A Green Method for Preparation of Self-Organized Organic Nanoparticles of a Free Base Tetrakis(pentafluorophenyl)porphyrin

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Abstract

Supramolecular systems that include their self-assembled and self-organized systems are promising components of advanced materials because of their rich photochemistry, stability, and proven enhanced catalytic activity. While inorganic nanoparticles are widely studied, the formation of organic nanomaterials is more recent, and porphyrinoids are at the forefront of this research. Here we present a *green eco-friendly* method to prepare a colloidal solution of a free base 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, $TPPF_{20}$, using miscible host-guest solvent method. The aggregation of porphyrinoid to form colloidal solution was initially identified by opaqueness of solution and the further confirmed by UV-visible absorption spectroscopy. The broadening of strong absorption peak in the range of 380-475 nm, called Soret band and also the redder shift in low energy Q-bands is an indicative of aggregation of porphyrin to form their nanoparticles solution. A simple light scattering experiment, Tyndall Effect, also proves the formation of particles (aggregation of porphyrinoid) in the colloidal solution. We have used a miscible host-guest solvents method to prepare organic nanoparticle of $TPPF_{20}$ as a model of *Green Chemistry* as ~89% solvent system is water.

Introduction

Porphyrins: Porphyrins are heterogenous macrocyclic compounds with four pyrrole units joined together by methine bridges. These are an important class of organic compounds as they possess unique optical, photophysical magnetic and chemical properties that enable a wide range of applications such as in photonics, catalyst for environmental remediations, therapeutics etc. The basic structure of a free base porphyrin is shown in figure 1a. Many porphyrins are naturally occurring; one of the best-known
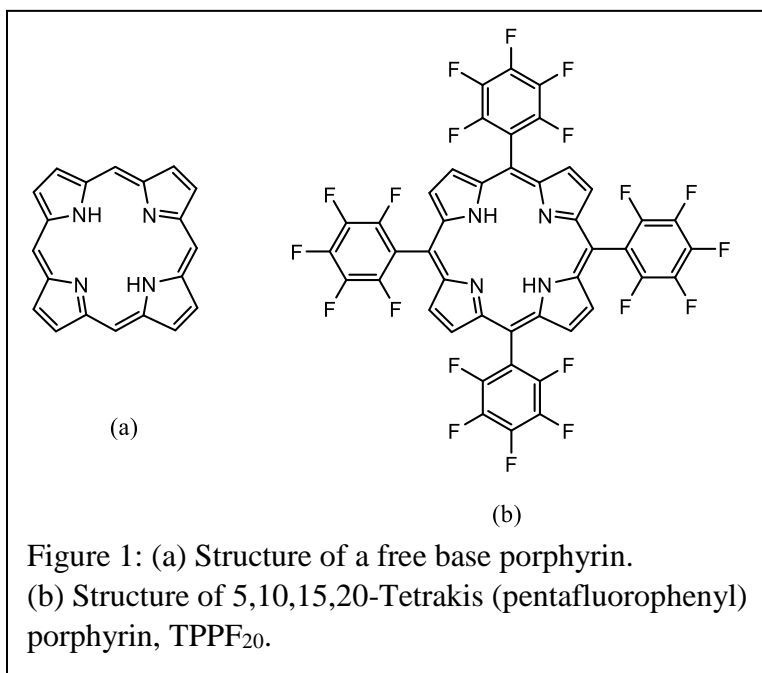

Figure 1: (a) Structure of a free base porphyrin. (b) Structure of 5,10,15,20-Tetrakis (pentafluorophenyl) porphyrin, $TPPF_{20}$.

porphyrins is heme (iron containing porphyrin), the pigment in red blood cells and a cofactor of

the protein hemoglobin. Other biologically important porphyrins include a magnesium porphyrin responsible for green pigment of plants (chlorophyll), a cobalt porphyrin, which are a common vitamin of Vitamin B_{12} family (cyanocobalamin) and many more. Porphyrins have been extensively studied for a wide range of other applications such as to develop sensors for environmental pollutant detection and remediation- to make components for solar cells for solar energy harvesting to photosensitizer for photodynamic therapeutic treatment of cancers.

Supramolecule: A supramolecular system is formed when the small building block molecules interact with each other either by non-specific interactions such as dispersion forces, dipole-dipole interactions or by specific interactions such as coordinate bond, hydrogen bonding are the foundations on which life builds complex functional materials. Supramolecular systems can be categorized as: (a) self-assembled systems in which building blocks are arranged in an ordered fashion is intolerant of errors/defects, whereas (b) self-organized systems results in formation of non-discrete systems that are dynamic in nature and are more tolerant of errors/defects. [1, 2] Porphyrinoids are ideal organic components for material chemistry— especially photonics, sensors, and molecular sieves—because they are remarkably robust under a variety of conditions. Also, the porphyrin core can be easily bind with a wide range of metal atoms via coordinate bond further helps to finetune their optical as well as redox properties. Nature exploits these optoelectronic properties of porphyrin supramolecular systems to harvest solar energy, transfer electrons, and as redox catalysts. [2] The properties of many nanoscaled particles are substantially different than those of bulk materials composed of the same atoms or molecules.

Organic Nanoparticles: The synthesis and applications of inorganic nano-materials composed of metals, metal oxides, ceramics etc. have been well reviewed in literature, [3, 4] but studies on the nanoparticles composed of organic molecules, other than lipids, are more recent [5-7] and porphyrinoids are at the forefront of this research. [8, 9] The inorganic nanoparticles are more robust and structurally static compare to organic nanoparticles that are dynamic in nature as the forces that held the organic molecules to form organic nanoparticles are week intermolecular forces and can easily adapt to the environmental conditions. [10] The methods used for the preparation of both inorganic as well as organic nanomaterials involves the use of either toxic metals, halogenated solvents, pH of reaction medium and other vigorous conditions such as high temperature, use of lasers. In addition to strong conditions, these methods also require heavy instrumentation that results in high cost. These all limits the development of advanced materials for their applications for modern society.[4] Therefore, there is a strong need to develop a green eco-friendly and cost-effective method to prepare nanomaterial for their applications.

Here, we are presenting a simple, quick and eco-friendly method to prepare organic nanoparticles of a free base 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, $TPPF_{20}$, by mixing host-guest solvent method reported earlier by Drain and coworkers [8,9]. The structure of $TPPF_{20}$ is shown in figure 1b. The formation of colloidal nanoparticles was confirmed by opaqueness of the solution, absorption spectra and also by scattering of light, that indicates the presence of small particles in solution.
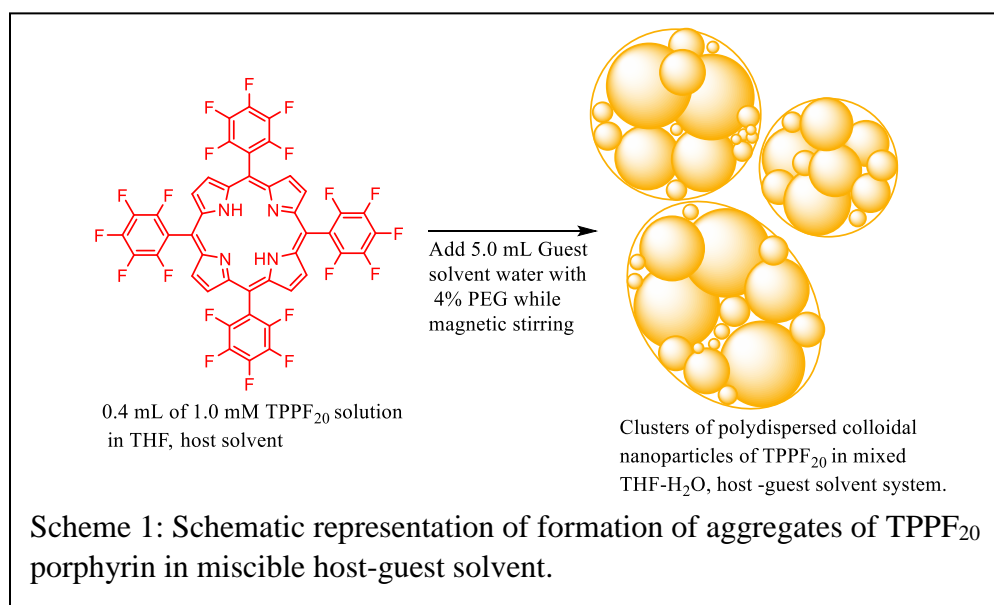
Experimental Details:

Materials and Instrumentation: 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TPPF$_{20}$), Tetrahydrofuran (THF) and polyethyleneglycol monomethylether (PEG$_{164}$) were purchased from Sigma Aldrich Chemicals Co. Electronic spectra were recorded on Cary Bio-3 UV/Vis spectrophotometer.

Preparation of Colloidal solution of organic nanoparticles (ONPs): 1 mM stock solution of TPPF$_{20}$ was prepared in THF. Then 0.4 mL portion of stock solution of TPPF$_{20}$ in THF was mixed with 0.2 mL of polyethylene glycol, PEG$_{164}$ in a 10 mL vial at room temperature. The solution was magnetically stirred. To this mixture solution then 5.0 mL of distilled water was added while magnetic stirring over a time period of 60 seconds and then the solution was further stirred under the same environmental conditions for another 2-3 minutes.[9, 11]

UV-visible Absorption Spectroscopy: The UV-visible absorption spectra of the stock solution of TPPF$_{20}$ in THF and the corresponding nanoparticles in water were recorded using baseline with THF and water respectively.

Results and Discussion:

Preparation of ONPs of TPPF$_{20}$: A colloidal nanoparticle solution of a hydrophobic porphyrin TPPF$_{20}$ is prepared by adding water to a solution of TPPF$_{20}$ in THF, mixing host-guest solvent method at room temperature. A small amount of PEG as stabilizer was added to the above mixture solution to increases the stability of the nanoparticles formed. The method of miscible host-guest solvent using a variety of host solvents such as THF, DMF, DMSO CH$_3$OH, and CH$_3$CN has already been successfully explored for a variety of porphyrinoids [8] and their related tetrapyrrole macrocycles. A schematic representation that shows the formation of clusters of colloidal nanoparticles in solution is shown in scheme 1.

0.4 mL of 1.0 mM TPPF$_{20}$ solution in THF, host solvent

Add 5.0 mL Guest solvent water with 4% PEG while magnetic stirring

Clusters of polydispersed colloidal nanoparticles of TPPF$_{20}$ in mixed THF-H$_2$O, host -guest solvent system.

Scheme 1: Schematic representation of formation of aggregates of TPPF$_{20}$ porphyrin in miscible host-guest solvent.

The formation of ONPs of TPPF$_{20}$, their size and stability depend on both: a) the nature of the intermolecular forces between TPPF$_{20}$, host solvent THF, Guest solvent water and the polyethylene glycol stabilizer, and b) the mode of mixing-magnetic stirring versus manual mixing. These factors also control the organization of the porphyrins into nanoaggregates. The addition of guest solvent water to the solution of porphyrin in host THF/PEG while magnetic stirring results into the formation of colloidal solution of TPPF$_{20}$, figure 2. The presence of stabilizer, PEG plays a crucial role to determine the stability of the nanoparticles formed. Manual mixing of solution of porphyrin in THF with water in the absence of PEG leads to the formation of precipitate, figure 2.
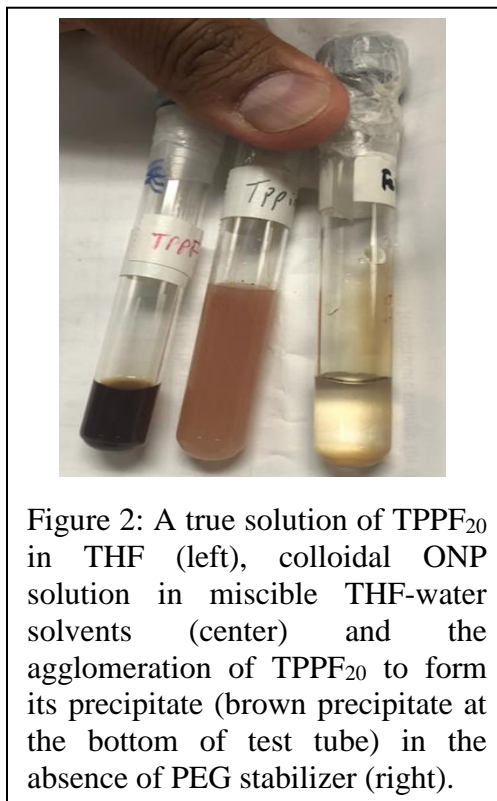

Figure 2: A true solution of TPPF$_{20}$ in THF (left), colloidal ONP solution in miscible THF-water solvents (center) and the agglomeration of TPPF$_{20}$ to form its precipitate (brown precipitate at the bottom of test tube) in the absence of PEG stabilizer (right).

Characterization of ONP:

(a) *Visual confirmation*: A clear transparent solution of TPPF$_{20}$ in THF was compared with its colloidal solution in water. The opaqueness of the colloidal solution is indicative of the presence of particles in the colloidal solution. Light always travels in a straight path; when light is deflected by the particles in the colloidal solution confirmed by its changed path, indicates that the size of particles must be big enough to block the vision, simultaneously the particles are small enough that cannot be seen through the naked eye, figure 2.

(b) Light scattering by ONPs: One traditional well-known characteristic of light is that it always travels in a straight path without any deflection. When a beam of light from a laser light source passed through the true solution of porphyrin in THF it passes without any scattering clearly

indicates the dissolved porphyrin particles in solution, figure 3(left). However, a small scattering can be seen in the left image of figure 3 is due to the scattering of light by glass, but not by the solution. On the other hand, when a beam of light from the same light source passes through the colloidal nanoparticles solution the entire test tube glows with the emission of pinkish-red light, indicates a strong scattering of light, figure 3(right). This clearly shows that the colloidal solution must be having particles that are big enough to deflect the path of the light. The multiple light scattering in the vicinity of the solution results in the strong fluorescence by the tube containing colloidal solution. This scattering of light by the colloidal nanoparticles solution is known as Tyndall effect.
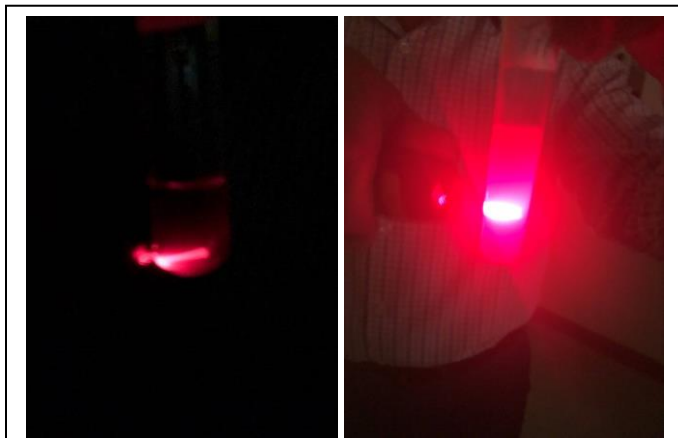

Figure 3: A beam of light passes straight through true solution of $TPPF_{20}$ with **NO** scattering of light. NOTE: A small scattering is observed because of glass (left). Scattering of light when it passes through the colloidal solution of $TPPF_{20}$ indicated by strong illumination (right).

(c) UV-visible absorption spectra: Absorption spectra of both colloidal nanoparticles solution in water and true solution of $TPPF_{20}$ in THF were recorded and compared. Figure 4 shows the absorption spectra of $TPPF_{20}$ nanoparticles and of its component molecule in THF. The component $TPPF_{20}$ molecule in THF shows a sharp narrow absorption band, Soret band at 406 nm along with four low energy Q-bands in the range of 485-650 nm. A broadening of the Soret Band was observed for the colloidal nanoparticle solution. Also, both the Soret band peak and the four low energy Q-bands shifter towards the redder end of the electromagnetic spectrum is an indicative of the agglomeration of the porphyrins into its colloidal solution. A detailed list of absorption peaks for both true solution of $TPPF_{20}$ and its colloidal nanoparticles solution are listed in table 1.
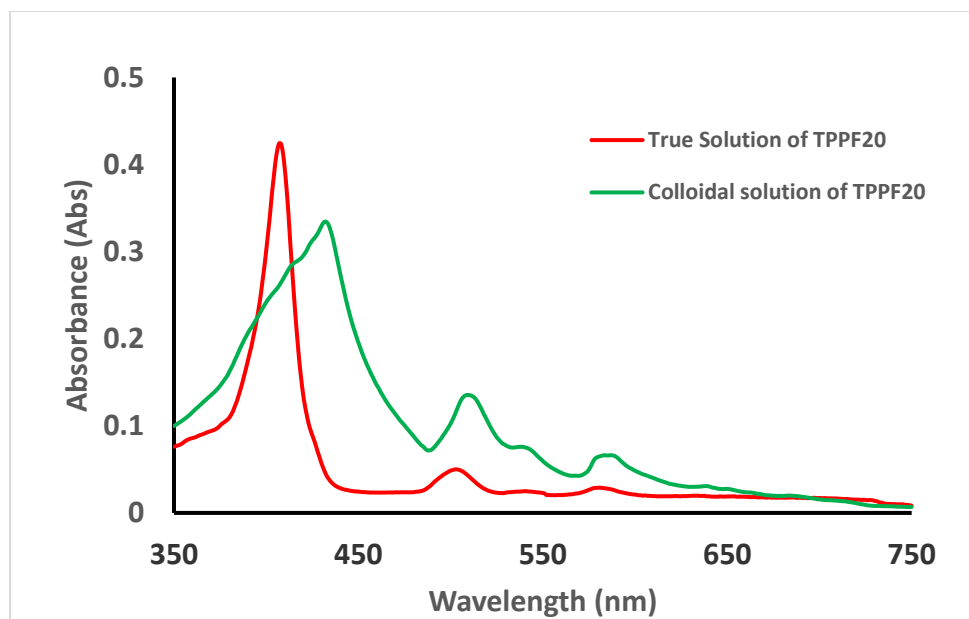
Figure 4: UV-visible absorption spectra of true solution of TPPF$_{20}$ in THF (red) and its colloidal nanoparticles (ONPs) solution in THF-H$_2$O mixed solvent system (green).

Table1: Absorption band peaks that includes for TPPF$_{20}$ in THF and its nanoparticles solution in THF-water mixed solvent.

	Absorption Peaks	
	Soret absorption band (nm)	Low energy Q-bands (nm)
TPPF$_{20}$ in THF	406	505, 542, 578, 632
Colloidal nanoparticles solution in THF-water mixed solvent	430	512, 547, 583, 644

Structural planarity of porphyrins macrocycles allows them to interact via two different ways to form their aggregates: edge-to-edge interaction leads to the formation of J-type aggregates and/or face-to face interaction also called π-stacking leads to the formation of H-type aggregates. Both J and H- types of aggregates possess different spectral features. In general, the formation of J-type aggregates were confirmed by the redder shift of the low energy Q-bands and/or also by the appearance of a shoulder on the red end of the Soret band, whereas for H-type of aggregates these above mentioned changes in the absorption band appears at the blue end of the electromagnetic spectrum. [9, 12] A small shoulder at 414 nm towards the blue end clearly indicates the formation of H-aggregates in the colloidal nanoparticle solution of TPPF$_{20}$. However, both the splitted Soret band together with the broadened and red-shifted Q-bands in the optical spectra suggest the presence of both types of aggregates in ONPs solution.

Conclusions:

In conclusion, we have used a previously reported [9,11] green eco-friendly method for the preparation of colloidal nanoparticles of TPPF$_{20}$ a free base porphyrin without using high energy and heavy instrumentation. The significance of this method lies in its simplicity and low-cost instrumentation that makes this method to be ideally to be used by both academia and industrially for other component molecules. The stability of the nanoparticles depends upon the presence of stabilizer. In the absence of stabilizer porphyrin particles further aggregates in THF-water solvent system to form its precipitate. The broadened, splitted and red shifted Soret band along with the low energy Q-bands in the optical spectra suggest both J- and H- types of interactions in the nanoparticles. This method of miscible host-guest solvent to prepare ONPs of TPPF$_{20}$ represents a model of *Green Chemistry* as ~89% solvent in the colloidal solution is water.

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