



## Microwave assisted synthesis, photophysical and redox properties of (phenothiazinyl)vinyl-pyridinium dyes



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### ABSTRACT

New cationic cyanine dyes, containing electron donor 10-alkyl-phenothiazine and electron acceptor pyridinium units connected through a vinylene bridge were conveniently synthesized by microwaves assisted condensation of phenothiazine carbaldehyde with methylpyridinium salts in dry media. Their photophysical properties revealing strong absorption bands in 440–470 nm region ( $\epsilon \approx 10^4$ – $10^5$ ) and large Stokes shifts of fluorescence emission (610–750 nm) in solid state were supported by computational data using TDDFT level of theory. The redox behavior of PVP was studied by means of electrochemical and biocatalytical oxidation processes.

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### 1. Introduction

Experimental and theoretical studies regarding the photophysical and electrochemical properties of various organic compounds containing extended  $\pi$ -conjugated electron systems enabled the preparation of molecular components suitable for diverse advanced photonic applications. Derivatives containing the phenothiazine core displayed characteristic UV–Vis absorption and emission properties, as well as low and reversible oxidation potentials and thus, taking benefit of the summative electron releasing effects of the nitrogen and sulfur atoms attached to the aromatic rings, phenothiazine appears as a potential heterocyclic candidate in the design of push–pull chromophore systems. Only a fairly weak electronic communication between heterocyclic cores was observed in alkynyl bridged diphenothiazinyl compounds [1], but dumbbell-shaped diphenothiazines bridged by conjugatively linked (hetero)aromatic moieties proved to be redox-active and strongly luminescent [2]. Linear vinylene linked

oligophenothiazines were tested as fluorescent probes for chemosensors [3] and phenothiazinyl merocyanines synthesized from phenothiazinyl aldehydes and N-methylrhodanine or indan-1,3-dione displayed a broad range of fine-tunable redox properties, deep-colored absorption bands and intense emission with large Stokes shifts [4]. Phenothiazinyl rhodanylidene acetic acid merocyanine dyes [5] and phenothiazinyl-vinyl-bipyridine ligand and its Ru(II) complexes [6] were successfully tested as chromophores for applications in dye sensitized solar cells. Terpyridinyl-styryl-phenothiazine ligand and its complexes exhibited good one and two photon excited fluorescence properties [7]. (Pyridinyl)vinyl-phenothiazine as push–pull chromophore system provided fluorophore-switching and potential near infrared sensor application [8] as well as biomarkers in cell biology [9].

Continuing our preoccupation for the identification of new phenothiazine based chromophores with potential applications in materials science or molecular biology [10] in this work we bring evidences of new cationic cyanine dyes obtained by the condensation of phenothiazine-carbaldehyde with methylpyridinium salts. The exploitation of the advantages induced by the dielectric heating allowed us the development of a facile, rapid and more ecofriendly microwave assisted synthetic protocol. Experimental

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**Table 1**  
Crystal data and structure refinement.

	<b>3</b>	<b>7</b>
Formula	C <sub>24</sub> H <sub>25</sub> IN <sub>2</sub> S	C <sub>24</sub> H <sub>25</sub> IN <sub>2</sub> S
Formula weight	500.42	500.42
Temperature [K]	130(2) K	130(2) K
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /n	C2/c
Unit cell		
<i>a</i> [pm]	1735.95(3)	3225.40(9)
<i>b</i> [pm]	749.54(1)	747.54(1)
<i>c</i> [pm]	1740.71(3)	2087.92(6)
$\alpha$ [°]	90°	90°
$\beta$ [°]	103.144(2)°	117.908(4)°
$\gamma$ [°]	90°	90°
Volume [nm <sup>3</sup> ]	2.20561(6)	4.4487(2)
<i>Z</i>	4	8
$\rho$ (calc.) [mg/m <sup>3</sup> ]	1.507	1.494
$\mu$ [mm <sup>-1</sup> ]	1.558	1.545
<i>F</i> (000)	1008	2016
Crystal size [mm <sup>3</sup> ]	0.2 × 0.1 × 0.03	0.4 × 0.4 × 0.2
$\theta_{\text{Min}}-\theta_{\text{Max}}$ [°]	2.97–30.51	2.90–30.51
Index ranges	–24 ≤ <i>h</i> ≤ 24 –10 ≤ <i>k</i> ≤ 10 –24 ≤ <i>l</i> ≤ 24	–46 ≤ <i>h</i> ≤ 46 –10 ≤ <i>k</i> ≤ 10 –29 ≤ <i>l</i> ≤ 29
Reflections collected	32,948	38,113
Indep. refl. [R(int)]	6735 [0.0366]	6796 [0.0301]
Completeness to $\theta_{\text{Max}}$	99.9%	99.9%
<i>T</i> <sub>Max</sub> – <i>T</i> <sub>Min</sub>	1 – 0.95929	1 – 0.90006
Restraints/parameters	0/353	80/364
Goof	1.048	1.041
<i>R</i> <sub>1&gt;2</sub> σ( <i>I</i> )/ <i>R</i> <sub>1(all)</sub>	0.0261/0.0361	0.0263/0.0344
<i>wR</i> <sub>2&gt;2</sub> σ( <i>I</i> )/ <i>wR</i> <sub>2(all)</sub>	0.0509/0.0544	0.0574/0.0608
Residual e-density [e/Å <sup>3</sup> ]	0.411/–0.377	0.732/–0.493

evidences of photophysical properties of the new (phenothiazinyl) vinyl-pyridinium (PVP) dyes were brought by means of UV–Vis absorption/emission spectroscopy and were completed by theoretical DFT computational studies. Their redox behavior was emphasized by electrochemical and biocatalytic oxidation experiments.

## 2. Experimental

### 2.1. Materials and methods

Flash chromatography was performed on silica gel 60 (particle size 0.032–0.063 mm). Thin layer chromatography was performed on Merck DCAlufolien, silica gel 60 F<sub>254</sub> and components were visualized by UV VL-4LC.

The melting points were determined in capillaries with an Electrothermal 9100 instrument. Elemental analysis was carried out using Thermo Flash EA 1112 CHN analyzer.

#### 2.1.1. Spectral measurements

NMR spectra (1D, DEPT, 2D-COSY, 2D-HSQC and 2D-HMBC) were recorded at room temperature on Bruker Avance instruments (<sup>1</sup>H/<sup>13</sup>C: 400 MHz/100 MHz or 300 MHz/75 MHz) in solution (deuteriated solvents (CDCl<sub>3</sub> or DMSO).

EI-MS spectra were recorded on a GC-MS QP 2010 Shimadzu mass spectrometer.

UV–Vis absorption spectra were recorded in solvent with a Perkin Elmer Lambda 35 spectrometer; Fluorescence emission spectra were recorded in solid state with a Perkin Elmer PL 55 spectrofluorometer.

Stopped-Flow spectrometer SFM-300/S BioLogic Science Instruments with standard configuration for UV–Vis absorbance optical mode was employed for fast mixing and observation of the kinetics of biocatalytic oxidation reactions.

IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer with scanning between 4000 and 600 cm<sup>-1</sup> using ATR sampling of the neat substance.

The X ray crystallographic data (Table 1) were collected using a CCD Oxford Xcalibur S diffractometer, MoK $\alpha$  radiation ( $\lambda = 71.073$  pm),  $\omega$ -scan mode. Data reduction was carried out with CrysAlisPro including empirical absorption correction with SCALE3 ABSPACK [11]. The structures were elucidated by direct methods using SIR 92 [12] and were refined using SHELXL-97 [13]. Anisotropic refinement of all non-hydrogen atoms with the exception of the minor 14% disordered part in **7**. The cationic part of compound **7** was found to be disordered over two positions with a ratio of 0.86(1):0.14(1). For **3** a difference-density Fourier map was used to locate all Hydrogen atoms at the final stage of the structure determination, whereas for **7** all H-atoms were calculated on idealized positions using the riding model. Structure figures were generated with ORTEP and DIAMOND [14]. Thermal ellipsoids are drawn at 50% probability if not otherwise mentioned and in Fig. 1 below only the major 86% fraction of the disordered molecule **7** is presented. CCDC 946801 (**3**) and 946802 (**7**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

EPR spectra were measured at liquid nitrogen temperature with a BRUKER-BIOSPIN EMX spectrometer operating at the X-band (9.5 GHz). The EPR parameters were: 100 KHz modulation frequency, microwave power 10 mW, modulation amplitude 2 G; time constant 10 ms; scan time 60 s; number of scans 5; receiver gain 10<sup>4</sup>. Spectral simulations were performed using a rigid limit simulation POWFIT program with simplex optimization method [15].

#### 2.1.2. Electrochemical measurements

The oxidation potentials were determined by cyclic voltammetry measurements using a Potentiostat/Galvanostat/ZRA Reference 600, with a typical three-electrode setup composed of platinum (1 mm) working electrode, platinum and Ag/AgCl as auxiliary and reference electrodes. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in dry dichloromethane purged with argon prior to a measurement. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was employed as internal standard.

### 2.2. Synthesis

All chemicals used were of reagent grade. Microwaves assisted syntheses were performed in a CEM Discover microwave reactor (300 W maximum power, mono-mode irradiation, pressurized reaction vessel, software control) using 20 mL sealed reaction vessels.

10-methyl-10Hphenothiazin-3-carbaldehyde was prepared according to our previously reported microwaves assisted procedure [16]

*N*-alkyl-methylpyridinium salts were prepared according to literature procedures.

**N-methyl-2-methylpyridinium iodide** m.p. = 223 °C from methanol (224 °C, ethanol, [17]) EI-MS *m/z*:107(100%).

**N-ethyl-2-methylpyridinium iodide** m.p. = 122 °C from diisopropyl ether (123 °C, diethyl ether, [17]) EI-MS *m/z*: 121(43%).

**N-butyl-2-methylpyridinium iodide** m.p = 101 °C from diisopropyl ether (98 °C, ethanol, [17]) EI-MS *m/z* 149(35%).

**N-hexyl-2-methylpyridinium iodide** light yellow oil, yield 45% from petroleum ether [light-yellow oil [18]] EI-MS *m/z* 177(58%).

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