



# Poly (ethylene oxide) tethered trans-porphyrin: Synthesis, self-assembly with fullerene (C<sub>60</sub>) and DNA binding studies



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## ABSTRACT

*trans*-Porphyrin containing phenyl group at both ends was synthesized via corresponding dipyrromethanes (DPM) in the presence of TFA and DDQ. The polyethyleneglycole (PEG) chains were attached at the *trans* positions of ABA type porphyrinic moiety. The prepared PEGylated porphyrin (with PEG arms at the periphery) P-(PEO)<sub>2</sub> was self-assembled into spheres of uniform diameter while their DMF solution was dialyzed into water. Furthermore, the addition of fullerene (C<sub>60</sub>) to P-(PEO)<sub>2</sub> caused complexation between porphyrin and fullerene which lead to interesting and trenchant morphology having worm like lateral aggregates. The assembly process and the as-prepared edifices were characterized using UV–vis absorption spectroscopy and the morphology of these assemblies was investigated using transmission electron microscope (TEM). Furthermore, the DNA binding with porphyrin aggregates has been demonstrated via electrochemical (cyclic voltammetric) response of screen printed electrodes modified. The obvious increase in redox current disclosed the intermolecular interactions of the adducts with the DNA. These studies of unprecedented adducts can further be explored for potential applications in biosensors.

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## 1. Introduction

In last few decades, inspired by the nature a great variety of porphyrin derivatives have been synthesized and is still the impetus for the current fabrication of smart materials e.g. sensors, biosensors, drug carriers and solar cells [1,2]. Primarily these derivatives have been used as sensitizers in both natural and artificial systems for their ultrafast electron injection [3], small splitting and prolonged excited state life time [4], higher absorption coefficients and stability [5] along with the other uses of photochemistry and construction of hybrid materials [6]. Similarly, much attention has been made to explore molecular assemblies and their organization which is governed by the cooperative interactions of various noncovalent bonds, such as hydrophobic interaction,  $\pi$ – $\pi$  stacking, and electrostatic interaction, where the hydrogen bonding gives additional driving as well as regulating forces. Porphyrin has also attracted the researchers to the distinct dependence of its mode of self-assembly on the peripheral substituent [7], additionally; the axial ligand and protonation at the core could also affect the aggregation behavior of porphyrin substantially [8]. Similarly, porphyrins can be

incorporated into the micelles resulting in the alteration of their mode of aggregation and location [9].

On the other side, in nature, photo induced electron transfer is the core of natural photosynthesis process, which is a multistep and unidirectional in nature, where the spatial arrangement of donor-acceptor (D-A) chromophores of transmembrane protein is very important. Hence the construction of D-A conjugated systems with restricted spatial arrangement is very attractive field of research in mimicking of natural photosynthesis process [10]. In this avenue, porphyrin-fullerene conjugates act as excellent electron donor-acceptor building blocks and have been widely used to optimize the light harvesting and electron transfer efficiency by adjusting the distance and orientation of individual units by *face-to-face* and *edge-to-edge* alignment [11,12]. *trans*-Porphyrin could help better to construct porphyrin based well defined architectures by linear substitution patterns, and are the key components of model systems including mimicking of enzyme models, photosynthesis, optical properties, catalysts, sensors, small molecule receptors and so on [13]. To be specific *trans*-substituted porphyrins, decorated with functional groups at the periphery of 18 $\pi$ -electron system, have been synthesized by MacDonald type synthesis to give wide range of substituents at the periphery positions [14]. For the possible utility of *trans*-porphyrin in well-defined architectures, and their structural specificity compared to general meso-A4 porphyrins, they have

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great importance in bio-mimicry which further depends on the functionalities attached as meso-substituents, because the terminal functional groups have vital role in self-assembly and surface attachment [15,16].

Furthermore, the porphyrin with its nature of unique aromatic scaffolds endowed quite important DNA binding potency, especially the noncovalent interactions of DNA (both double stranded and single stranded) with porphyrin, which have been studied using NMR, spectroscopy, biophysical studies and molecular modeling [17,18]. For the stronger interactions, the smart engineering of particular porphyrin molecules is the most influential factor of porphyrin ligands in hosting the DNA [19] that have potential applications in anti-cancer drugs.

To improve the solubility and functionality, this study aims to explore the synthesis and characterization of double PEGylated porphyrins and further to study their morphological changes during complexation with fullerene. The morphology of the self-assembled architectures was investigated using transmission electron microscope (TEM) and the molecular attachments were characterized using UV-vis absorption spectra. Moreover, we studied the DNA binding to these self-assembled architectures via electrochemical (cyclic voltammetric) responses of screen printed electrodes modified with these adducts. To the best of our knowledge, it is the first time to study the DNA attachment with porphyrin/fullerene assembled architectures.

## 2. Experimental

### 2.1. Materials

Pyrrole ( $C_4H_5N$ , 98%), benzaldehyde ( $C_6H_5CHO$ , 99%), 4-hydroxybenzaldehyde ( $HOC_6H_4CHO$ , 97%), poly(ethylene oxide) (1000 g.mol<sup>-1</sup>), N, N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), Trifluoroacetic acid (TFA), 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ), and triethylamine were purchased from Sigma-Aldrich and Aladdin. Fullerene ( $C_{60}$ , 99.5%) was purchased from Bucky, USA and used as received. All the solvents and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. or Shanghai Lingfeng Chemical Reagent Company and were used as received.

### 2.2. Characterization

<sup>1</sup>H NMR spectra were recorded at 400 MHz, using BRUKER AV400 Spectrophotometer. The samples were dissolved in  $CDCl_3$ , and measured using tetramethylsilane (TMS) as an internal reference. Gel permeation chromatography (GPC) measurements were performed with Styragel HR3-HR4 (7.8 × 300 mm) columns equipped with Waters 1515 isocratic HPLC pump and Waters 2414 Refractive Index Detector with flow rate of 1 mL/min, and the instrument was calibrated using polystyrene standards. UV-vis. Spectroscopy traces were recorded at SHIMADZU UV-2550 UV spectrophotometer using 2.5 mL sample in quartz Cuvettes with 1 cm beam path length, at room temperature. Fluorescence measurements were performed at Varian's Cary Eclipse fluorescence spectrophotometer at room temperature with and the excitation wavelength is 420 nm. In order to avoid spectral distortions very dilute solutions were used for both UV and fluorescence measurements. Transmission electron microscopy (TEM) images were taken on a JEOL JEM1400 electron microscope operated at 100 kV. A 5 μL droplet of self-assembly aggregate solution (0.5 mg/mL) was directly dropped onto a copper grid (300 mesh) coated with a carbon film, followed by drying at room temperature. Surface morphologies of modified electrodes was investigated with scanning electron microscopy (SEM) by using TESCAN VEGA 3 and dynamic light scattering measurements for particle size determination were performed at NICOMP TM 380ZLS of PSS-NICOMP particle size systems, USA.

### 2.3. Synthesis of 2,2'-(phenyl methyl)bis(1H-pyrrole)/(phenyl-dipyromethane), DPM

Phenyl-dipyromethane was synthesized by the reported method [20], where distilled pyrrole (17 mL, 245 mmol) was placed in a round bottom flask followed by the addition of benzaldehyde (1 mL, 9 mmol, 1.0 equiv) under Ar, at room temperature. After stirring the mixture for 5 min, trifluoroacetic acid (TFA) (0.225 mL, 0.9 mmol, and 0.10 equiv.) was added drop wise and stirring was continued for another 5 min under Ar atmosphere followed by quenching of the reaction with 0.1 M NaOH. In the vigorously stirring mixture ethyl acetate was added and then washed with  $H_2O$  and dried over  $Na_2SO_4$ . Orange oil was obtained after removal of the solvent in reduced pressure while the crude product was collected from ethanol/water as yellowish crystals, (1.0 g, and yield 46%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ , Fig. 5), δ ppm: 7.92 (bs, 2H, NH-pyrrole), 7.22–7.35 (m, 3H, phenyl), 6.7 (d, 2H, α-pyrrole), 6.2 (t, 2H, β-pyrrole), 5.85 (d, 2H, β-pyrrole), 5.50 (s, 1H, C-CH-C), the spectrum is provided as Supplementary Fig. S1.

### 2.4. 5,15-Bis(4-hydroxyphenyl)-10,20-diphenyl porphyrin, (P-(OH)<sub>2</sub>)

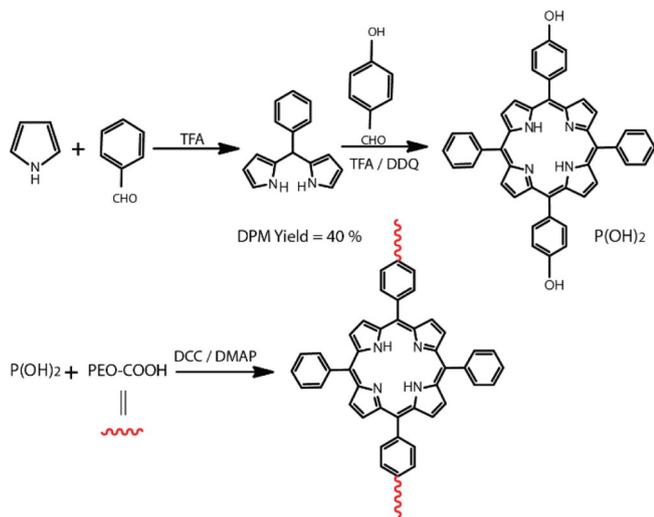
trans-Porphyrin was synthesized according to the following procedure [21,22], where 2, 2'-(phenyl methyl)bis(1H-pyrrole), DPM (0.225 g, 1 mmol), and 4-hydroxybenzaldehyde (0.123 g, 1 mmol) were added in 800 mL of dichloromethane and stirred under Ar bubbling for 20 min. Then 10 mL DCM solution of TFA (0.131 mL, 1.7 mmol) was added with dropper in Ar atmosphere and stirred for 3 h followed by the addition of DDQ (0.23 g, 1.5 mmol) with vigorous stirring for 1 h and the reaction was quenched with triethylamine (3–5 mL). At the end the resultant solution mixture was passed through a pad of silica gel to collect the first band, which was concentrated under vacuum and the product was precipitated by DCM/methanol, (0.04 g, yield 18%). The product was characterized by <sup>1</sup>H NMR as shown in Fig. 5.4 (400 MHz,  $CDCl_3$ ), δ ppm: 8.8 (d, 8H, β-pyrrole), 8.25 (d, 4H, meta-phenyl), 8.15 (d, 4H, ortho-phenyl), 7.75 (m, 10H, ortho/meta/para-phenyl), –2.77 (s, 2H, NH-pyrrole), the spectrum is given as Fig. S2.

### 2.5. Synthesis of PEGylated trans-porphyrin, P-(PEO)<sub>2</sub>

The doubly PEGylated trans-porphyrin was obtained by DMAP and DCC assisted esterification of hydroxyl functionalized porphyrin (P-OH<sub>2</sub>) and PEO-COOH (1000 Da) according to the reported method [15] which gave the target molecule of P-PEO<sub>2</sub>. Typically, P-OH<sub>2</sub> (0.025 g, 0.04 mmol), PEO-COOH (0.085 g, 0.15 mmol) and DMAP (0.004 g, 0.04 mmol) were dissolved in dry DCM at 10 °C under  $N_2$ , and after 20 min stirring, 10 mL DCM solution of DCC (0.032 g, 0.15 mmol) was drop wise added to the mixture. The reaction mixture was stirred for 48 h at room temperature, and then solvent was evaporated under reduced pressure and the product was precipitated in cold ether. The product was characterized by gel permeation chromatography and <sup>1</sup>H NMR, <sup>1</sup>H NMR ( $CDCl_3$ , 400 MHz): 8.85 (d, 8H, β-pyrrole), 8.23 (d, 8H, ortho-phenyl), 7.8 (m, 9H, meta/para-phenyl), 7.56 (d, 2H, meta-phenyl), 4.25 (t, COOCH<sub>2</sub>), 3.65 (m, OCH<sub>2</sub>CH<sub>2</sub>O), 3.4 (s, CH<sub>3</sub>O), 2.63 (m, OCOCH<sub>2</sub>CH<sub>2</sub>OCO), –2.73 (s, 2H, NH-pyrrole), the <sup>1</sup>H NMR spectrum is provided as Fig. 2.

### 2.6. Morphology investigation of P-(PEO)<sub>2</sub> and its complexation with C<sub>60</sub>

Due to their homophilic nature, these ABA type trans porphyrins might have variety of solvent options for their self-assembly studies. Different solubility profiles of various segments of this poly (ethylene oxide)-porphyrin-poly (ethylene oxide) (PEO-P-PEO) tri-block molecule could expectedly give interesting morphology. Here the self-assembly of P-(PEO)<sub>2</sub> and P-(PEO)<sub>2</sub>-C<sub>60</sub> were studied in DMF via dialysis in the selective solvent ( $H_2O$ ) that assembled these adducts concordant



**Fig. 1.** Schematic representation of synthesis route for P-(PEO)<sub>2</sub> starting from pyrrole and benzaldehyde.

by their natural affinities. Initially, P-(PEO)<sub>2</sub> was dissolved in DMF as stock solution. Aliquot of stock solution was added into 3 mL of DMF to make the total solution concentration at  $1 \times 10^{-4}$  M which is above the critical micelles concentration (the critical micelles concentration was estimated by UV–vis spectra, as discussed below), then the solution was subjected to dialysis into water by placing it in dialysis membrane (MWCO = 3500 Da). The changes in color after dialysis was observed.

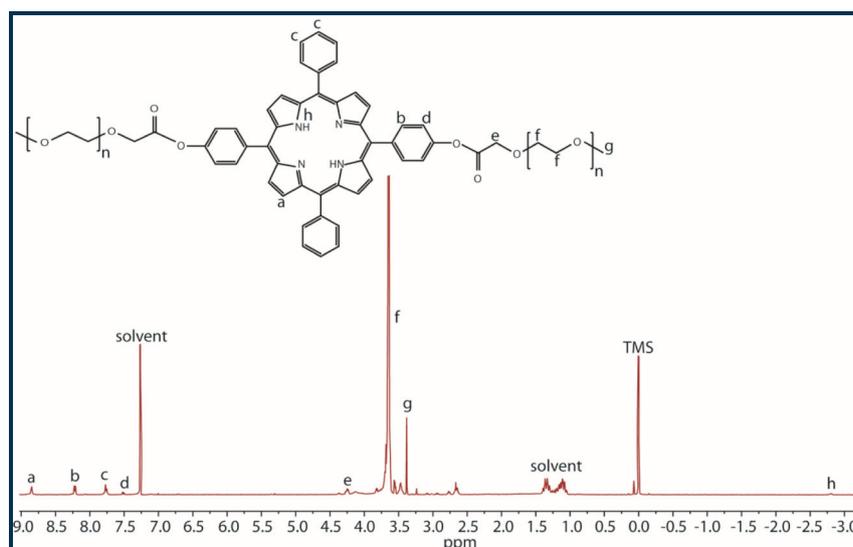
### 2.7. DNA attachment studies of P-(PEO)<sub>2</sub>

The water soluble trans porphyrins were expected to give better DNA attachment with central part of the PEGylated moiety which will further broaden the knowledge of DNA attachment with porphyrins. DNA of the sequence 5'-GCAGTTGATCCTTTGGATACCCTGG-3 was used in this study, prior to the experimentation, initial heat treatment was performed to obtain the single strands of DNA. In 2 mL of porphyrinic solution ( $1 \times 10^{-5}$  M) equimolar concentration of DNA (40  $\mu$ L of DNA stock solution) was added and the resulting solution was incubated for 10 min before the analysis. The changes in the voltamograms of different porphyrinic assemblies indicated the complexation with DNA.

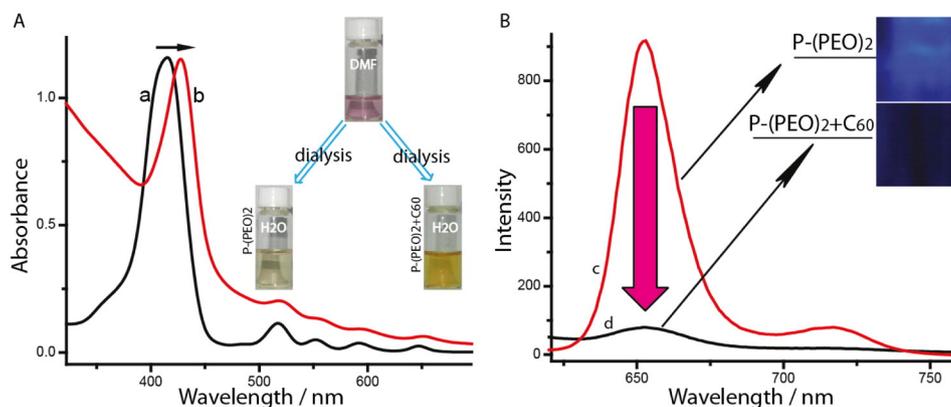
## 3. Results and discussion

As the spectral properties are the finger prints for aggregation, initially the UV–vis spectra were analyzed for the aggregation of adduct in aqueous solvent. Poly (ethylene oxide) arms associated with the porphyrin, Fig. 1 made the molecule soluble in water, which showed typical absorption bands due to in-plan  $\pi$ - $\pi^*$  transition [23], named as soret band. In absorption spectra one intense soret band appeared at 417 nm and four (relatively weak) Q bands at 516, 551, 592, and 647 nm. Moreover, at very low concentration, porphyrin was found in monomeric form in water, as can be evidenced from the UV–vis spectra of P-(PEO)<sub>2</sub> in water at  $2.5 \times 10^{-6}$  to  $2 \times 10^{-5}$  M, (Fig. S6). The critical micelle concentration (CMC) can also be deduced from the UV–vis titration of the aqueous solution, as shown in Fig. S6, the gradually increasing concentration of porphyrin in the water solution showed increasing soret band intensity, while the splitting of soret band into two aggregation bands at 407, 420 nm, was occurred between  $5 \times 10^{-5}$  and  $1.0 \times 10^{-4}$  M, that gives an idea of the presence of CMC between these two values [24]. Hence, the morphological investigations of P-(PEO)<sub>2</sub> were conducted above the CMC at  $1.0 \times 10^{-4}$  M.

Furthermore, the soret band of P-(PEO)<sub>2</sub>-C<sub>60</sub> aggregates shows red shift, indicating the presence of slipped face-to-face J aggregates [25] of porphyrin-fullerene that could further be correlated with the morphology observed by transmission electron microscopic studies. On the other side, on complexation of these amphiphilic porphyrins with pristine C<sub>60</sub> there was a clear red shift of about 13 nm, from 415 nm to 428 nm, in the soret band of porphyrin and visible color change of the solution which was a characteristic of these molecular level interactions of donor-acceptor (porphyrin-fullerene) moieties [26], as shown in Fig. 3A. The color of the solution was light pink which was faded away after dialysis, as can be seen from Fig. 3A. This porphyrin-fullerene complexation was also corroborated by fluorescence quenching of porphyrin as shown in Fig. 3B. The fluorescent images also elaborated the quenching hypothesis [27], as the porphyrin-fullerene complex showed less fluorescent image in dark background as compared to the porphyrin solution. One more possible change in the original spectra of porphyrin is the decrease in absorption intensity of the soret band, but here during the dialysis turgidity of dialysis membrane caused dilution of the solution approximately up to two times, which also caused a significant decrease in the intensity of the soret band, therefore the decrease in the soret intensity due to porphyrin-fullerene complexation could not be quantified in the present case.



**Fig. 2.** <sup>1</sup>H NMR spectra of P-(PEO)<sub>2</sub>, showing typical porphyrinic protons along with the ethylene oxide protons at 3.6 ppm.



**Fig. 3.** (A) UV-vis absorption spectra of P-(PEO)<sub>2</sub> nanospheres (a) and P-(PEO)<sub>2</sub>-C<sub>60</sub> aggregates (b), the inset showing visual appearance of the solutions and (B) fluorescence emission spectral changes on complexation of P-(PEO)<sub>2</sub> with fullerene after dialysis in H<sub>2</sub>O (inset showing the fluorescent images of the solutions).

Transmission electron microscopy of aqueous solutions of P-(PEO)<sub>2</sub> shows spherical aggregates of highly monodispersed nature, as shown in Fig. 4a. The sample was prepared by first dissolving P-(PEO)<sub>2</sub> in DMF, a good solvent for all the segments, then gradual dialysis of DMF solution into water, in which central porphyrinic part of P-(PEO)<sub>2</sub> is insoluble. The porphyrin in DMF could arrange itself freely, while the slow dialysis in water permits the gradual removal of DMF and addition of water to the micelles solution. It is noteworthy, that the annealing time (rate of solvent interchange during the dialysis) which apparently seizes morphology at the core, is an important factor for the morphology of such aggregates.

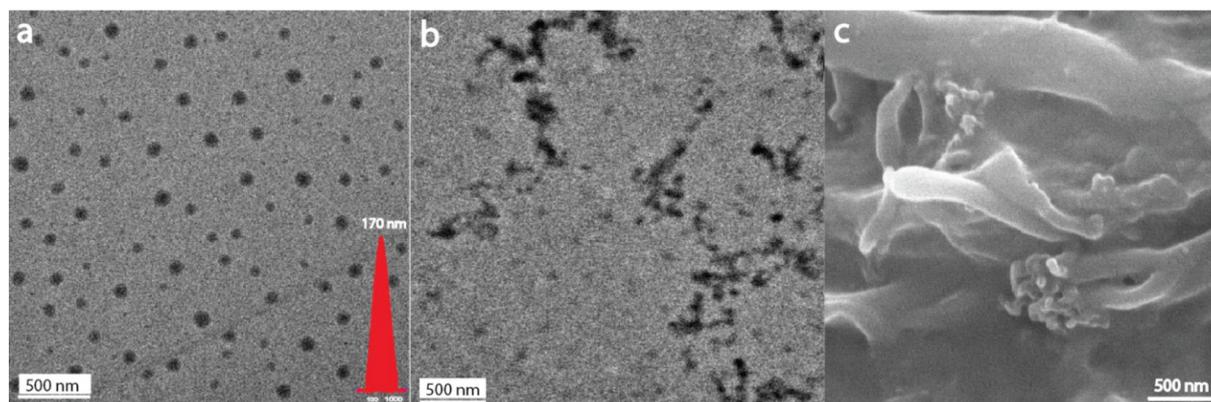
In these aggregates porphyrin moieties were encapsulated with in polymeric matrix of PEO. The average size of the spherical aggregates was found to be about 80 nm as depicted in the following TEM micrographs, however the hydrodynamic diameter was found to be 170 nm which is in good agreement with dry and wet calculations of the diameter [28]. Interestingly, the lateral aggregates of 100 nm width and varied length were observed, when these PEGylated porphyrins were complexed with C<sub>60</sub> in DMF followed by the dialysis into water, as shown in Fig. 4b. Deducing from the spectral (red shift of sorlet band) and microscopic observations, these lateral aggregates could be considered as face-to-face aggregates of alternating porphyrin-fullerene molecules.

Cyclic voltammetry was performed to evaluate the electrochemical behavior of self-assembled aggregates of P-(PEO)<sub>2</sub> and its C<sub>60</sub> complexes by modifying carbon based screen printed electrodes. Fig. 5 represents cyclic voltammetry curves of bare electrode, P-(PEO)<sub>2</sub> nanospheres modified electrode and P-(PEO)<sub>2</sub>-C<sub>60</sub> aggregates modified

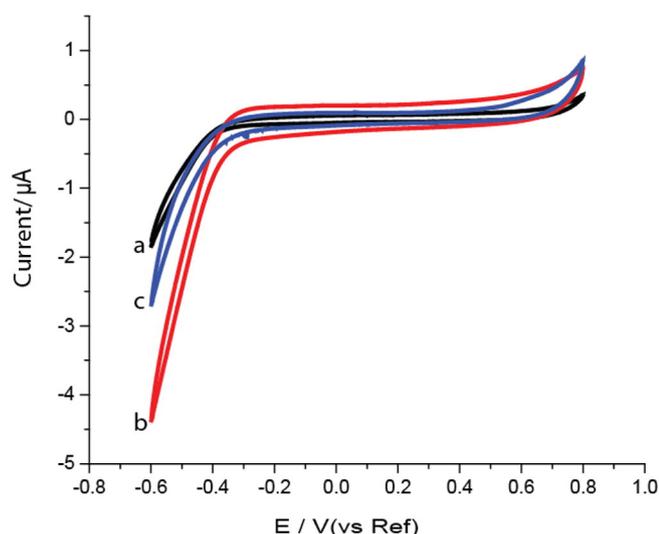
electrodes against DNA. It was observed that although the characteristic oxidation reduction peaks of porphyrin and fullerene were absent in either case however with the modification of electrode the current was significantly increased which shows the enhanced conductivity of the electrodes, modified with self-assembled nanoparticles [29]. Additionally, on complexation of P-(PEO)<sub>2</sub> with C<sub>60</sub>, being the donor-accepter pair, current should be increased, but it was decreased as compared to P-(PEO)<sub>2</sub> spheres. This unexpected change could be attributed to the uniformity and specific orientation of the porphyrin molecules with respect to the fullerene. Apparently the more number of active sites and larger surface of the nanospheres resulted in increased current as compared to lateral aggregates of P-(PEO)<sub>2</sub>-C<sub>60</sub> complexes.

#### 4. Conclusion

The doubly PEGylated trans-porphyrin was successfully synthesized and characterized with NMR and SEM analysis. The enhanced solubility profile of the P-(PEO)<sub>2</sub> made it susceptible to form various self-assemblies including highly monodispersed nanospheres of 80 nm diameter and trenchant lateral aggregates with and without C<sub>60</sub> complexation, respectively. The aggregates were characterized both in wet and dry states by optical and spectroscopic studies. The practical perspectives of these adducts for DNA attachment were also demonstrated with the help of electrochemical characterization in aqueous solutions. These findings will help to further explore the applications of these types of porphyrin derivatives and their self-assembled aggregates in both energy and the biomedical fields.



**Fig. 4.** TEM micrographs of self-assembled (a) P-(PEO)<sub>2</sub> ( $M_w = 2700$  Da), and (b) the complex of P-(PEO)<sub>2</sub> and C<sub>60</sub> showing highly monodispersed spherical aggregates of the average size ca. 80 nm and lateral aggregates with varying length, (c) SEM lateral assemblies of P-(PEO)<sub>2</sub> and C<sub>60</sub> complex. The inset of (a) showing the hydrodynamic diameter ( $R_h = 170$  nm) of spherical aggregates of P-(PEO)<sub>2</sub>.



**Fig. 5.** Cyclic voltammograms of bare screen printed electrode (a), P-(PEO)<sub>2</sub> nanospheres modified electrode (b) and P-(PEO)<sub>2</sub>-C<sub>60</sub> aggregates modified electrodes (c) against DNA at a scan rate of 50 mVs<sup>-1</sup> in the potential range of  $-0.6$  V to  $0.8$  V.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.molliq.2016.11.059>.

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