groups respectively. We observe also peaks corresponding to penta-charged species that arise from oxidation processes at the metal center (Fe<sup>2+</sup> → Fe<sup>3+</sup>), and tri-

charged species which correspond to  $[\text{Fe}_2\text{SubPc}_3(\text{OTf})]^{3+}$  (Figure 3). However, no evidence on the formation of tetrahedral  $\text{Fe}_4\text{SubPc}_4$  species was found in any of the experiments.



**Figure 3.** ESI-MS spectrum of the the assembly of **C<sub>3</sub>-SubPc1** with  $\text{Fe}(\text{OTf})_2$  in  $\text{d}_7$ -DMF at  $80^\circ\text{C}$ .

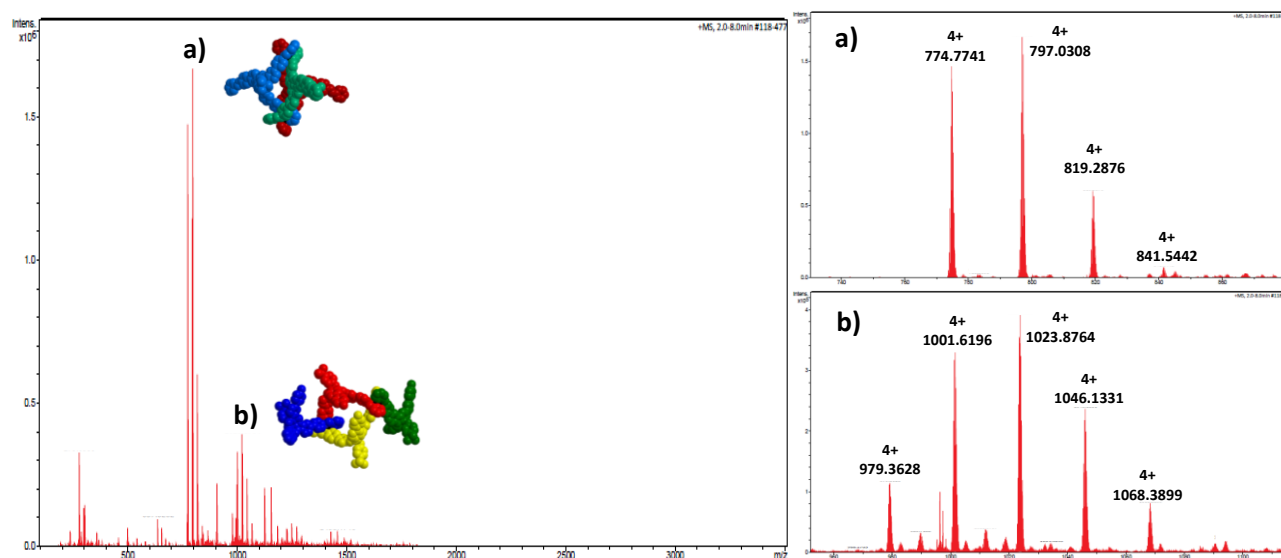


**Figure 4.** a) **Self-assembly experiment 2** where i)  $\text{DMF-d}_7$ ,  $\text{Fe}(\text{OTf})_2$ ,  $45^\circ\text{C}$ , 24 h. b) Modelized structure of the  $[\text{Fe}_2\text{SubPc}_3]^{4+}$  helicate (HyperChem release 8.0.9 for Windows, Molecular Modeling System, n.d.).

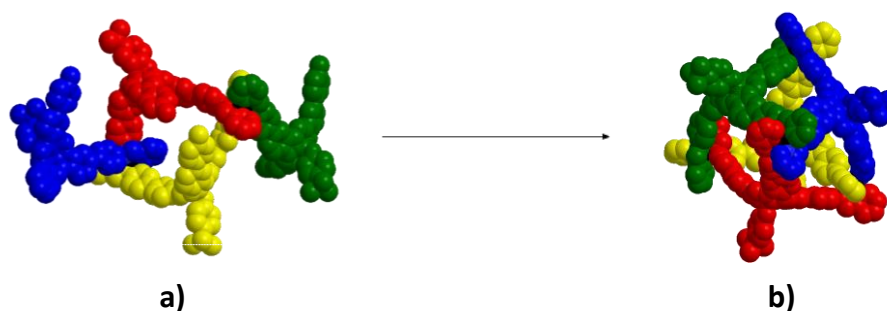
Both the solvent and temperature used in the self-assembly experiments have a strong impact on the type of metallo-organic structure obtained. For that reason, we turned again to  $\text{CD}_3\text{CN}$ , which is the most widely used solvent for building metallo-supramolecular ensembles by dynamic covalent self-assembly, and we sorted out the solubility issue by using iron (II) triflimide  $\text{Fe}(\text{NTf}_2)_2$  (**self-assembly experiment 3**) [21]. Also in this case, we performed  $^1\text{H}$ -NMR measurements on freshly prepared samples, after 24 h heating at  $45^\circ\text{C}$  and additional 24 h heating at  $80^\circ\text{C}$ , where we could observe broadening of the signals of the SubPc protons. In the ESI MS measurements of the solution after heating at  $45^\circ\text{C}$ , we observed the same sets of peaks for different  $[\text{Fe}_2\text{SubPc}_3]^{4+}$  and  $[\text{Fe}_2\text{SubPc}_3]^{5+}$  species, and also peaks with a tetra-charged pattern but with larger  $m/z$  values (Figure 5). The analysis of these peaks confirmed that they correspond to  $[\text{Fe}_2\text{SubPc}_4]^{4+}$  species, which have only six of the twelve iminopyridyl moieties involved in the octahedral coordination to two  $\text{Fe}(\text{II})$  centers (Figure 6a). Important peaks of this series are  $m/z = 1023.8764$ ,  $1046.1331$  and



1068.3899, which correspond to species endowed with two, three and four free-iminopyridine units, respectively. These species remain after heating to 80°C. When changing to DMF-d<sub>7</sub> and Fe(NTf<sub>2</sub>)<sub>2</sub> (**self-assembly experiment 4**), we could see the same pattern of [Fe<sub>2</sub>SubPc<sub>3</sub>]<sup>4+</sup> and [Fe<sub>2</sub>SubPc<sub>4</sub>]<sup>4+</sup> complexes. Noteworthy, [Fe<sub>2</sub>SubPc<sub>4</sub>]<sup>4+</sup> species recall the structure of a tetrahedral complex (Figure 6b), but lacking two Fe(II) coordinations.



**Figure 5.** ESI-MS experiment of **self-assembly experiment 3**: C<sub>3</sub>-SubPc1 + 2-formylpyridine + Fe(NTf<sub>2</sub>)<sub>2</sub>, t = 24 h, 45°C, in CD<sub>3</sub>CN. a) [Fe<sub>2</sub>SubPc<sub>3</sub>]<sup>4+</sup> species; b) [Fe<sub>2</sub>SubPc<sub>4</sub>]<sup>4+</sup> species.



**Figure 6.** Model of a [Fe<sub>2</sub>SubPc<sub>4</sub>]<sup>4+</sup> complex (a), with only six of the twelve iminopyridyl moieties involved in the octahedral coordination to two Fe(II) centers, which can be considered as non-closed precursor of a hypothetical M<sub>4</sub>L<sub>6</sub> tetrahedron (b). Modeling with HyperChem release 8.0.9 for Windows, Molecular Modeling System, n.d.

## CONCLUSIONS

We have applied subcomponent self-assembly conditions for the formation of metallo-supramolecular structures from appropriately functionalized SubPcs. Two isomeric, C<sub>1</sub>-SubPc1 and C<sub>3</sub>-SubPc1 derivatives have been independently prepared, and the tritopic C<sub>3</sub>-SubPc1 ligand has been tested under different assembly conditions, using 2-formylpyridine and different Fe(II) salts, solvents and temperatures, in the search of helicate-type Fe<sub>2</sub>SubPc<sub>3</sub> structures and/or Fe<sub>4</sub>SubPc<sub>4</sub> tetrahedral capsules. The formation of the metallo-supramolecular ensembles has been followed by

mass spectrometry (ESI direct injection techniques) and, under the different conditions applied, the assembly into Fe<sub>2</sub>SubPc<sub>3</sub> helicates and/or Fe<sub>2</sub>SubPc<sub>4</sub> structures was confirmed. Interestingly, the latter can be considered as open precursors of face-centered, Fe<sub>4</sub>SubPc<sub>4</sub> tetrahedral complexes, but, unfortunately, the closed cage was not formed. Further experiments will be focused on the search of conditions that lead the assembly towards the formation of this interesting type of SubPc-based tetrahedral cages.

## ACKNOWLEDGEMENTS

Financial support from Comunidad de Madrid, Spain (S2013/MIT- 2841, FOTOCARBON), and Spanish MICINN (CTQ2014-52869-P) is acknowledged.

## REFERENCES

- 1 a) Cook T. R., Stang P. J. *Chem. Rev.* 2015; 115: 7001–7045.
- 2 Belowich M. E., Stoddart J. F. *Chem. Soc. Rev.* 2012; 41: 2003–2024.
- 3 Zarra S., Wood D. M., Roberts D. A., Nitschke J. R. *Chem. Soc. Rev.* 2015; 44: 419–432.
- 4 Bilbeisi R. A., Clegg J. K., Elgrishi N., Hatten X. de, Devillard M., Breiner B., Mal P., Nitschke J. R. *J. Am. Chem. Soc.* 2012; 134: 5110–5119.
- 5 Roberts D. A., Castilla A. M., Ronson T. K., Nitschke, J. R. *J. Am. Chem. Soc.* 2014; 136: 8201–8204.
- 6 Mahata K., Frischmann P. D., Würthner F. J. *Am. Chem. Soc.* 2013; 135: 15656–15661.
- 7 Wood D. M., Meng W., Ronson T. K., Stefankiewicz A. R., Sanders J. K. M., Nitschke J. R. *Angew. Chem. Int. Ed.* 2015; 54: 3988–3992.
- 8 Rizzuto F. J., Wood D. M., Ronson T. K., Nitschke J. R. *J. Am. Chem. Soc.* 2017; 139: 11008–11011.
- 9 Musser A. J. P., Neelakandan P., Richter J. M., Mori H., Friend R. H., Nitschke J. R. *J. Am. Chem. Soc.* 2017; 139: 12050–12059.
- 10 a) Claessens C. G., González-Rodríguez D., Torres T. *Chem. Rev.* 2002; 102: 835–854. b) Claessens C. G., González-Rodríguez D., Rodríguez-Morgade M. S., Medina A., Torres T. *Chem. Rev.* 2014; 114: 2192–2277.
- 11 Caballero E., Fernández-Ariza J., Lynch V. M., Romero-Nieto C., Rodríguez-Morgade M. S., Sessler J. L., Guldi D. M., Torres T. *Angew. Chem. Int. Ed.* 2012; 51: 11337–11342.
- 12 Winterfeld K. A., Lavarda G., Guilleme J., Sekita M., Guldi D. M., Torres, T., Bottari, G. J. *Am. Chem. Soc.* 2017; 139: 5520–5529.
- 13 Perez E. M., Martin N. *Chem. Soc. Rev.* 2008; 37: 1512–1519.
- 14 de la Torre G., Bottari G., Torres T. *Adv. Energy Mater.* 2016: 1601700.
- 15 Claessens C. G., Torres T. *J. Am. Chem. Soc.* 2002; 124: 14522–14523.
- 16 Sánchez-Molina I., Grimm B., Krick Calderon R. M., Claessens C. G., Guldi D. M., Torres T. *J. Am. Chem. Soc.* 2013; 135: 10503–10511.
- 17 a) Claessens C. G., Gonzalez-Rodriguez D., del Rey B., Torres T., Mark G., Schuchmann H.-P., von Sonntag C., MacDonald J. G., Nohr R. S., *Eur. J. Org. Chem.* 2003; 14: 2547–2551. b) Sánchez-Molina I., Grimm B., Krick Calderon R. M., Claessens C. G., Guldi D. M., Torres T., *J. Am. Chem. Soc.* 2013; 135: 10503–10511.
- 18 Claessens C. G., Torres T., *Tetrahedron Letters.* 2000; 41: 6361–6365.
- 19 Ronson T. K., Meng W., Nitschke J. R., *J. Am. Chem. Soc.* 2017; 139: 9698–9707.
- 20 Fazio E., Haynes C., de la Torre G., Nitschke J. R., Torres T., submitted article.
- 21 Roberts D. A., Pilgrim B. S., Cooper J. D., Ronson T. K., Zarra S., Nitschke J. R., *J. Am. Chem. Soc.* 2015; 137: 10068.