



Electropolymerized phenothiazines for the photochemical generation of singlet oxygen



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ARTICLE INFO

Article history:

Received 4 June 2014

Received in revised form 1 July 2014

Accepted 7 July 2014

Available online 23 July 2014

Keywords:

Singlet oxygen

Phenothiazines

Photosensitizers

Photochemical generation

Electropolymerization

ABSTRACT

The selected group of five amine-derivative phenothiazines was used to form their electropolymerized films in aqueous acidic solution with the aim to assess their ability to generate singlet oxygen. The films were characterized using cyclic voltammetry, UVVis spectroelectrochemistry, and Raman spectroscopy. The data of all the films were compared with properties of their monomer analogs. It was demonstrated that the electrochemically prepared films similarly to the known process of the corresponding monomers in solution phase are able to generate singlet oxygen in a photochemical surface process activated by laser radiation. These photogeneration process of the short-living species was monitored using the selected trap, which is detectable using UVVis spectroscopy. The effectiveness of the surface photogeneration reaction for each polymeric structure was determined in terms of half-life of the trap decay. The presented heterogeneous process of singlet oxygen photogeneration is believed to extend the area of applications of that highly oxidative reactant as compared to known homogeneous systems employing unbounded active species.

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1. Introduction

Singlet oxygen due to its strongly electrophilic character is under high research interest in the areas of fine chemicals synthesis [1], wastewater treatment [2], and medicine, including photodynamic therapy [3] and blood sterilization [4]. Though its lifetime in the diluted gas phase is relatively long (72 minutes) due to the molecular interactions, it is shorten in solution phase to micro- or milli-second level. Therefore *in situ* generation processes including photogeneration are the only effective routes in applications of singlet oxygen. Lately, attention is paid to systems based on surface immobilization of photoactive molecules aimed to produce that form of oxygen using solid materials. The surface modified solids show some distinctive features, like easiness of operation, simple product purification, etc. Beside, the surface immobilized molecules in contrast to any fluid phase exhibit both better stability against oligomerization/aggregation and higher photostability [5]. Two binding routes of the photoactive molecule can be distinguished: non-covalent immobilization in polymer matrix, like

e.g. cellulose acetate [6], and covalent bonding with the polymer matrix [7–9]. In the first case a high antimicrobial activity was obtained [10], however these materials are less stable due to photoactive molecule leakage and destruction of polymer matrix by free radicals. Covalent bonding of dyes with polymer matrix like polystyrene, polyamide, poly(methyl methacrylate) is obtained via chemical reaction of the matrix functional groups with suitable dyes. The last is generally a complicated multistep procedure, also the formation process is sensitive to the supporting material surface.

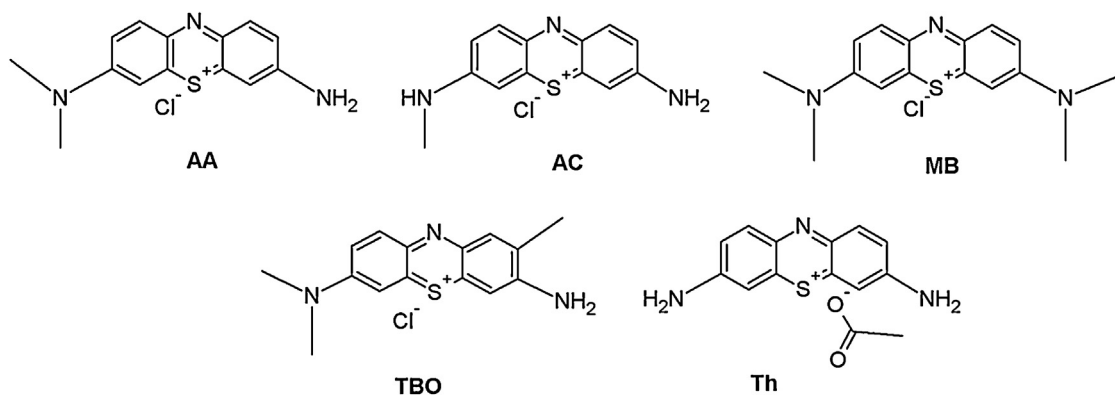
There are several known groups of compounds capable to generate singlet oxygen, including dyes and aromatic hydrocarbons [11], porphyrines [12], phthalocyanines [13], transition metals complexes [14] or semiconductors oxides [15]. Among them, phenothiazine derivatives are often explored, because of their considerable photosensitizing efficiency and other chemical and physical properties, which can be easily tuned [16,17]. Furthermore, the electrochemical properties of phenothiazines allow to use that molecule as monomer in electropolymerization processes [18–20]. The obtained polymers were applied earlier in sensors of glucose [21], NADH [22] nitrogen oxide (V) [23], and theophylline [24]. The area of applications includes also solar batteries [25,26] and biofuel cells [27].

In this work we demonstrate that thin film of polymeric forms of phenothiazines, which can easy be formed on electrode surface

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Scheme 1. Structures of phenothiazines derivatives: azure A (AA), azure C (AC), methylene blue (MB), toluidine blue (TBO), thionine (Th).

is capable to photogenerate effectively singlet oxygen. The studies were focused on each of five selected phenothiazine derivatives that were electropolymerized on ITO substrate in aqueous solutions. The group of phenothiazine monomers includes Azure A (AA), Azure C (AC), Methylene Blue (MB), Toluidine Blue O (TBO), and Thionine (Th). The effectiveness of the polymeric phenothiazines in the photogeneration process activated by laser visible radiation was monitored in organic solution phase containing 1,3-diphenylisobenzofuran (DPBF) that selectively traps photogenerated $^1\text{O}_2$.

2. Experimental

2.1. Chemicals

Five amine-derivative phenothiazines were selected as monomers for further electrochemical polymerization. The group included azure A (AA), azure C (AC), methylene blue (MB), toluidine blue (TBO) and thionine (Th). Their structures are shown in [Scheme 1](#).

AA (purity >90%) and TBO (purity >88%) were purchased from Sigma Aldrich, AC (purity >90%) was obtained from Fluka, MB (purity >92%), Th (purity >90%) and 1,3-diphenylisobenzofuran (DPBF, purity >97%) were purchased from Across Organics. The Britton-Robinson (BR) buffer solution of pH 4.45 was used as the electrolyte solution. It was prepared with analytical grade H_3PO_4 (85%), CH_3COOH (99.9%) and H_3BO_4 ; all obtained from POCH. Organic solvents, methanol (purity >97%) and carbon tetrachloride (purity 99.9999%) were obtained from Across Organics.

2.2. Apparatus

Electrochemical measurements were carried out using the CHI 660C electrochemical workstation (CH Instruments Inc.). A conventional three-electrode system was employed with a glassy carbon disc electrode (GC, EDAQ, 1 mm dia.) or ITO/glass electrode (PGO, 1 cm^2 of exposed surface area) as a working electrode, Ag/AgCl (saturated KCl) as a reference electrode, and GC rod as a counter electrode. The electrodes mounted in Teflon holder were placed in the conical 2 mL electrochemical cell.

Spectroelectrochemical UVVis measurements were carried out using Hewlett Packard 8452A spectrometer and OMNI 90 (Cypress) potentiostat in 10 \times 4 mm quartz cuvette (Hellma Analytics). The cuvette volume was limited to less than 2 mL, when ITO/glass electrode was mounted in it as the working electrode, Ag|Ag $^+$ electrode as a reference electrode and platinum wire as a counter electrode. In the case of solution spectroelectrochemistry a thin layer configuration of the cell was arranged in the conventional 1 cm quartz

cuvette with 0.08 mm Teflon spacer between the cuvette wall and ITO electrode cut to the size of the cuvette.

Raman spectra for each polymer were recorded *ex-situ* using ITO electrode as a support using Renishaw inVia Raman Microscope (Renishaw, Inc., New Mills, UK) that was equipped with diode excitation laser with 50 mW maximum power at the wavelength 633 nm. The laser intensity was then reduced to 1–5% of its power by using a set of neutral density filters at the exit of the objective. The acquisition time was 6 s and spectral resolution was 2 cm^{-1} . The raw spectra were subjected to procedures of smoothing and baseline subtraction using Renishaw software.

The effectiveness of singlet oxygen photogeneration was measured by monitoring of absorption spectra for DPBF using Hewlett Packard 8452A UVVis spectrometer. The standard 10 \times 2 mm quartz cuvette (Hellma Analytics) applied in these measurements was arranged as a quasi-thin layer cell having a cavity of 10 mm pathlength and thickness of 0.9 mm. This cavity was created between the cuvette wall and the ITO electrode, which was cut to the size fitting the cuvette. As an excitation light source the diode laser (Oxxius 150 mW model LBX-638-150-ELL-PP) was employed with emission wavelength of 638 nm and laser power adjusted to 20 mW. Since the laser produces an elliptic beam (4 mm height, 1 mm width) to enlarge the illumination area a scanning mirror (General Scanning Inc.) driven by AC voltage of 50 Hz frequency was applied that allowed effectively illuminate near 0.5 cm^2 of the active surface. In that arrangement the analyzing beam of the spectrophotometer passes adjacent, along the sample, whereas the laser beam oriented perpendicularly to it illuminates the active layer without any distortion to the spectra.

2.3. Procedures

• Electropolymerization of phenothiazines

In electrochemical polymerization of the phenothiazine derivatives the cyclic voltammetry (CV) was employed, typically within the potential range -0.3 V to +1.2 V, at the scan rate 0.1 V/s. The process was carried out in the 1 mM phenothiazine in the buffered solutions of pH 4.45. The second step after electropolymerization was a conditioning step, which led to complete oxidation of polymer by holding the working electrode under a constant potential of 0.6 V for 2 min. Tests of the modified electrodes were performed at the potential range -0.3 V to +0.8 V in the pure electrolyte solution. Part of these tests were performed to assess a stability of polymer films (see SD). Then the film was exposed to CCl_4 + MeOH mixture for a given period of time (up to 2 h) before the control CV record in the appropriate buffer solution.

• UVVis spectroelectrochemistry

Spectroelectrochemical UVVis measurements for the films deposited on ITO electrode were carried out in the buffer solution

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