Preparation and Characterization of Porphyrin Nanoparticles

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Supporting information

General method: UV-Vis absorption spectra were obtained on a Carey 1 spectrophotometer. DLS experiments were performed with a PD2000DLS (Precision Detector), using nonlinear regularization without normalization and with a spherical normalization which both gave statistically similar results. The reported distributions are in number density. AFM experiments were performed with a PicoSPM (Molecular Imaging) coupled with an SPM 1000 Electronics, Revision 8 (RHK Technology). Images were typically collected at scan rates of 1 – 4 Hz. All data are collected in air at room temperature (22 ± 3 ^{o}C). Standard Si_3N_4 tips (Veeco) with nominal tip radius of curvature 20-60 nm and spring constant of ~ 0.12 N/m. Porphyrin 2H**2**, 2H**3**, 2H**4**, 2H**5** and 2H**6** were purchased from Aldrich and used as received. Porphyrin Fe(III)**1** was synthesized according to Groves, J. T.; Moeller, S. M. *WO 00/75144*; Porphyrin 2H**7** was synthesized according to Littler, B. J.; Ciringh, Y.; Lindsey, J. S.; *J. Org. Chem.,* **1999**, *64*, 2864-2872.

AFM sample preparation: the glass slide (Corning) was rinsed thoroughly with deionized water and methanol. After the glass slide was completely dried at room temperature, several drops of porphyrin nanoparticle solution (from pyridine) was transferred to the slide via a pipette. AFM images were taken after the solvent was completely evaporated at room temperature. The AFM studies were to evaluate the integrity of the various nanoparticles on surfaces because this is the likely environment that they will be used for numerous applications. Though an effort was made to use conditions that would allow the particles to be deposited without significant aggregation, there is no *a priori* reason that the structure on surfaces should be the same as in solution. The table (Table SI-1) summarizes the DLS and AFM data.

Preparation method and DLS measurements for porphyrin nanoparticles in table 1:
2H**2**: 1.9mg 2H**2** porphyrin was dissolved in 4ml DMSO to make a stock solution. 0.4ml stock solution was transferred to a test tube followed by addition of 50 μl triethylene glycol monomethylether. After 1 minute, 5ml water was added to this mixture and a glass rod was used to stir the mixture. The resultant nanoparticles were used for DLS measurement. The result is shown in figure 5.

2H**3**: 1.0mg 2H**3** porphyrin was dissolved in 4ml DMSO to make a stock solution. 0.4ml stock solution was transferred to a test tube followed by addition of 50 μl triethylene

glycol monomethylether. After 1 minute, 5ml water was added to this mixture and a glass rod was used to stir the mixture. The resultant nanoparticles were used for DLS and UV-Vis. measurements. The results are shown in figure 6&7.

2H**4**: 3.0mg 2H**4** porphyrin was dissolved in 4ml DMSO to make a stock solution. 0.4ml stock solution was transferred to a test tube followed by addition of 50 μl triethylene glycol monomethylether. After 1 minute, 5ml water was added to this mixture and a glass rod was used to stir the mixture. The resultant nanoparticles were used for DLS and UV-Vis. measurements. The results are shown in figure 8&9.

2H**5**: 1.5mg 2H**5** porphyrin was dissolved in 4ml DMSO to make a stock solution. 0.4ml stock solution was transferred to a test tube followed by addition of 50 μl triethylene glycol monomethylether. After 1 minute, 5ml water was added to this mixture and a glass rod was used to stir the mixture. The resultant nanoparticles were used for DLS and UV-Vis. measurements. The results are shown in figure 10&11.

2H**6**: 0.7mg 2H**6** porphyrin was dissolved in 4ml pyridine to make a stock solution. 0.4ml stock solution was transferred to a test tube followed by addition of 50 μl triethylene glycol monomethylether. After 1 minute, 5ml water was added to this mixture and a glass rod was used to stir the mixture. The resultant nanoparticles were used for DLS and UV-Vis. measurements. The results are shown in figure 12&13.

2H**7**: 1.6mg 2H**7** porphyrin was dissolved in 4ml DMSO to make a stock solution. 0.4ml stock solution was transferred to a test tube followed by addition of 50 μl triethylene glycol monomethylether. After 1 minute, 5ml water was added to this mixture and a glass rod was used to stir the mixture. The resultant nanoparticles were used for DLS and UV-Vis. measurements. The results are shown in figure 14&15.
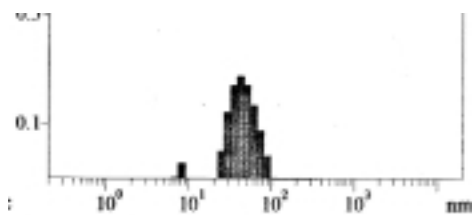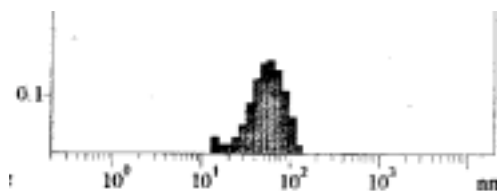

Figure 5. DLS characterization of 2H**2** nanoparticles.
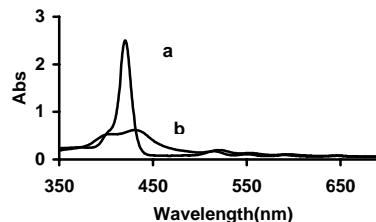

Figure 6. DLS characterization of 2H**3** nanoparticles.

Figure 7. UV-Vis. Spectra. 2H**3** in DMSO (a) and its nanoparticles in water (b).
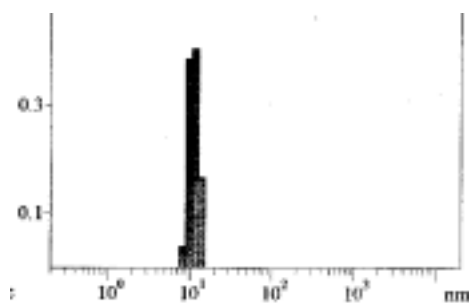
Figure 8. DLS characterization of 2H**4** nanoparticles.
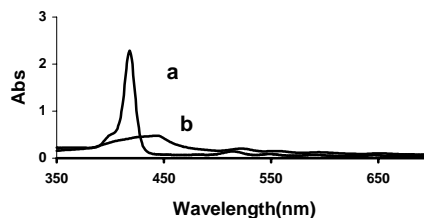

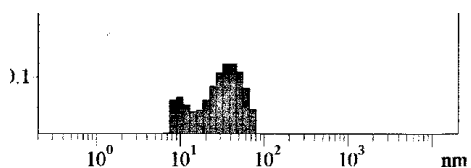Figure 9. UV-Vis. Spectra.   2H**4** in DMSO (a) and its nanoparticles in water (b).

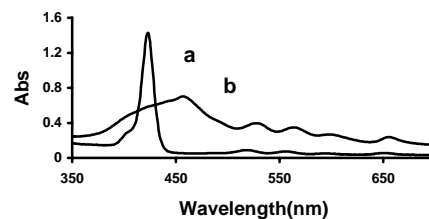Figure 10. DLS characterization of 2H**5** nanoparticles.

Figure 11. UV-Vis. Spectra. 2H**5** in DMSO (a) and its nanoparticles in water (b).
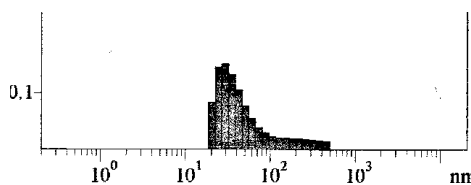

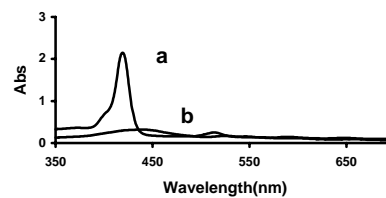Figure 12. DLS characterization of 2H**6** nanoparticles.

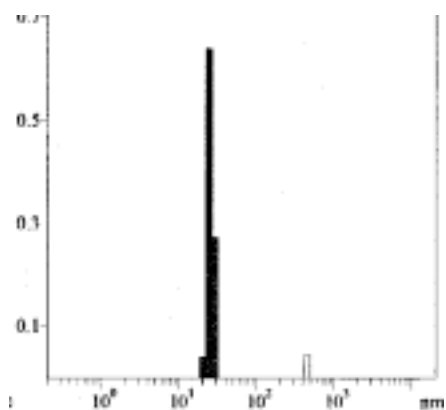Figure 13. UV-Vis. Spectra. 2H**6** in pyridine (a) and its nanoparticles in water (b).
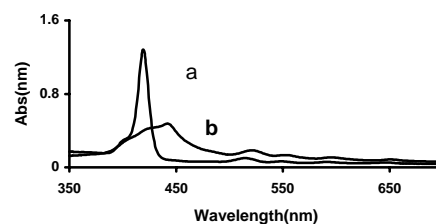
Figure 14. DLS characterization of 2H**7** nanoparticles.

Figure 15. UV-Vis. Spectra. 2H**7** in DMSO (a) and its nanoparticles in water (b).

	DLS[1] norm=0	DLS norm=0	
Porphyrin	DMSO (radius, nm)	Pyridine (radius, nm)	Size by AFM (nm)[4]
2	46[2] ($\pm$40)[3]	141 ($\pm$46)	aggregates[5]
3	58 ($\pm$47)	208 ($\pm$62)	66 ($\pm$ 33)
4	11 ($\pm$ 4)	35 ($\pm$18)	78 ($\pm$ 23)
5	34 ($\pm$30)	131 ($\pm$71)	aggregates
6	70 ($\pm$50)	70 ($\pm$39)	61($\pm$ 14)
7	24 ($\pm$6)	33 ($\pm$8)	63 ($\pm$20)

[1] DLS norm=3, sphere, yields similar sizes and distributions.

[2] Number weighted average of particle size

[3] Numbers in parentheses are the size distributions.

[4] Numbers in parentheses are the first standard deviation of the distribution.

[5] In these systems listed as 'aggregates" the particles agglomerate on the surface to such an extent that an accurate size distribution based on individual particles can not be made by AFM.

Table SI-1. Summarization of the DLS and AFM data.

Comment on the UV-Visible spectra. The sharp peaks of the split Soret bands implies two types of aggregates in the given nanoparticle solution. The substantially broadened spectra also indicate aggregation; however, there is no reason that the nature of the aggregates in the nanoparticles should be the same for each different porphyrin (i.e. the relative orientation(s) of the chromophores in the nanoparticles may differ depending on the porphyrin). Solvent, substituent, and derivitization effects can be ruled out as the cause of the spectral changes. The batch-to-batch consistency of the DLS, UV-Visible and AFM implies that the internal structure of the chromophores in the nanoparticle is also consistent.