Preparation of Self-Organized Organic Nanoparticles of Perfluorophenylporphyrin

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Abstract

Porphyrin supramolecular systems are well proven to serve as promising components for advanced materials because of their unique physicochemical, optoelectronic, and magnetic properties. Here we present the colloidal nanoparticle solution of a free base 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, $TPPF_{20}$, using mixed solvent method. The formation of nanoparticles was confirmed by the opaqueness of solution and also by UV-visible absorption spectroscopy. The broadening of Soret band in the range of 370-480 nm as well as the redder shift in low energy Q-bands is an indicative of aggregation of porphyrin to form their nanoparticles solution. Light scattering experiment, Tyndall Effect, also proves the formation of bigger particles in the colloidal solution.

Introduction

Supramolecular systems originate by the spontaneous association of building blocks such as atoms, ions or molecules that are the foundations of any functional materials. Supramolecular systems broadly classified into two categories: self-assembly and self-organized systems. Self-assembled systems are those in which the building block are arranged in a fashion that results in discrete supramolecular structures that have long rage ordered arrangement and are also intolerant of errors/defects, whereas in a self-organized systems the building blocks are arranged in less orderly pattern and leads to the formation of non-discrete supramolecular systems, that are dynamic in nature and are more tolerant of errors/defects. The intermolecular forces that results the supramolecular system formed when the small building block molecules interact are either non-specific interactions such as dispersion forces, dipole-dipole interactions or specific interactions such as coordinate bond, hydrogen bonding are the foundations on which life builds complex functional materials. [1, 2] Porphyrinoids are ideal organic components for advanced material chemistry- especially in photonics, sensors, vehicles for drug delivery etc. The skeleton structure of a simple porphyrin is shown in fig 1a. Nature exploits the unique optoelectronic properties of porphyrin supramolecular systems to harvest solar energy, transfer

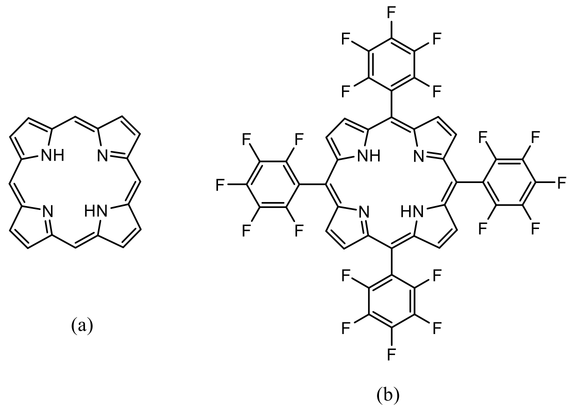


Figure 1: (a) Structure of a free base porphyrin. (b) Structure of 5,10,15,20-Tetrakis (pentafluorophenyl). porphyrin, $TPPF_{20}$.

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.

The studies on synthesis and application of organic nanoparticles is relative new compare to the inorganic nano-materials composed of metals, metal oxides, ceramics etc. [3, 4] and porphyrinoids are at the forefront of this research. [5-7] The methods used for the preparation of both inorganic as well as organic nanomaterials involves strong experimental conditions, toxic chemicals and special instrumentation/techniques that all limits the development of advanced materials for their applications for modern society.[4] Therefore, there is a strong need to develop a simple and cost-effective method to prepare nanomaterial for their applications.

Here, we are presenting a simple, quick and cost-effective 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 [5, 6]. 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:

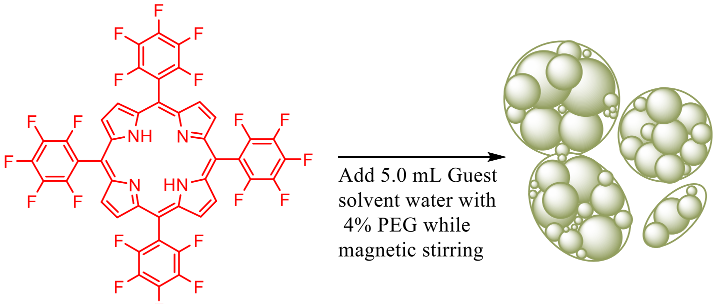
Materials: 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ($TPPF_{20}$), Tetrahydrofuran (THF) and polyethyleneglycol monomethylether (PEG_{164}) were analytical grade and purchased from Sigma Aldrich Chemicals Co.

Preparation of Colloidal solution of organic nanoparticles (ONPs): A stock solution of $TPPF_{20}$ was prepared by dissolving 2 mg of it in 2 ml THF (1mM solution). Then 400 μL portion of this stock solution of $TPPF_{20}$ in THF was mixed with 200 μL of polyethylene glycol, PEG_{164} in a 10 mL vial at room temperature. 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.[6, 8]

UV-visible Absorption Spectroscopy: The absorption spectra were recorded on Cary Bio-3 UV/Vis spectrophotometer. UV-visible absorption spectra of the stock solution of $TPPF_{20}$ in THF and the corresponding nanoparticles in water-THF mixed solvent system were recorded using baseline with THF and water respectively.

Results and Discussion:

Preparation of ONPs of $TPPF_{20}$: Mixing of miscible host-guest solvent method is used to prepare a colloidal nanoparticle solution of $TPPF_{20}$, a free base porphyrin at room temperature. To 0.4 mL portion of a stock solution (1 mM) of $TPPF_{20}$ in THF, a small amount (0.2 mL) of PEG as stabilizer was added. PEG serves as a bridge between the organic solution of $TPPF_{20}$ in THF and water and causes the stabilization of the nanoparticles formed. A schematic representation that shows the formation of clusters of colloidal nanoparticles of $TPPF_{20}$ in miscible host THF and guest water solvent system is shown in scheme 1.



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

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

Clusters of polydispersed colloidal nanoparticles of $TPPF_{20}$ in mixed $THF-H_2O$, 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 several factors such as (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 vortex missing or manual mixing, and (c) temperature. These factors also control the organization of the porphyrins into nanoaggregates and so nanoparticles formed are dynamic in nature. 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.

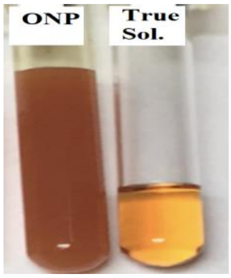


Figure 2: Colloidal ONP solution in miscible THF-PEG-water solvent system (left) and a true solution of $TPPF_{20}$ in THF (right).

Characterization for colloidal organic nanoparticle formation:

(a) *Visual confirmation*: A true solution of $TPPF_{20}$ in THF is clear and transparent while its colloidal solution in miscible solvent system is opaque. The opaqueness of the colloidal solution is indicative of the aggregation of small particles in the colloidal solution (figure 2).

(b) Light scattering by colloidal nanoparticles solution: A well-known traditional characteristic property of light is that it travels in a straight path without any deflection. When a beam of light from a laser light source hit the true solution of porphyrin in THF, it passes through the solution without any deflection or scattering clearly indicates the presence of dissolved porphyrin particles in solution, figure 3(left). On the other hand, a strong scattering of light in all direction was observed when the light from same light source was passed through the colloidal nanoparticles solution and the entire test tube glows with the emission of pinkish-red light, figure 3(right). This scattering of light by the colloidal nanoparticles' solution is known as Tyndall effect. This clearly

shows that the colloidal solution must be having particles that are big enough to deflect the path of the light. Note, a small scattering of light can be seen in the left image of figure 3 is due to the scattering of light by glass, but not by the solution.

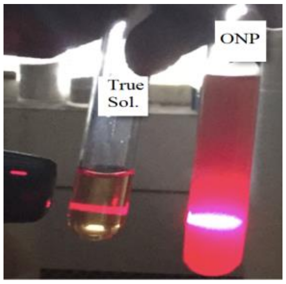


Figure 3: A beam of light passes straight through true solution of $TPPF_{20}$ with **NO** scattering of light. NOTE: A small scattering is observed because of glass (left). Scattering of light when it passes through the colloidal solution of $TPPF_{20}$ indicated by strong illumination (right).

(c) UV-visible absorption spectra: Absorption spectra of both colloidal nanoparticles solution and true solution of $TPPF_{20}$ in THF were recorded and compared, Figure 4. A strong sharp absorption peak at 406 nm (Soret band) observed for component $TPPF_{20}$ molecule in THF gets broadened between 370-470 nm range shows the aggregation of component porphyrin molecules to make their nano clusters. Also, the bathochromic shift for both the Soret band peak as well as the four low energy Q-bands for colloidal nanoparticles is indicative of agglomeration of the porphyrins into its colloidal solution. Appearance of small shoulders on both side of the broadened Soret band

Porphyrins can aggregate side wise and leads to the formation of J-type aggregates, where as their face-to-face interaction leads to the formation of H-aggregates. Both J and H- types of aggregates possess different spectral features. In general, the formation of J-type aggregates was confirmed by the appearance of a shoulder on the red end of the Soret band, whereas for H-type of aggregates a shoulder appears at the blue end of Soret band. [6, 9] 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.

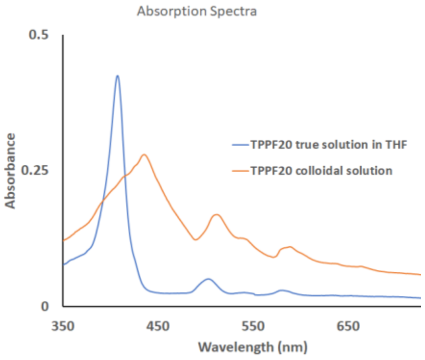


Figure 4: UV-visible absorption spectra of true solution of $TPPF_{20}$ in THF (blue) and its colloidal nanoparticles (ONPs) solution in THF-H_2O miscible solvent system (orange).

Conclusions:

In conclusion, we have used a previously reported [6, 8] miscible host-solvent solvent method for the preparation of colloidal nanoparticles of $TPPF_{20}$ a free base porphyrin under ambient conditions. 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. Formation of opaque colloidal solution and light scattering is an indicative of formation of porphyrin nanoparticles. The stability of the nanoparticles depends upon the presence of stabilizer. In the absence of stabilizer porphyrin particles aggregates quickly in THF-water solvent system to form its precipitate.

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