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Complete List of Authors:	Montero-Campillo, M. Merced; Universidad Autonoma de Madrid, Quimica M $\diamond$, Otilia; Universidad Autonoma de Madrid Yanez, Manuel; Universidad Autonoma de Madrid,
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Beryllium Subphthalocyanines Self-Assembling Properties

M. Merced Montero-Campillo,^a Otilia Mó^a and Manuel Yáñez^{a,*}

^aDepartamento de Química, Módulo 13, Universidad Autónoma de Madrid
Campus de Excelencia UAM-CSIC
Cantoblanco, 28049 Madrid (Spain)

*e-mail: manuel.yanez@uam.es

This paper is dedicated to Russ Boyd and Arvi Rauk, two excellent scientists and two excellent friends.

ABSTRACT

Beryllium subphthalocyanines have been recently shown to be suitable candidates for photochemical devices if combined with appropriate donor systems. The ability of beryllium subphthalocyanines to self-assemble is explored for the first time by means of Density Functional Theory calculations. Free dimers of beryllium subphthalocyanine and their corresponding complexes with water and pyridine are computed at the wB97X-D/6-311+G(d,p) level of theory. In contrast with the behavior reported for beryllium phthalocyanines, for beryllium subphthalocyanines, beryllium-aza-nitrogen intermolecular interactions are observed, suggesting that these species are likely to self-assemble. Aggregates of related structures such as beryllium subporphyrazines with axial groups confirm the importance of hydrogen bonds in the stacking.

KEYWORDS

Subphthalocyanines, Subporphyrazines, Beryllium, Self-assembling, Intermolecular interactions, Non covalent interactions

INTRODUCTION

Fundamental biological functions such as photosynthesis or cellular respiration are carried out by porphyrins, a huge, relevant family of macrocycles in organic synthesis.¹⁻² From a structural point of view, porphyrines are highly conjugated systems that generate nowadays as much interest as in the early years, in particular in material science and medicine.³⁻⁷ Many analogues of porphyrins have been obtained in the last years in the search for new materials, as for instance subphthalocyanines (**SubPc**) or subporphyrazines (**SubPz**).⁸⁻¹¹ These **SubPc** compounds (see Figure 1) are non-planar contracted porphyrinoids containing a 14 π electron aromatic core and present a very promising photochemical behavior.¹² As shown by previous experimental and theoretical studies,¹³⁻¹⁵ photochemical properties of **SubPc** compounds depend strongly on the peripheral and axial substituents, as well as on the nature of the cation that occupies the central cavity.

Figure 1. Porphyrin (**P**), phthalocyanine (**Pc**), subphthalocyanine (**SubPc**) and subporphyrazine (**SubPz**).

In this field the synergy theory-experiment has been shown to be particularly useful, since *ab initio* or Density Functional Theory (DFT) calculations may provide useful *a priori* information on the expected behavior of particular derivatives prior to any synthesis attempt. This approach permits to save much time and efforts in the preparation of compounds for which it is possible to predict, on theoretical grounds, whether they are going to have low or null photochemical activity, or on the contrary to focus the efforts in the synthesis of those systems for which a high photochemical activity is predicted.¹⁶⁻²¹

In this direction, very recently, beryllium subphthalocyanines were shown to be able of absorbing light in the visible region.²² This fact is a new evidence of the chemical versatility of beryllium, whose ability to behave as an effective Lewis acid, by forming beryllium bonds, opens a door to modulate or completely modify the intrinsic physicochemical properties of its conjugated Lewis base.²³⁻²⁵

When the final goal is to design compounds with a high potential photochemical activity, it is not enough to verify that indeed this is the case for isolated systems. The preparation of the devices to be used in practical applications requires the active compounds to be able to form large enough molecular assemblies, which can work as a molecular wire. This is actually the main objective of this paper, to investigate the self-assembling capacity of Be derivatives which have been recently found to be good components of photovoltaic devices, in view of the photochemical activity of the isolated systems.

In order to study the stacking behavior of **BeSubPc** compounds, it is convenient to review what is already known about related structures such as beryllium phthalocyanine dimers and their complexes with other molecules.²⁶⁻³⁰ Beryllium phthalocyanine (**BePc**) forms monoclinic crystals belonging to the $P2_1/c$ space group. **BePc** exhibits also a planar D_{4h} symmetry at the molecular level, as well as **Pc** complexes of Cu(II), Ni (II), Mg(II) and others. In practice, **BePc** and **MgPc** are particular with respect to other **Pc** complexes due to their high affinity for water molecules and oxygen from air.²⁶ However, as revealed by X-ray technique studies, **BePc** has an additional peculiarity in the way it interacts with itself in the crystalline structure.²⁶ Whereas weak Mg-aza N intermolecular interactions are present in **MgPc**,

an interaction that is also present in other d-cation **Pc** complexes, it has been claimed that no Be-aza N interactions are present in the stacks of **BePc** due to the small size of Be(II).²⁶

BePc in contact with air is transformed to a hydrated form, **BePcH₂O**, in which Be(II) has a four plus one coordination number.²⁶ Water molecules have been shown to be essential in the stabilization of the crystalline structure, as **BePcH₂O** units together with solvent molecules, as for example pyridine, form stable dimers in which several hydrogen bonds are involved (see Figure 2).²⁹ Also, **BePc** forms stable complexes with 4-picoline (4-Mepy) in which this ligand occupies the axial position, having Be(II) a four plus one coordination and escaping from planarity as in the case of water molecules.²⁸

Figure 2. Two **BePcH₂O** units together with pyridine solvent molecules form stable dimers.²⁹

To the best of our knowledge, no information about stacking of **BeSubPc** complexes has been reported yet, although some particular stacked structures with boron analogues **BSubPc**, with axial and peripheral fluorine substituents, have been already studied.³¹ Curved structures of **BSubPc(F,R)** complexes behave differently to **BePc** when crystallizing. This is not only due to the different size and shape of the macrocycles or differences between Be and B atoms, but also to the R substituents which largely affect the packing along the three dimensions and determine the supramolecular organization.³¹ In the **BSubPc** crystal, parallel columns of aggregates are distorted along the c axis, avoiding the alignment of the B-F bonds. Additionally, F-N intermolecular distances are considerably shorter than the sum of the corresponding van der Waals radii. The short distance between monomers was studied through DFT

calculations, concluding that the reason behind this shortening is the cooperativity effect that increases with the number of monomers included in the aggregates.

In order to study how Be**SubPc** molecules could form dimers, Be**Pc** was taken as a starting point. In this work, dimers of Be**SubPc** are investigated by means of Density Functional Theory (DFT) calculations, providing some clues about the kind of intermolecular interactions that these molecules with a promising photochemical behavior can lead to. Depending on the relative orientation of the monomers and the presence of axial groups or other molecules in the environment, such as solvent molecules, different kinds of non-covalent interactions will dominate the stacking process. Aggregates up to three units of beryllium subporphyrazines (Be**SubPz**) are also studied, as a suitable model for Be**SubPc** self-assembling processes. The arrangement of building blocks of these compounds are crucial for the construction of any device.

COMPUTATIONAL DETAILS

Electronic structure calculations were carried out by using the Gaussian09 code.³² It is of crucial importance that van der Waals interactions are included when considering Be**SubPc** n-mers. With this purpose, the wB97X-D/6-311+G(d,p) level of theory was used to model the interaction between monomers.³³⁻³⁴ This latter functional includes empirical dispersion and long range corrections and its performance has been recently compared with B97D, B97-D3 and APFD functionals to study π - π stacking systems.³⁵ Also, the electron density at the bond critical points (BCP) of the Be-N bonds was calculated by means of the Atoms in Molecules (AIM) theory.³⁶⁻³⁷ We used NCIPLOT (NCI, Non Covalent Interaction) program to characterize the non-covalent interactions, which are accompanied by low reduced gradient and low-density values.³⁸⁻³⁹ These regions of real space can be located by using gradient isosurfaces on which a blue-green-red color code can be projected. This color is related to the sign of the second eigenvalue of the electron-density Hessian and allows to distinguish, in 3D representations, between strong attractive non covalent interactions (blue) and strong repulsive non covalent interactions (red), whereas very weak interactions, of order of Van der Waals magnitude, appear in green. Although not represented in this work, quantitative values can also be easily visualized by using 2D-NCIPLOT diagrams.

RESULTS AND DISCUSSION

Self-assembling properties of BeSubPc compounds at the wB97X-D/6-311+G(d,p) level of theory are presented in this section. Firstly, it is important to take into account the shape that these molecules present, which is going to be crucial for their association processes. With the only exception of SubPc in which carbon is the central atom,⁴⁰ all other SubPc complexes with different cations as central atoms are cone-shaped structures. This is also the case for beryllium subphthalocyanine and subporphyrizine (SubPz) complexes, as recently reported in the literature.²² As mentioned in the Introduction, BePc observed stacked structures will be used as a starting point for our studies, for which no Be aza-N interactions seem to exist (CSD Refcode ZZZNHK01).²⁶ To confirm this point for an isolated dimer in vacuum, we have fully optimized the geometry of the simplest BePc dimer, containing hydrogen atoms as peripheral substituents. In the dimer, the monomers conserve their planar structure and beryllium cation is placed over the π cloud of the neighboring cyclopentadiene ring, as represented in Figure 3A. The distance between beryllium and the molecular plane of the other monomer being 3.3 Å. This distance is consistent with previous observations for related crystalline structures (see distances in back-to-back dimers in Ref. 28, CSD Refcode WIJZEV).^{26,28}

Figure 3. (A) BePc dimer optimized structure at the wB97X-D/6-311+G(d,p) level of theory. (B) NCIPLOT of the BePc dimer. Be (yellow and pink color) and N (blue color) atoms are labeled in both pictures for the sake of comparison.

In agreement with what was claimed in the literature for the crystalline structure, no direct beryllium – aza nitrogen interactions are observed. This latter point has been

confirmed by looking at the NCIPLOT of the system (see Computational Details), for which no other interactions than van der Waals interactions between monomers were found. These weak interactions are visualized in Figure **3B** as an extensive green surface located in between both monomers. In the same picture, other interactions within each monomer are visualized, as for instance strong repulsion (red color) between nitrogen atoms in the core of the structure and attractive interactions (blue color) in Be-N bonds. The arrangement observed in the BePc dimer is a typical π - π stacking between planar aromatic structures.

BeSubPc units without any other axial or solvent moiety may form dimers in which the monomers have the same or opposite orientations (**A** and **B** in Figure 4). It should be noticed that in both cases the Be cation is able to connect with the neighboring molecule through a Be-N non-covalent intermolecular interaction, which is a remarkable difference with respect to the previous BePc case. If we compare this situation with that observed in Figure 3, it is clear that the curvature of the molecule favors the interaction with the aza-nitrogens, leading to Be-N distances of 2.166 Å (same orientation, Figure 4A) and 1.846 Å (opposite orientation, Figure 4B). By looking at the results obtained through the QTAIM approach, the difference between these two distances is reflected in the corresponding density values at the bond critical points (BCPs) of the N-Be bond in both cases, which are 0.021 and 0.048 a.u., respectively. A larger interaction energy is observed for the 4B structure with respect to the 4A structure (-186.0 kJ/mol vs -168.7 kJ/mol), the interaction energy defined as the energy difference between the complex and the monomers within the geometry of the complex. Also, in the 4B structure, an unexpected bonding path between two N atoms of the monomers appears, apparently triggered by the Be-N interaction in the dimer with opposite orientation. This N-N interaction is characterized by a density value of 0.042 a.u. at its BCP (see also Table S1). At that same position, the NCIPLOT analysis shows a repulsive interaction in the N-N bond path, due to the formation of the beryllium and nitrogen four-membered ring, unlike the very attractive Be-N interactions (see Figure 4D). This constitutes another nice example of cases where the overlap between the electron densities of two neighboring atoms leads to the appearance of a BCP even though not a real bond between them exists.

Figure 4. BeSubPc dimers with two different orientations (A) and (B) at the wB97X-D/6-311+G(d,p) level of theory. Pictures (C) and (D) correspond to the NCIPLLOT of (A) and (B), respectively. Be (yellow and pink color) and N (blue color) atoms are labeled in all pictures for the sake of comparison.

Regarding the ability of BeSubPc to add axial molecules, we studied the interaction of the subphthalocyanine through the Be cation with a water molecule, on the basis that it will be easily hydrated as BePc is (CSD Refcode XEGFEV).²⁶ As expected, BeSubPc interacts with water as BePc does (see Figure 5A), similarly also to the arrangement showed with fluorine or chlorine as axial substituents.²² The distance between Be and O from water is 1.760 Å and the N-Be-N angle 103.8°, in the same range of values found with the previously mentioned axial groups.

These molecules could be able to trap other small molecules present in the environment when forming aggregates, such as solvent molecules, as previously

observed in BePc dimers (CSD Refcode PEDPUL, see Figure 2).²⁹ By including water and pyridine (Py) in presence of two BeSubPc units, we effectively obtain a stable dimer in which water molecules help bringing together both monomers through hydrogen bonds. This (BeSubPcH₂OPy)₂ dimer along with its non-covalent interaction network is shown in Figure 5B (see also Table S2). In view of these structures, it is reasonable to think that BeSubPc might as well coordinate other similar molecules such as 4-Mepy, as observed for the phthalocyanine derivative (CSD Refcode WIJYUK).²⁸

Figure 5. (A) BeSubPc with water in axial position (BeSubPcH₂O), (B) BeSubPc dimer with water and pyridine molecules ([BeSubPcH₂OPy]₂, distances are in Å), (C, D) two different orientations of the NCIPLOT picture of BeSubPcH₂OPy dimer. All structures were obtained at the wB7X-D/6-311+G(d,p) level of theory. Be (yellow and pink color) and N (blue color) atoms are labeled in all pictures for the sake of comparison.

Very interestingly, cooperativity between weak interactions plays an important role in the BeSubPcH₂OPy dimer. This is evidenced by the reinforcement of Be-O bonds in the dimer (1.663 and 1.665 Å) with respect to the isolated BeSubPcH₂O system (1.760 Å, Figure 5A). This time, the Be-N interactions found in the pure dimer (Figure 4) are replaced by an extensive network of hydrogen bonds and van der Waals interactions between both macrocycles (see Figure 5B). The net of attractive non-covalent interactions revealed by the NCIPLOT analysis involves hydrogen bonds of different types (O-H, N-H) and beryllium bonds (Be-O) (see Figures 5C-D). Arrangements in molecular wires supported on hydrogen bonds such as CH $\cdots$ F bonds have been observed in packing in the solid state in BSubPc arrays.⁴¹

Figure 6. Monomer, dimer and trimer of BeSubPzH₂O units, respectively, at the wB97X-D/6-311+G(d,p) level of theory. At the bottom of the figure the zenithal views of the dimer and trimer are shown. Be (green color) and N (blue color) atoms are labeled to facilitate their identification.

From the complexes described to this point, it is evident that the assembling between units is strongly conditioned by other molecules such as water or solvent molecules that might change the balance between strong non-covalent interactions (i.e., hydrogen bonds) and extensive van der Waals interactions. Whereas dimers as that shown in Figure 4B are stabilized by strong non-covalent interactions, others present also π - π stacking areas (see Figure 5D). This lead us to wonder how these structures would self-assemble along a one-dimensional arrangement including an axial group and which forces would predominate. The organization of supramolecular structures by adding new monomer units is largely dependent on the nature of the axial and peripheral substituents, as well as on their respective sizes. Moreover, directional strong non-covalent interactions may help to the formation of aggregates. In this sense, cooperative effects are related to the dipole moment, this property being essential for the construction of molecular wires in one dimension.

Following a similar study to that developed for BSubPz,³¹ we have investigated the aggregation process from one to three monomer units of beryllium subporphirazines (BeSubPzH₂O, see Figure 6 and Table S3), a smaller and much affordable system from the computational point of view that has similar photochemical properties to those of BeSubPc.²² The BeSubPz core is identical to that of BeSubPc, but lacks of peripheral benzene rings. For these BeSubPzH₂O aggregates, we looked at the directionality of the structure, the dipole moment and the complexation energies. Results are collected in Table 1 and Figure 6.

Table 1. Complexation energies (kJ/mol), geometrical parameters and dipole moment (D) of (BeSubPzH₂O)_x (x=1-3) aggregates at the wB97X-D/6-311+G(d,p) level of theory. Complexation energy is defined as the energy released in the reaction $n \cdot \text{BeSubPzH}_2\text{O} \rightarrow (\text{BeSubPzH}_2\text{O})_n$.

Aggregate	E _{int} (kJ/mol)	μ (D)	Be-O distances (Å)	ρ (a.u.)
BeSubPzH ₂ O	0.0	4.00	1.763	0.045
(BeSubPzH ₂ O) ₂	-81.8	8.23	1.718, 1.758	0.051, 0.046
(BeSubPzH ₂ O) ₃	-167.4	12.89	1.712, 1.709, 1.755	0.052, 0.053, 0.046

Figure 7. (A) NCIPlot of the $(\text{BeSubPzH}_2\text{O})_3$ structure obtained at the wb97X-D/6-311+G(d,p) level of theory. (B) Hydrogen bonds between monomers involving water molecules. Be (yellow and pink color) and N (blue color) atoms are labeled in both pictures for the sake of comparison.

One variable that evidences the effect of adding monomers to the aggregate is the Be-O distance. In $\text{BeSubPzH}_2\text{O}$, this distance is pretty similar to that in $\text{BeSubPcH}_2\text{O}$ (1.763 Å vs 1.760 Å). On going from the monomer ($\text{BeSubPzH}_2\text{O}$) to the dimer ($(\text{BeSubPzH}_2\text{O})_2$) and trimer ($(\text{BeSubPzH}_2\text{O})_3$), this distance is shortened, as shown in the sequence of Be-O distances in Table 1. The shortest distance is the one observed in the trimer, 1.709 Å, which, besides, corresponds to the intermediate monomer of the chain. Density values on the corresponding Be-O bond critical points (BCPs) are in agreement with these observations.

Figure 7 shows the different interactions involved in the $(\text{BeSubPzH}_2\text{O})_3$ aggregate. Axial groups (in this case water molecules) play a crucial linking role in the

aggregate, similarly to the $\text{CH}\cdots\text{F}$ bonds previously described for **BSubPc** arrays.⁴¹ In this case, water is responsible for the hydrogen bond interactions between monomers ($\text{O-H}\cdots\text{N}$, $\text{OH}\cdots\text{C}$). The QTAIM analysis shows density values for these hydrogen bonds between 0.010 and 0.012 a.u. (see also Table S4). These hydrogen bonds appear in blue color in the corresponding NCIPLOT (see Figure 7A) and can be easily visualized in Figure 7B. Also, some other weak interactions between neighboring units are present, allowed by the curvature of the structure (green surfaces in Figure 7A).

Regarding the variation of the dipole moment on forming the aggregate, there is an increment of 0.23D from **BeSubPzH₂O** to (**BeSubPzH₂O**)₂, and even larger increasing (0.89D) is observed for the (**BeSubPzH₂O**)₃ structure. The aggregate gains stability by adding new units, in agreement with increasing values for the complexation energies, which passes from -81.8 kJ/mol in the dimer to -167.4 kJ/mol in the trimer.

It is important to note the helicoidal arrangement of the monomers, as evidenced by the zenithal views of the aggregates in Figure 6. This arrangement has also been observed very recently in **BSubPc** polymers,⁴² in which the authors relate the existence of the head-to-tail (convex-concave) stacking with the high dipole moment and the presence of hydrogen bonds, in agreement with our findings based on topological methods for **BeSubPz** aggregates. The role played by water in our survey is similar to the one played by fluorine in **BSubPc** supramolecular structures,⁴²⁻⁴³ showing that core-core interactions are fundamental to create long-range ordered structures in these systems.

CONCLUSIONS

The study of dimers of **BeSubPc** has revealed the presence of Be-N intermolecular interactions, unlike in the **BePc** dimer case, by coupling either the concave or the convex faces of the monomers. This survey has also been extended to dimers including water and pyridine molecules, which can form a stable network of non-covalent interactions between monomers. Taking **BeSubPz** as a good model for **BeSubPc**, the aggregate formed by three monomer units ((**BeSubPzH₂O**)₃) has large dipole moment and interaction energy values, which are clear driven forces for the self-assembling. Again, nitrogens are essential for the formation of hydrogen bonds between neighboring units along the molecular wire. In summary, these systems, with a

promising photochemical activity, are likely to self-assemble forming molecular wires. In this case, π - π stacking is not dominant, as occurred in BePc. Also importantly, core-core interactions triggered by Be itself and the axial group are as important as the peripheral substituents to achieve a long-range ordered structure, as previously observed in BSubPc related systems.

SUPPORTING INFORMATION

Cartesian coordinates and QTAIM results from some selected structures are available at <http://...>

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