12th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-12) 1-30 November 2008
http://www.usc.es/congresos/ecsoc/12/ECSOC12.htm & http://www.mdpi.org/ecsoc-12

[A008]

Ultrasonic method for the preparation of organic nanoparticles of porphyrin

Mohamad Mehdi Kashani Motlagh*,Rahmatollah Rahimi,Marziye Javaheri Kachousangi

Department of chemistry, university of science and technology ,Iran

Abstract

We report the synthesis and optical properties of organic porphyrin nanoparticles with narrow size distribution and well dispersibility. Nanoparticles were produced by a combination of the reprecipitation and sonication method and termed the “ultrasonic method”. The TPClPP nanoparticles were stable in solution without precipitation for at least 30 days. No self-aggregation of the constituent porphyrin chromophores was confirmed. The TPClPP nanoparticles exhibited interesting optical properties; a large bathochromic shift in the absorption spectra.

Keywords: Porphyrin nanoparticles; Optical properties

1-Introduction

Many of unique properties of nanoscaled materials can not be obtained by the corresponding atomic,molecular,polymeric or macroscopic materials,especially electronic,photonic and magnetic properties.

The porphyrinoids(porphyrins,porphyrazines,phthalocyanines and corrols)display a rich variety of photonic properties that can be modulated by endocyclic or exocyclic metal ion coordination,peripheral functional groups and the environment of the macrocyclic system.

For the formation of 10-500nm materials from supramolecular polymers and aggregates of porphyrins,the key issue is how to stabilize and isolate systems of the desired dimensions with acceptable polydispersity and in high yields .There are three basic strategies for the stabilization of nanoscaled supramolecular materials.(1)stabilizing agents that are either grafted onto the porphyrin monomers or added into the solution can prevent agglomeration of the nanoparticles and result in stable colloidal dispersions[1].Stabilizers include compounds that have little or no structural organization in the solvent such as polyethylene glycolsand surfactants that have metastable structures in solution such as cetyltrimethylammonium bromide(CTAB).Metastable structures may in fact be used to template the formation of nanoparticles-aggregates or crystals.(2)it is possible to kinetically trap the self-organized material by removing the conditions that allow equilibrium[2,3].Practically, this often means isolating the nanoparticles on a surface and/while removing them from solution[3,4,5].(3)adjusting the environmental conditions favor or force the formation of isolated nano aggregates by, for example, encapsulation into a solid or a gel matrix[6,7].Each of these strategies has advantages and disadvantages that depend on the function and application of the material.

---

*Corresponding author:E-mail address:m.kashani@iust.ac.ir

There are a variety of possible applications of porphyrin nanoparticles that derive from the photonic properties of both the component molecule and the nanoscaled dimensions of the particle.Many of these nanoparticles, when the porphyrin contains a redox-active transition metal (e.g.Fe,Co.Mn)are more efficient catalysts on a per porphyrin basis than the individual porphyrins adsorbed onto supports.The fluorescence properties of nanoparticles containing the free base or closed-shell metalloporphyrins or the phosphorescence of these or other metalloderivatives such as the Pd(II) and Pt(II) can be exploited for sensors and displays.

In this psper,we report synthesis of porphyrin nanoparticles via sonication method.There are a few reports on the synthesis of porphyrin nanoparticles[8,9,10,].Synthesis of nanoparticles via sonication method have been reported for other dyes and organic materials but have not been worked much for porphyrins[11,12,13].

2-Results and discussion

Structure of porphyrin nanoparticles

Nanoparticles consist of sub-domains of the macrocycles and solvent/stabilizer-filled voids or channels of unknown size and distribution ,so that the number of chromophore per nanoparticle is substantially less.The structural organization of the porphyrins within the nanoparticles likely depends on the specific structure of the macrocycle used because this dictates the intermolecular interactions between the porphyrins ,the solvent and the stabilizer.

Optical properties

The UV-vis spectra of porphyrin nanoparticles are significantly different compared to the spectra of the corresponding porphyrin solutions(fig1).Soret bands are found to be broadened and/or split. The arrangement of macrocycles in aggregates generally fall into two types,"J"(edge-to-edge)interactions are characterized by red shifts and "H"(face-to-face)interactions are characterized by blue shifts[?].The optical spectra suggest both types of interactions in the nanoparticles and are well understood to be indicative of electronic coupling of the chromophores. The extent of J versus H aggregation depends on the specific porphyrin used.

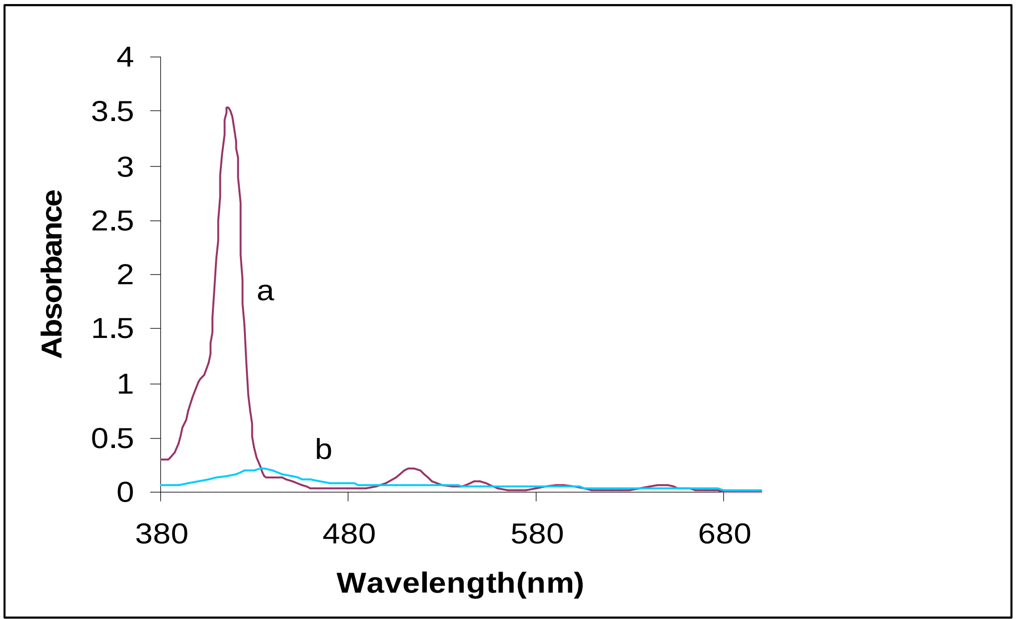


Fig .1. UV-vis spectra of: (a)TClPP in chloroform,(b)nanoTClPP

Effect of volume of water(guest solvent)
Volume of water did not have major effect on the position of soret and Q bands of porphyrin nanoparticles but with increasing volume of water as a guest solvent absorbance of porphyrin nanoparticles decreased.In UV-vis spectra,organic nanoparticles of porphyrin in comparison to their monomer ones redshifted and broadened.

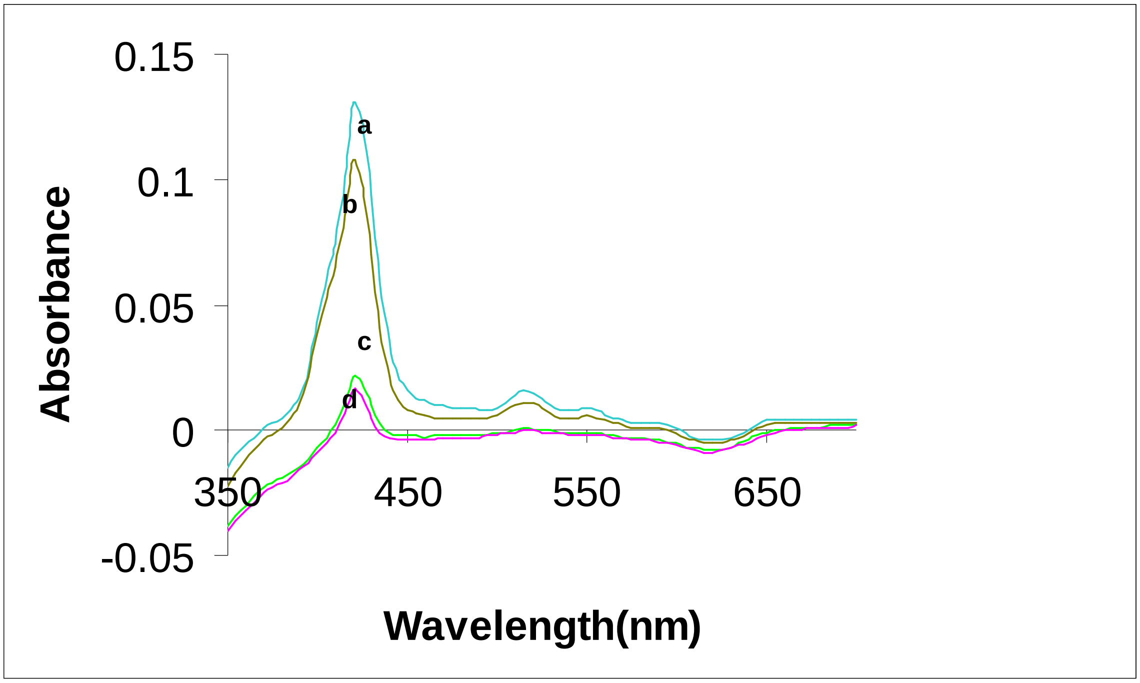


fig.2.UV-vis spectra:effect of volume of guest solvent: (a) :10ml,(b)20ml,(c)30ml,(d)40ml

Effect of concentration of solutions of porphyrin
The widest range of particle sizes can be achieved by varying the concentration of the macrocycle in the host solvent(fig3). The formation of the porphyrin nanoparticles likely represents a process governed by kinetics as well as the equilibrium of intermolecular interactions between all the components. The importance of kinetics is supported by the strong dependence of particle size on concentration in the host solvent. largest particles form at the lowest concentrations. At the highest porphyrin concentration in the host solvent, there are some differences in the intermolecular interactions of the chromophores since a ~15% broadening of the Soret band is observed compared to the lowest concentration The observed larger nanoparticles at lower concentrations may indicate that there is a minimum, critical aggregate size that nucleates the growth, and smaller particles eventually aggregate into larger ones.

Effect of time of sonication
Time of ultrasonic process has a profound effect on the particle size of the porphyrin nanoparticles. At less time as shown in fig 4, porphyrin nanoparticles have sharper peaks and stronger absorbance, this indicates that with increasing the time of sonication ,the number of porphyrin nanoparticles become more and number of porphyrins per each unit of nanoparticle increases.

Mixing
The rate and efficiency of mixing the host and guest solvents have a profound effect on the size and stability of the porphyrinic nanoparticles—especially when metalloporphyrins are used. In general for a given derivative and using the same rate of addition, the greater the mixing the smaller the nanoparticles. Stirring

rates were varied by controlling the spin of a magnetic stirrer and with and without the sonication and sonication assumed to be the most efficient. Smaller and stable porphyrin nanoparticles were formed only with sonication.

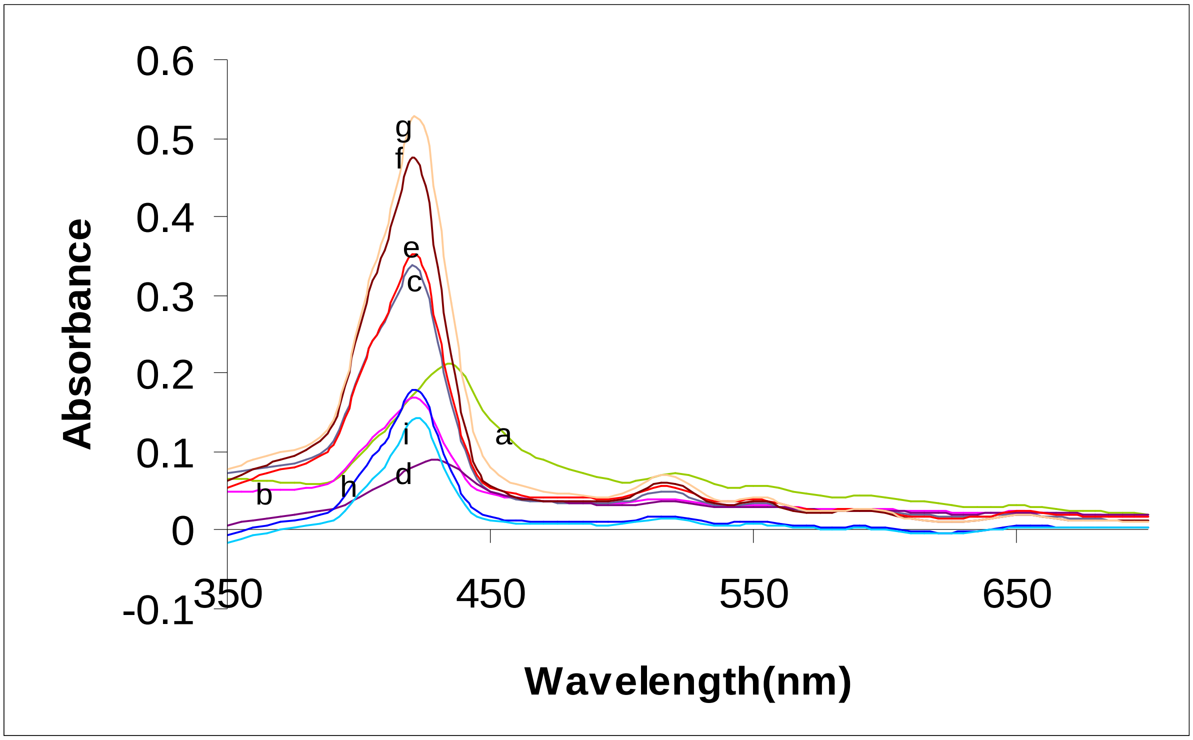


Fig. 3.UV-vis spectra: effect of concentration: (a)200µl,(b)250µl,(c)300µl,(d)350µl,(e)400µl, (f)450µl,(g)500µl,(h)150µl,(i)100µl

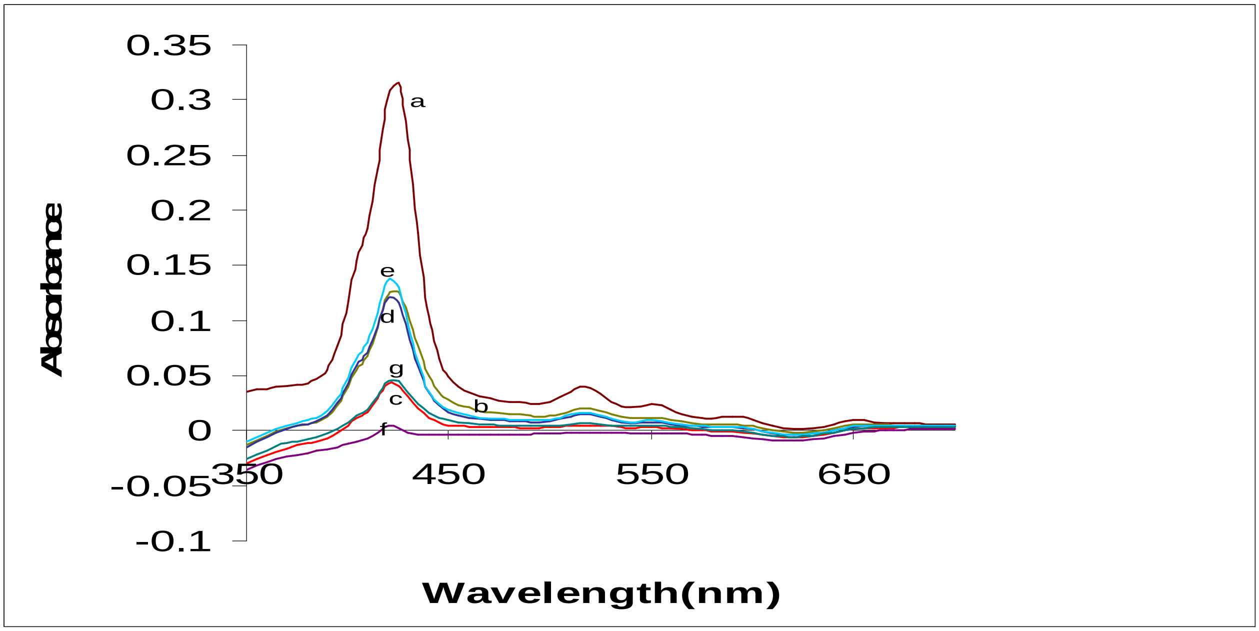


Fig.4.UV-vis spectra .time of sonication: (a)5min,(b)10min,(c)15min,(d)20min,(e)25min,(f)30min,(g)40min

Well-dispersed TMPyP nanoparticles

The SEM images of the porphyrin nanoparticles are shown in Fig. 5. The particles are spherical in shape and the average size is 200 nm. These nanoparticles were stable in solution without precipitation stored under dark at room temperature for at least 30 days. These images confirm the preparation of porphyrin nanoparticles via ultrasonic method and The porphyrin nanoparticles are held together by hydrophobicand Π-stacking effects.

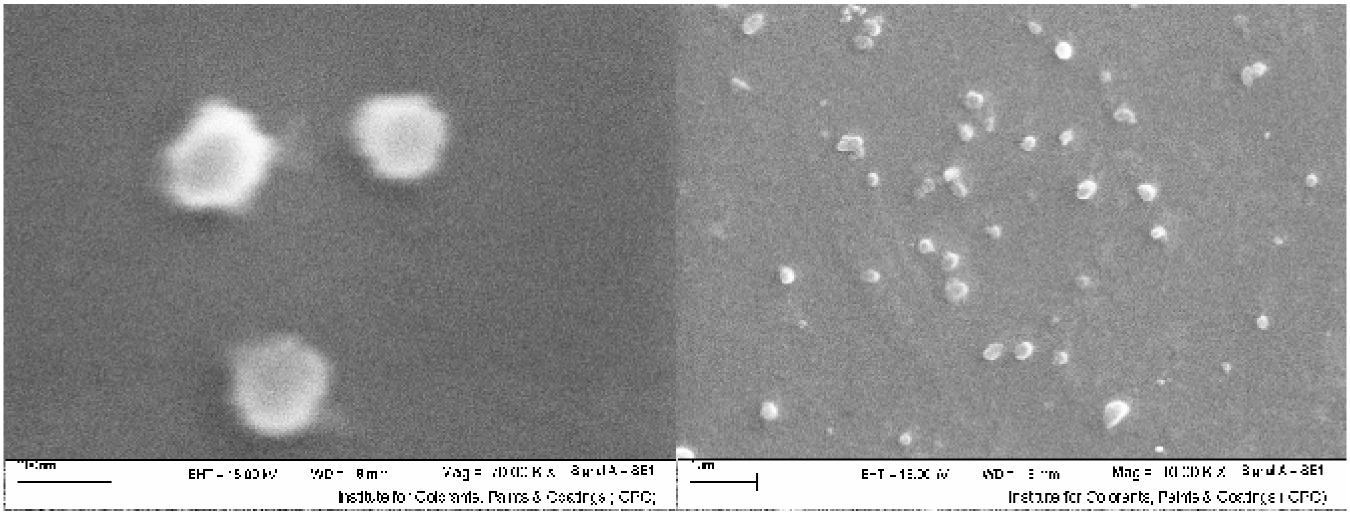


Fig.5.SEM images of porphyrin nanoparticles

Optical properties of TClPP nanoparticles

Fig. 6 shows typical fluorescence spectra of TPClPP nanoparticles along with that of aqueous TPClPP solution (0.01 mM) excited at 270 nm. the addition of stabilizer neither quenched the fluorescence of solution-phase TPClPP nor altered its spectral shape.The fluorescence spectra of TPClPP nanoparticles exhibited a bathochromic shift compared to that of the solution sample, corresponding to the behavior observed in the absorption. In nanoparticle samples, the Soret band and Q bands exhibit a bathochromic shift compared to those of the aqueous solution. Regarding the red shift of the Soret band, four explanations have been proposed in the past [14,15,16,17]: (i) protonation of the porphyrin ring nitrogens, (ii) solvent (or matrix) effect, (iii) aggregation of porphyrin molecules and (iv) flattening of the porphyrin molecule caused by the twisting of four phenyl moieties. In mechanism (i), a highly acidic solution induces the protonation of the porphyrin ring. The pH of the solutions containing the nanoparticles were measured to be 7.1–7.3. the observation of four Q bands for the nanoparticle samples makes this mechanism implausible because diprotonated porphyrins show only two Q bands due to the *D*4h symmetry of the chromophore. In mechanism (ii), although the absorption band maxima depend on the refractive index of solvents or matrices, very minor spectral shifts of the Soret band (~2 nm) have been revealed for the TPClPP molecule when the solvents are largely varied. Thus, this mechanism is also not the main reason of the large red shift of the Soret band. In mechanism (iii), two types of molecular aggregates involving dipolar coupling are considered with unique electronic and spectroscopic properties: J- and H-type aggregates. When chromophores such as porphyrins are parallel aligned, two new excitonic bands are generated according to a simple exciton theory: one with higher energies and the other with lower than the monomer energy level. In J aggregates, transitions only to the low energy states of the exciton band are allowed. As a consequence, J aggregates exhibit a red-shifted absorption band with respect to the monomer band, and are characterized by almost no Stokes-shifted fluorescence that has a very high quantum yield. In H aggregates, on the other hand, transitions only to the higher level are allowed, yielding a blue shift of the absorption peak. Another consequence of the dipolar coupling in the H aggregate is quenching of fluorescence caused by a rapid internal conversion to the lower energy level and a subsequent forbidden transition to the ground state,therefore a shift of the Soret band to longer wavelengths should be attributed to the self-association of porphyrins into J-type aggregates. The estimated fluorescence quantum yields of the TPClPP nanoparticle systems are quite similar to that of the solution-phase TPClPP so that J-type self-aggregation does not occur in the nanoparticles.The origin of the large red shift of the Soret band is then reasonably attributed to a flattening of the porphyrin molecule(mechanism (iv)).

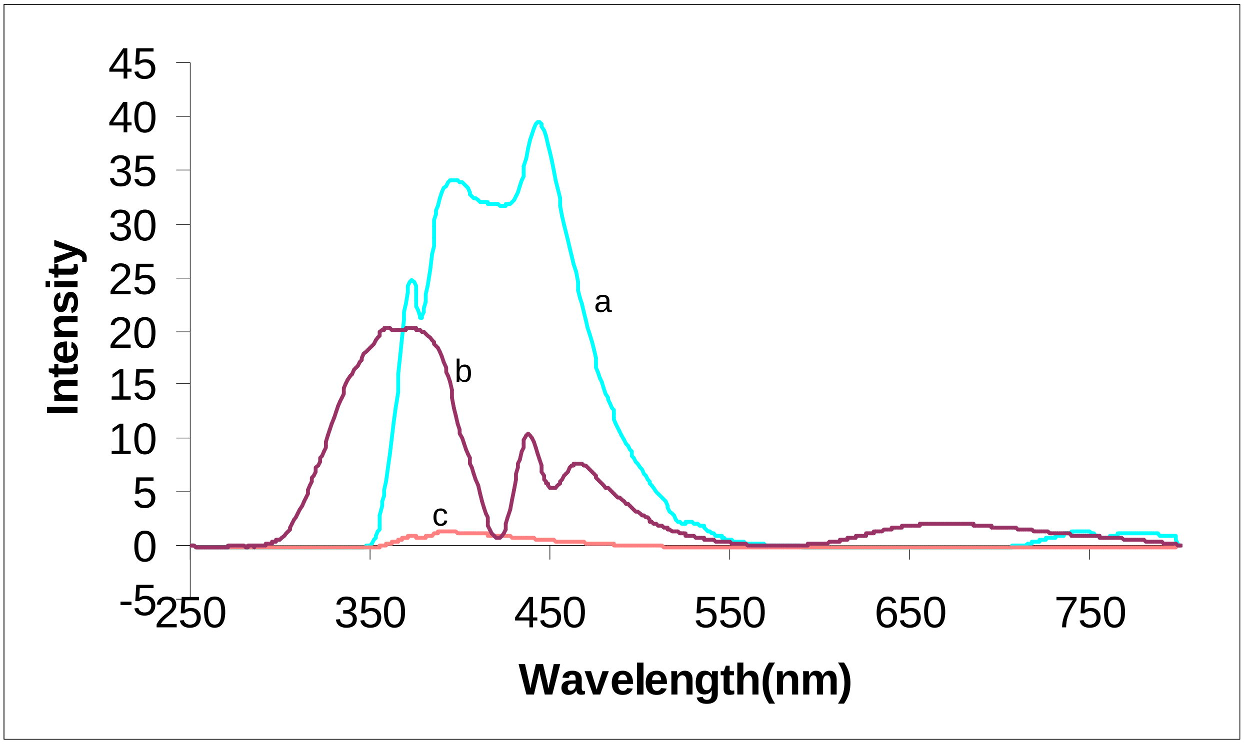


Fig.6. Fluorescence spectra of: (a)TPClPPnanoparticle;(b)solution of 0.005g porphyrin in 20ml of chloroform;(c)solution of 0.005g porphyrin in 5 ml porphyrin

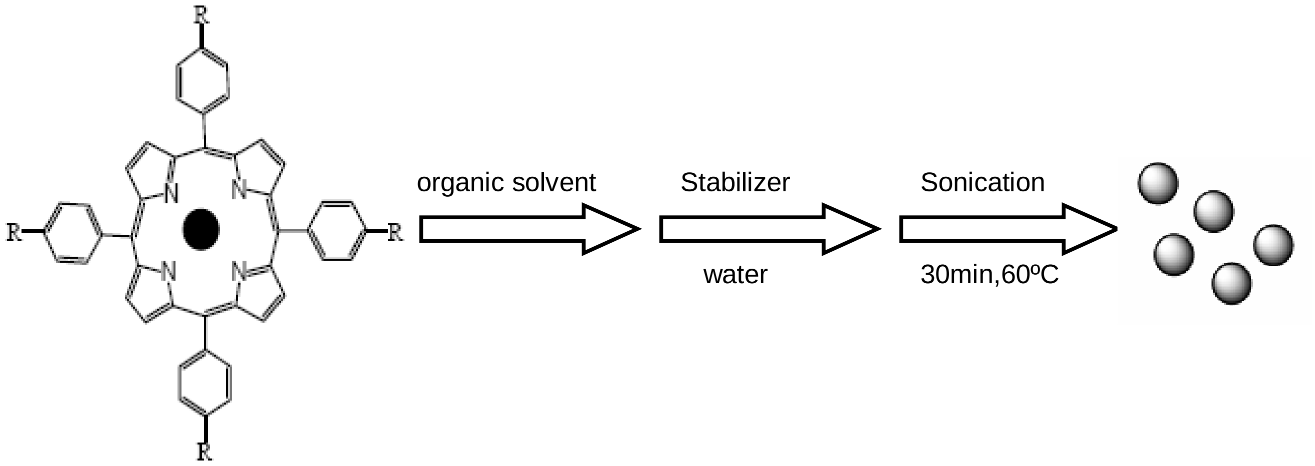
3-general experimental procedure

Chemicals and Instruments

TPClPP was prepared according to Adler-Longo method.DMF was used as a solvent and purchased from Merk and used as received. Tri ethylene glycol mono methyl ether was used as a stabilizer and purchased from Merk.UV–vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorometer. The morphology and size of TPClPP nanoparticles were observed with a Hitachi S-4800 scanning electron microscope (SEM).

Synthesis of TPClPP nanoparticle

The porphyrin [tetra(para-chlorophenyl)porphyrin] nanoparticles were prepared by means of sonication technique. A typical preparation procedure as follows: 100 µL stabilizer(tri ethylene glycol mono methyl ether) was added to 200µL of stock solution in DMF (1.22 mM for TPClPP), followed by adding 20 mL water with vigorous mixing and after that was sonicated for 30 min at 60ºC.In this research,the effect of different agents on the size of nanoparticles via UV-vis spectra was examined.



References

[1] Gong, X.; Milic, T.; Xu, C.; Batteas, J.D.; Drain, C.M.*J. Am. Chem. Soc.* **2002**, *124*, 14290–14291.
[2] Milic, T.; Garno, J.C.; Smeureanu, G.; Batteas, J.D.;Drain, C.M. *Langmuir* **2004**, *20*, 3974–3983.
[3] Y. Diskin-Posner, R. K. Kumar and I. Goldberg, New J. Chem.,**1999**, 23, 885–890.
[4] B. Moulton and M. J. Zaworotko, Curr. Opin. Solid State Mater.Sci., **2002**, 6, 117–123.
[5] T. S. Balaban, A. Eichhofer and J.-M. Lehn, Eur. J. Org. Chem.,**2000**, 24, 4047–4057.
[6] T. S. Balaban, R. Goddard, M. Linke-Schaetzel and J. M. Lehn, J.Am. Chem. Soc., **2003**, 125, 4233– 4239.
[7] Philp, D.; Stoddart, J.F. *Angew. Chem. Int. Ed.* **1996**,*35*, 1154–1196.
[8]Xia-Hua Li,Zong-Hong Xie,Hong Min,Yue-Zhong Xian,Li-Tong Jin,Electroanalysis 19,**2007**,No.24,2551-2557
[9]Amporn Sane,Shelby Taylor,Ya-Ping Sun,Mark C.Thies.Chem.Comm.,**2003**,2720-2721
[10]Xianchang Gong,Tatjana Milic,Chag Xu,James D.Batteas,Charles Michael Drain,J.Am.Chem.Soc,**2002**,124,14290-14291
[11]Lun Wang,Ling Dong,Gui-Rong Bian,Le-Yu Wang,Ting-Ting Xia,Hong-Qi Chen,Anal Bioanal Chem,**2005**,382,1300-1303
[12]Kun Wang,Jing-Juan Xu,Kai-Shi Tang,Hong-Yuan Chen,Talanta,67,**2005**,798-805
[13]Xinran Zhang,Yongfeng Wang,Yan Ma,Yingchun Ye,Yuan Wang,Kai Wu,Langmuir,**2006**,22,344-348
[14] P.M.R. Paulo, S.M.B. Costa, J. Phys. Chem. B 109 (2005) 13928
[15] K. Kalyanasundaram, M. Neumann-Spallart, J. Phys. Chem. 86 (1982)5163
[16] S. Takagi, T. Shimada, M. Eguchi, T. Yui, H. Yoshida, D.A. Tryk, H.Inoue, Langmuir 18 (2002) 2265
[17] L. Ukrainczyk, M. Chibwe, T.L. Pinnavaia, S.A. Boyd, J. Phys. Chem.98 (1994) 2668;