Green Method of Preparation of Organic Nanoparticles of a Porphyrinoid and their Characterization by Absorption Spectroscopy

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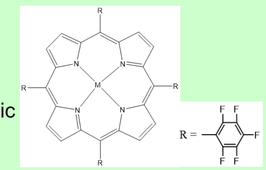
Abstract

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 are more recent, and porphyrinoids are at the forefront of this research. Porphyrinoids are well exploited by both nature and scientists for wide variety of applications. Porphyrin based supramolecular systems are recently reported to accelerate their catalytic properties. Here we present a *green eco-friendly* method to prepare a colloidal solution of a free base 5,10,15,20-tetrakis(pentafluoro)phenyl porphyrin using miscible host-guest solvent method. The aggregation of porphyrinoid to form colloidal solution was initially identified by opaqueness of solution and the further characterized by UV-Visible absorption spectroscopy. Broadening of soret band at 410 nm and also the red shift of Q-bands indicates the aggregate formation. A simple light scattering experiment, Tyndall Effect, also proves the formation of particles (aggregation of porphyrinoid) in the colloidal solution. The broadening of soret band and red shifted Q-bands indicates the formation of porphyrin nanoparticles. Our organic nanoparticle formation system represents a model of *Green Chemistry* as ~89% reaction solvent is water.

Introduction

Porphyrins

- Tetrapyrrole macrocycle with four pyrrole subunits connected via methine bridges.
- They have unique optoelectronic and physicochemical properties.
- For example: Heme in hemoglobin is an iron porphyrin and Chlorophyll, a green pigment of plant is Mg-Porphyrin.



M = Fe, Co, Ni, Mg etc. for metalloporphyrinoids
= H, for free base porphyrin.

Figure 1: Structure of a porphyrinoid.

Porphyrin Supramolecular System

- Atoms or molecules interacted by non-covalent forces.
- Supramolecular porphyrinoid materials are of current interest in photonics, catalysts, and biological activities.
- A *self-assembled* system is highly ordered and intolerant of errors, whereas a *self-organized* system is less ordered and is more tolerant of errors.

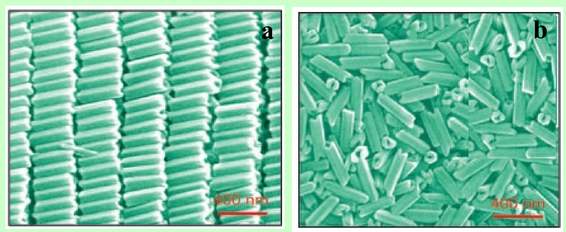


Figure 2: Self-assembled porphyrin nanoprism (**a**) and self-organized porphyrin nanoprisms (**b**). (taken from *J. Am. Chem. Soc.*, 2005,127, 17090-17095).

Organic Nanoparticles (ONPs)

- ONPs are aggregates of organic molecules, dynamic in nature and are composed of sub domains.

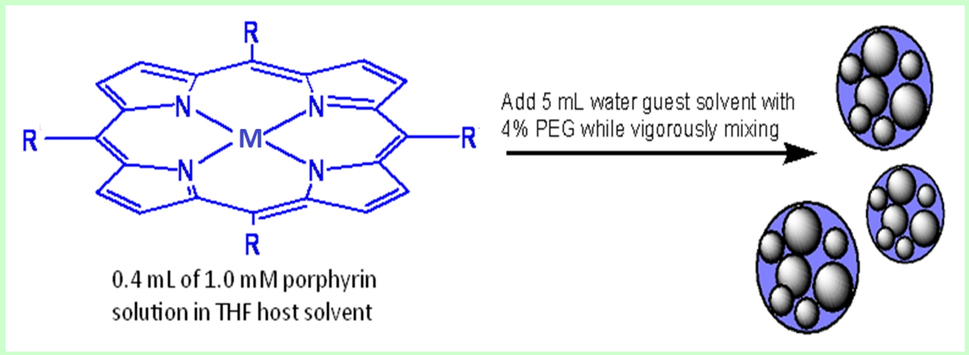


Figure 3: Schematic representation of formation of aggregates of porphyrinoids in miscible host-guest solvent.

Green Method for ONP Preparation

Experimental Details

- 1 mM stock solution (SS) of $TPPF_{20}$ in THF.
- 200.0μL of SS of $TPPF_{20}$ was then mixed with 100.0μL of polyethylene glycol (PEG).
- 2.5mL water was added slowly while magnetic stirring for over a time period of 60 seconds and then continuously stirring for another 2-3 minute until an pinkish-orange solution was obtained.

Characterization of ONP formation

- Formation of colloidal solution of $TPPF_{20}$ indicates the presence of nanoaggregates of porphyrin (figure 5), further confirmed by light scattering experiments (figure 6).
- Absorption spectra of true solution of Porphyrin in THF was compared with the spectra of colloidal solution.
- A broadening of Soret band and redder shift for both Soret band (by 11 nm) as well as for the Q–bands indicates the aggregation of porphyrin to form nanoparticles (figure 7).

Colloidal solution of Porphyrins ONPs

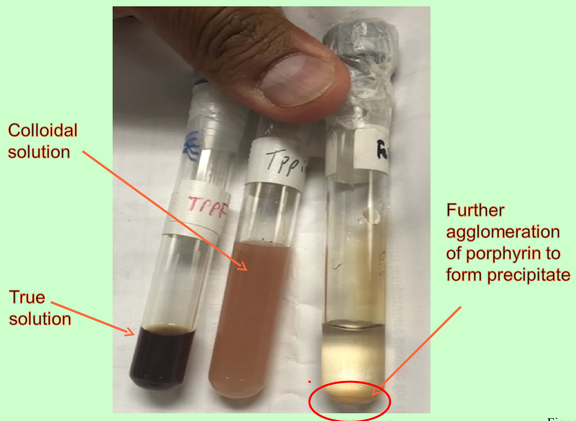


Figure 4: A true solution in THF (left), colloidal solution in miscible host-guest solvents (middle) and formation of precipitate (right) of a free base porphyrinoid, $TPPF_{20}$.

Light scattering by ONPs- Tyndall Effect

- Light scattering experiments were done in a dark room.

Figure 5: 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.

Figure 6: Scattering of light when it passes through colloidal solution of $TPPF_{20}$ indicated by strong illumination.

UV-Vis absorption spectra

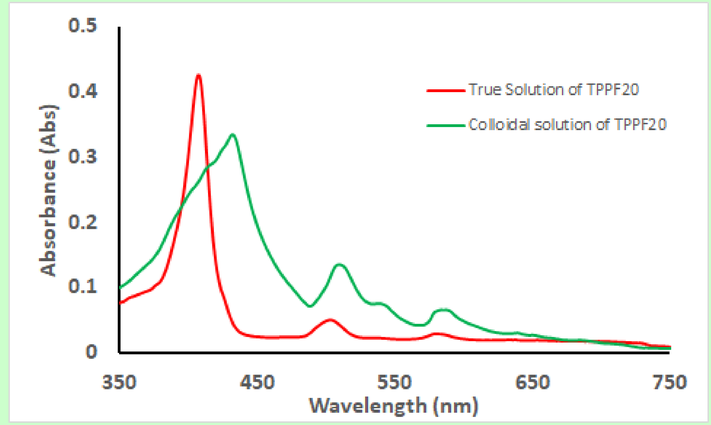


Figure 7: UV-Vis absorption spectra of porphyrin true solution (red) in THF and colloidal solution of porphyrin ONPs in water (green).

Conclusion

- Formation of aggregates of porphyrin is confirmed by the formation of opaque colloidal solution. Also, the
- Scattering of a beam of light by colloidal solytion indicates that particle size must be in a range of 100-1000 nm.
- Broadening of the Soret band (strong absorption band in the range of 400-450 nm indicates the formation of porphyrin aggregates.
- Soret band porphyrin ONPs shift to 434 nm compare to sore band for true solution of porphyrin at 408 nm.
- The shift in the Soret band and the low energy Q-bands for colloidal solution towards the redder end of the electromagnetic spectrum indicates the formation of porphyrin nanoparticles.
- A shoulder at **411 nm** (figure 7) at the blue edge of the Soret band of Porphyrin NP indicates the formation of H-aggregates .
- Formation of ppt (figure 4-right) indicates that the mode of mixing, and the ratio of miscible solvent plays a significant role for the formation of colloidal solution.
- Our method of ONPs formation represents a model of *Green Chemistry* as ~89% reaction solvent is water.

References

1) Aggarwal, A., Yu, Z. *Experiment 4: Synthesis of Nanoparticles.* LaGuardia Community College, NY. 2018 (lab handouts).
2) Gong, X.; Milic, T.; Xu, C.; Batteas, J. D.; Drain, C. M. *J. Am. Chem. Soc.* **2002**, *124*, 14290.
3) Drain, C. M.; Smeureanu, G.; Patel, S.; X.Gong; Garno, J.; Arijeloye, J. *New J. Chem.* **2006**, *30*, 1834.
4) V.N. R. Kishore. https://www.researchgate.net/post/why_maximum_
5) absorbance_occur_at_cut-off_wavelength_in_UV-vis_spectroscopy

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