

# PHthalOCYANINE-CONTAINING SUPRAMOLECULAR MATERIALS

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**Abstract:** *Phthalocyanines are among the most studied functional molecular materials with numerous applications in various scientific fields ranging from materials science, catalysis, nanotechnology to medicine. The intrinsic properties of these macrocycles and their molecular distribution can be modified by chemical functionalization. Conjugation of different functional units to phthalocyanine can also enhance the properties of these macrocycles, improving their performances as advanced functional materials. This literature study presents a short review of the current research of phthalocyanine-containing supramolecular materials, focusing on their hetero-arrays with different macrocycles such as porphyrins, subphthalocyanines and fullerene.*

**Keywords:** *supramolecular materials, phthalocyanines, hetero-arrays*

## 1. INTRODUCTION

Phthalocyanines (Pcs), macrocyclic compounds with a large  $\pi$ -conjugated system, absorb strongly in the red region of the spectrum (~670 nm), have a characteristic blue-green shade and exhibit extraordinary physical-chemical stability. Phthalocyanines are prepared and used as dyes and pigments, catalysts in photodegradation, chemical and gas detection sensors, optical recording media, conducting polymers and sensitizers in photodynamic therapy [1, 2].

Different functional units have been linked to Pcs in order to enhance their properties and functionalities and to improve their performance as advanced materials. Particular interest present some photo- and redox-active groups such as porphyrins, fullerenes and carotenoids mainly because the resulted conjugates exhibit potential applications in molecular photonics, photovoltaics and light-harvesting devices. In most conjugates, all the individual components are covalent linked while supramolecular hetero-arrays are relatively rare even though this self-assembly technique may lead to advanced molecular architectures with improved physical-chemical characteristics that are sometimes better than those of the individual counterparts. There are several methods used for obtaining such hetero-arrays, such as: axial coordination, hydrogen bonding, electrostatic forces, donor-acceptor interactions and host-guest interactions [3].

This short literature review will provide an overview of some researches in the field of phthalocyanine-

containing supramolecular arrays obtained by axial coordination.

## 2. AXIAL COORDINATED SUPRAMOLECULAR ARRAYS

Axial linkage of different phthalocyanines has been little studied compared to their porphyrins analogs even though this approach has been used to obtain various Pc-based hetero-arrays with porphyrins, subphthalocyanines, fullerene, etc. Noncovalent porphyrin-based ensembles are especially of great interest due to their resemblance to nature (which also depends on supramolecular assembly techniques), rich redox chemistry and photochemistry [4].

### 2.1. Phthalocyanine - Porphyrin hetero-arrays

Supramolecular aggregates of Pcs have received little attention, even though these tetrapyrrole derivatives exhibit unique physical-chemical properties. Arrays of mixed-porphyrin and Pc are mainly limited to some examples of covalently linked systems, sandwich-type complexes and face-to face aggregates arrays assembled by axial ligation [5].

The first report of the axial ligation between Pc and porphyrin derivatives was in 2000 [6] when zinc (II) 1,8,15,22-tetrakis(3-pentyloxy) phthalocyanine (1) was linked to *meso*-pyridyl porphyrin to form square-shaped building block. The structure of the resulted hetero-array was analyzed by <sup>1</sup>H-NMR and UV-Vis spectroscopy and the data obtained are consistent with an edge-to-face dyad. UV-Vis spectroscopy also showed that ground-state  $\pi$ - $\pi$  interactions between the perpendicular arranged

macrocycles are weak. When zinc (II) *meso*-tetra(*p*-tolyl)porphyrin was mixed with Pc (1), the formation of an edge-to-face hetero-arrayed dyad was also proven.

Imidazolyl-substituted porphyrins were also used to prepare dimeric Pc-porphyrin hetero-dyads and it was concluded that the two macrocycles are displayed orthogonal to each other so their intermolecular  $\pi$ - $\pi$  stacking can be avoided. The linkage between the *meso*-imidazolyl substituent and the zinc center of the Pc allows the formation of hetero-dyads stable in non-coordinating solvents such as chloroform, dichloromethane and toluene.

In another recent report, the synthetic methods of three covalently linked Pc-porphyrin heteropentamers formed after coupling four units of porphyrin to a central Pc, are described. The general reaction is a nucleophilic substitution between 1,8,15,22-tetra nitro phthalocyanines and [5-(4-hydroxy phenyl)-10,15,20-triphenyl porphyrins) as phenolic alcohols. These macrocycles were characterized by  $^1\text{H-NMR}$ , UV-Vis, IR, fluorescence and mass spectroscopy and showed a considerable red shift in the Pc Q-bands, confirming the electron-donating effects of the porphyrin derivatives [7].

## 2.2. Phthalocyanine - Subphthalocyanine hetero-arrays

In a report published in 2008, two pyridyl subphthalocyaninene (SubPc) derivatives were synthesized and axially linked to a series of zinc (II) and ruthenium (II) Pcs and the corresponding hetero-dyads were obtained. These hetero-dyads were characterized by UV-Vis spectroscopy and it was concluded that the ground-state interaction between the chromophores is weak.  $^1\text{H-NMR}$  and fluorescence spectroscopic methods were used to study the complexation processes and 1:1 binding stoichiometry was confirmed. Association constants were determined by fluorescence titration and it was observed that it has a higher value for ruthenium Pc than for zinc Pc. The molecular structure was also determined and confirmed by X-ray diffraction method [8].

Another method used for the preparation of SubPc-Pc dyads is palladium-catalyzed cross-coupling reaction between monoalkynyl-Pc and different monoiodo-SubPcs via  $\pi$ -conjugated alkynyl spacer. Cyclic voltammetry measurements revealed that the reduction potential of the SubPc unit can be decreased upon functionalization with different peripheral substituents. The resulted molecular ensembles exhibit special

features (highly efficient photoinduced electron-transfer, extraordinary absorptive cross section across the entire UV-Vis spectrum) making them ideal candidates for applications in fields where broadband light sources are required [9].

## 2.3. Phthalocyanine - Fullerene hetero-arrays

In a report published in 2002, the coordination between pyridine-linked fulleropyrrolidine ( $\text{C}_{60}\text{Py}$ ) and zinc (II) tetra-*tert*-butyl Pc -  $\text{ZnPc}(\text{t-Bu})_4$  was reported where the two macrocycles are linked through N – pyridine to the zinc center. Once photoexcited, the radical pair  $\text{ZnPc}(\text{t-Bu})_4^{\cdot+} - \text{C}_{60}\text{Py}^{\cdot-}$  is generated via intracomplex electron transfer route. The weak coordination that exists between  $\text{C}_{60}$  and Pc units eases the dissociation of the radical pair into  $\text{ZnPc}(\text{t-Bu})_4^{\cdot+}$  and  $\text{C}_{60}\text{Py}^{\cdot-}$ , free radical ions [10].

The assembly between zinc (II) tetra-*tert*-butyl-2,3-naphthalocyanine –  $\text{ZnNc}(\text{t-Bu})_4$  and fulleropyrrolidine with an imidazole coordinating ligand was also studied. Using electronic absorption spectroscopy it has been found that they form 1:1 supramolecular dyads by means of axial coordination. The association constant was measured in toluene only to emphasize that this dyad has good donor properties. In the optimized structure, the HOMO is located entirely in the  $\text{ZnNc}(\text{t-Bu})_4$  moiety while the LUMO is in the fullerene entity. These results are in close relationship with those obtained from cyclic voltammetry studied in *o*-dichlorobenzene [11].

## 3. CONCLUSIONS

The present paper provides a brief overview of phthalocyanine-containing supramolecular arrays obtained by axial coordination, a special attention being paid on the hetero-arrays with porphyrins, subphthalocyanines and fullerene.

Arrays formed by porphyrins and phthalocyanines are confined to some examples of covalently linked systems, sandwich-type complexes and face - to face aggregates arrays assembled by axial ligation. The structure of all these ensembles was proven by means of UV-Vis,  $^1\text{H-NMR}$ , IR, fluorescence and mass spectrometry measurements.

Different phthalocyanine-subphthalocyanine hetero-arrays were obtained with a 1:1 binding stoichiometry between the counterparts.

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