



Spectroscopic investigations of vinyl-substituted 10H-phenothiazine

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ARTICLE INFO

Article history:

Received 6 February 2009

Received in revised form

5 May 2009

Accepted 8 May 2009

Available online 28 May 2009

Keywords:

Phenothiazine

Fluorophores

Near infrared sensors

Charge transfer

Contact ion-pair

Spectral diversities

ABSTRACT

Different 10H-phenothiazine derivatives modified at their 3- and 3,7-positions with conjugated electron-deficient pyridine or pyridinium groups using ethenyl linkers are described. Spectral variations of 3-((E)-2-(Methylpyridium-4-yl)vinyl)-10H-phenothiazine iodide and 3,7-bis((E)-2-(Methylpyridium-4-yl)vinyl)-10H-phenothiazine diiodide, which are attributed to intramolecular charge transfer, electronic rearrangement and contact ion-pair mechanisms, were observed to be either base or ion dependent. Depending on the extent of deprotonation of the nitrogen atom in the 10-position of the phenothiazine core, donor–acceptor or push–pull systems provide fluorophore-switching and potential near infrared sensor application.

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1. Introduction

Near infrared (NIR) absorbing dyes and pigments are molecules of much current interest because of their potential applications in optoelectronic devices [1,2]. In particular, NIR dyes play prominent roles in medicinal chemistry and biotechnology [3–5]. Typically, functional dyes with significant bathochromic shifts are obtained by taking advantage of the strong donor-acceptor interactions in these molecules [6,7] or by extending the π -system of the chromophores [8,9]. However, most of these dyes exhibit complex architectures that require multi-step synthetic procedures resulting in poor yields.

The phenothiazine (PTZ) core has been an important moiety in heterocyclic chemistry since it was first reported in 1883 [10]. Many important pharmacological applications of PTZ are attributed to its stable radical cation heterocyclic form [11–13]. The well-defined electron-donating properties of PTZs [14–16] can be partially associated with electrophores to produce dyads and triads [17–20] that influence the oxidation potentials of PTZs, especially electronic substitutions in the 3- or 3, 7- positions. Thus, because of its ground-state intramolecular charge transfer (ICT) and excited-state photo-induced electron transfer (PET) properties, the phenothiazine is

widely used as organic light-emitting diodes (OLEDs) [21,22], acid–base dyes and pigments [23,24], semiconductors [14,25,26], chemical sensors [27] or near-IR dyes [28–31].

However, most of these applications use the protected PTZ structure with covalent substitutions on the nitrogen atom at the 10-position (10N–H). In the present study, we describe the convenient preparation of divinyl substituted 10H-phenothiazines at the 3- or 3, 7- positions (Scheme 1). The deprotonation of these PTZ derivatives at 10N–H is critically important and based on our results, fluorophores and NIR chromophores can be switched on by the loss of protons at 10N–H. We conclude that these alkaline NIR dyes, especially PTZ3 and PTZ4, are potentially useful for ionic sensor applications.

2. Experimental

2.1. Material

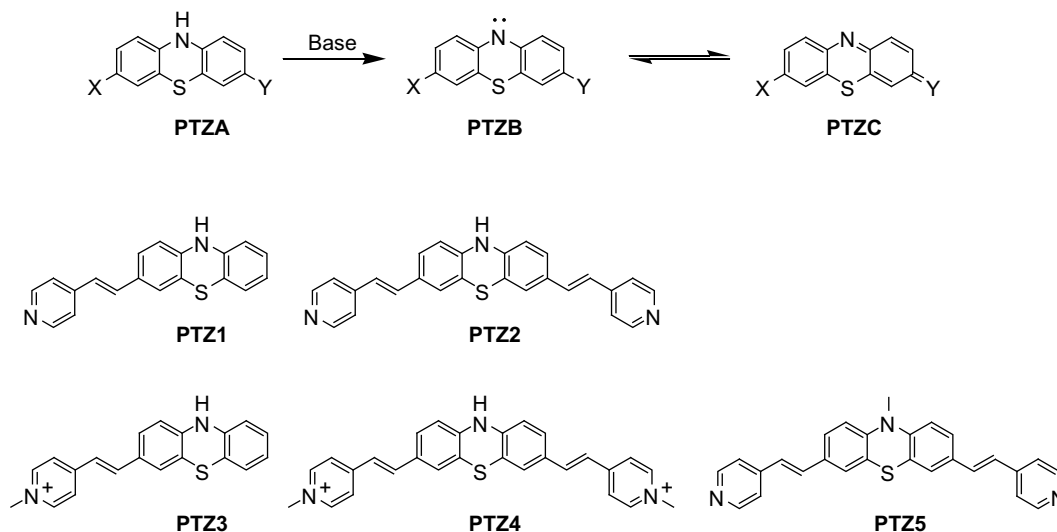
General chemicals were of the best grade available, supplied by Acros Organic Co., Merck Ltd., or Aldrich Chemical Co. and were used without further purification. Cell culture medium and organelle markers were from Invitrogen. All the solvents employed were of spectrometric grade.

2.2. Apparatus

Absorption spectra were taken on a Thermo Genesis 6 UV-visible spectrophotometer, and fluorescence spectra were recorded

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Scheme 1. The 3- or 3,7-divinyl substituted PTZ derivatives.

on a HORIBA JOBIN-YVON Fluoromas-4 spectrofluorometer with a 1 nm band-pass in a 1 cm cell length at room temperature.

2.3. Determination of quantum yields

The quantum yields of PTZ derivatives were determined according to the literature [32].

$$\Phi_u = \Phi_s \times (A_{fu} \times A_s \times \lambda_{exs} \times \eta_u) / (A_{fs} \times A_u \times \lambda_{exu} \times \eta_s)$$

Where Φ_u is quantum yield of unknown; A_f is integrated area under the corrected emission spectra; A is absorbance area at the excitation wavelength; λ_{ex} is the excitation wavelength; η is the refractive index of the solution; the subscripts u and s refer to the unknown and the standard, respectively. For the same λ_{ex} , we chose BMVC as the standard, which has the quantum yield of 0.25 in glycerol and 0.02 in DMSO [33].

2.4. General procedure for the synthesis of phenothiazine derivatives (Scheme 2)

Synthesis of these phenothiazines derivatives are shown in Scheme 1. 10H-phenothiazine containing solution was brominated with *N*-bromosuccinimide (NBS)/THF in additional funnel and then, followed by Heck coupling reaction [34] with 4-vinylpyridine or 4-methoxy styrene under catalyst Pd (OAc)₂. Methyl-pyridinium derivatives can be easily prepared by mean of addition of methyl iodine in acetone system.

2.4.1. Synthesis of 3-bromo-10H-phenothiazine (2)

A double-necked round bottomed flask was charged with phenothiazine (PTZ) 10 mmol in THF solution (20 mL). Then NBS (10 mmol) was dissolved in 20 mL THF and was added dropwise over 1 h with an addition-funnel. The reaction was stirred at ice bath until the complete consumption by TLC monitoring. The solvent was evaporated in vacuum and the residue purified via column chromatography (silica, ethyl acetate/hexane. 1:8, v/v, Rf = 0.38) to remove the dibromo-substituted side product. The final light green products were crystallized from acetone/EA. (yield: 55%). Data for **2**: ¹H NMR (400 Hz, DMSO-*d*₆): δ = 8.706(s, 1H), 7.122(dd, *J* = 8.4, 2.4 Hz, 1H), 7.095 (d, *J* = 2.4 Hz, 1H), 6.984 (ddd, *J* = 8.0, 7.6, 1.2 Hz, 1H), 6.896(dd, *J* = 7.6, 1.2 Hz, 1H), 6.750(ddd,

J = 7.6, 7.6, 0.8 Hz, 1H), 6.650(dd, *J* = 8.0, 0.8 Hz, 1H), 6.590(d, *J* = 8.4 Hz, 1H) ppm.

2.4.2. 3,7-Dibromo-10H-phenothiazine (3)

A double-necked round bottomed flask was charged with phenothiazine (PTZ) 10 mmol in THF solution (20 mL). Then NBS (22 mmol) was dissolved in 45 mL THF and was added dropwise over 1 h with an addition-funnel. The reaction was stirred in ice bath until the complete consumption by TLC monitoring. The solvent was evaporated in vacuum and the residue purified via column chromatography (silica, ethyl acetate/hexane. 1/8, v/v, Rf = 0.34). The final light green products were crystallized from acetone/EA. (yield: 70%). Data for **3**: ¹H NMR (400 Hz, DMSO-*d*₆): δ = 8.848 (s, 1H), 7.140 (dd, *J* = 8.0, 2 Hz, 2H), 7.113 (d, *J* = 2.0 Hz, 2H), 6.571 (d, *J* = 8.0 Hz, 2H) ppm.

2.4.3. 3,7-Dibromo-10-methyl-10H-phenothiazine (4)

Compound **3** (2 mmol) and NaH (3.5 mmol) were placed in a double-necked round bottomed flask with THF solution and stirred at room temperature. CH₃I (5 mmol) was added to the system after 30 min and refluxed for 2 h under N₂ condition. After the reaction finished, system quenched with trace of methanol and extracted with CH₂Cl₂/H₂O. The organic layer was dried by anhydrous MgSO₄ and filtered. The product was isolated by silica gel column chromatography using ethyl acetate/hexane (1/8, Rf = 0.4) solvent pairs as the eluent to afford white solid (yield: 75%). Data for **4**: ¹H NMR (400 Hz, DMSO-*d*₆): δ = 7.300 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.248 (d, *J* = 2.0 Hz, 2H), 6.810 (d, *J* = 8.4 Hz, 2H), 3.225 (s, 3H) ppm.

2.5. 3-((E)-2-(Pyridin-4-yl)vinyl)-10H-phenothiazine (PTZ1)

The compound **2** (5 mmol) was added into a high pressure bottle containing the mixture of palladium (II) acetate (8 mg, strem) and tri-*o*-tolyl phosphine (80 mg, Aldrich), then to which was added the solvent pair (triethylamine 5 mL/acetonitrile 15 mL) and 4-vinylpyridine (10 mmol, Merck). The bottle was sealed after bubbling 10 min with nitrogen. After keeping the system under ~105 °C for three days, the system was cooled to room temperature and then extracted with CH₂Cl₂/H₂O twice. The solvent was dried by MgSO₄ and evaporated in vacuum. The residue was chromatographed on silica gel by Hexane/Acetone (1/1). The orange solid compound was obtained by recrystallizing with acetone/EA (yield: 72%). Data for

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