

Synthesis and photophysical properties of a novel pyridinium salt based on dipicolinate



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ABSTRACT

A novel pyridinium salt based on dipicolinate, **PM-1** was synthesized from the corresponding neutral chromophore and enhanced two-photon absorption activity was obtained. The two-photon absorption cross section value is 6.8×10^2 GM. **PM-1** exhibits pronounced negative solvatochromism and possesses high absorption spectral sensitivities to pH and water content changes. **PM-1** could be used as pH probe and to measure the water content, particularly for less than 10%, in common water miscible organic solvents such as THF, 1,4-dioxane, acetone and methanol.

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1. Introduction

Research into molecular two-photon absorption (TPA) has received increasing attention owing to numerous applications in various areas such as three-dimensional optical data storage, up-conversion lasing, optical power limiting, microfabrication, photodynamic therapy and two-photon laser scanning fluorescence imaging [1,2]. Among the numerous compounds that possess nonlinear optical properties, “push–pull” molecules bearing pyridyl group as an acceptor have been widely studied [3,4]. When the pyridyl group is methylated, the cationic form can enhance the acceptor character of the pyridine group as well as the water solubility of the chromophore considerably [3,5–8].

It has long been known that UV–vis absorption spectra of chemical compounds may be influenced by the surrounding medium and that solvents can bring about a change in the position, intensity, and shape of absorption bands [9]. Several literature studies have been devoted to discuss the solvatochromism of styryl pyridinium dyes and found that the absorption maximum of these dyes depends on the polarity and hydrogen bonding ability of the solvents, and hypsochromic shifts were observed with increasing polarity of the solvent [10].

Water as an impurity in many organic solvents is usually detrimental to many chemical and industrial production processes, especially to electronics and fine chemicals. Thus, devising accurate and reliable water probing methods is very important, and is attracting more and more attention in recent years [11]. Recently, the use of multi-informational dye systems [12–14], which are convenient in terms of required instrumentation and skill, have been shown to be successful for measuring water content in organic solvents [15,16]. Some fluorescent water probes exhibit changes of their fluorescence lifetime and intensity with varying amounts of water content. In most cases, the fluorescence intensity decreases with increasing water content [17]. Thus, it is difficult to detect a trace amount of water in polar solvents by using these fluorescence probes [18].

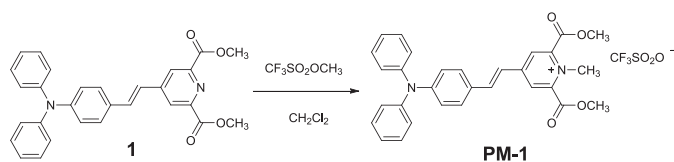
Much effort has also been made toward development of pH probes because of the importance of pH measurements in various scientific research areas and applications. Of the several methods available to determine pH, optical methods have several advantages including rapid response time, high signal-to-noise ratio and excellent pH-sensitivity [19–21].

We have reported previously the synthesis and two-photon absorption behavior of a D–π–A chromophore containing dipicolinate (compound **1**, Scheme 1) [1]. In this work, the methyl pyridinium salt of **1** was synthesized (compound **PM-1**, Scheme 1) and its linear absorption, fluorescence properties and TPA properties were investigated. Compound **PM-1** exhibits significant negative solvatochromism and high absorption spectral sensitivities

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Scheme 1. Synthetic route for compound **PM-1**.

to pH and water content changes, which makes it useful as a probe for pH and water content.

2. Experimental

2.1. General

Compound **1** was prepared according to our previous method [1]. Melting points were determined with an XT-4A apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker DRX 400 MHz spectrometer. Chemical shifts were reported in ppm relative to a Me_4Si standard. IR spectra were obtained on a Nicolet Avatar 370 DTGS spectrometer. Elemental analyses were performed by Atlantic Microlab. Steady-state emission and excitation spectra were recorded on Perkin Elmer LS55 instrument. Visible absorption spectra were determined on Perkin Elmer Lambda 35 spectrophotometer. A Ti:sapphire mode-locked fs laser system with regenerative amplifier (Spectra-Physics) was employed to carry out the experiments to investigate the TPA properties. The average output power of the amplifier is about 200 mW at wavelength of 800 nm with repetition rate of 1 kHz, and the pulse duration was about 140 fs. The open-aperture Z-scan technique was used to measure the TPA cross section.

2.2. Preparation of (*E*)-4-(4-(diphenylamino)styryl)-2,6-bis(methoxycarbonyl)-1-methylpyridin-1-ium trifluoromethanesulfonate (**PM-1**)

Compound **1** (62.0 mg, 0.2 mmol) was dissolved in 10 mL of dichloromethane (freshly distilled from CaH_2). To this solution was added dropwise a solution of methyl trifluoromethanesulfonate (0.01 mL, 0.2 mmol) [ed. Note: corrosive; hygroscopic] in dichloromethane (1.0 mL) and stirred for 36 h at 40 °C. The reaction mixture was then cooled to room temperature. The solvent was removed in vacuum and the residue was purified by column chromatography (ethyl acetate/petroleum ether, 1:1–2:1, v/v) to give **PM-1** (64.8 mg, 51.6%) as a purple red solid. m.p. 118–119 °C. ^1H NMR (400 MHz, DMSO- d_6 , ppm) δ 8.61 (s, 2H, PyH), 8.17 (d, J = 16.0 Hz, 1H, CH=CH), 7.66 (d, J = 8.8 Hz, 2H, ArH), 7.43 (dd, J = 16.4, 8.8 Hz, 5H, CH=CH, ArH), 7.25–7.15 (m, 6H, ArH), 6.93 (d, J = 8.7 Hz, 2H, ArH), 4.28 (s, 3H, N^+CH_3), 4.06 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, DMSO- d_6 , ppm) δ 165.1 (C=O), 155.9 (C), 146.6 (C), 145.9 (CH), 145.7 (C), 144.3 (=CH), 131.2 (CH), 130.9 (C), 130.2 (CH), 128.4 (=CH), 127.3 (C), 126.5 (CH), 123.7 (CH), 121.4 (CH), 121.3 (q, $J_{\text{C-F}}$ = 323 Hz, CF_3), 55.4 (CH $_3$), 45.4 (N^+CH_3). ^{19}F NMR (376 MHz, DMSO- d_6): –76.70. IR (KBr): 2956, 2923, 2853, 1750, 1578, 1490, 1444, 1366, 1261, 1171, 1106, 1034, 641 cm^{-1} . Anal. calcd for $\text{C}_{31}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_7\text{S}$: C, 59.23; H, 4.33; F, 9.07; N, 4.46; S, 5.10. Found: C, 59.33; H, 4.30; N, 4.47; S, 5.13.

3. Results and discussions

3.1. Synthesis

According to the literature, methyl pyridinium salt could easily be prepared from the corresponding neutral pyridine compound and methyl iodide [6,22]. Allain et al. reported the synthesis of

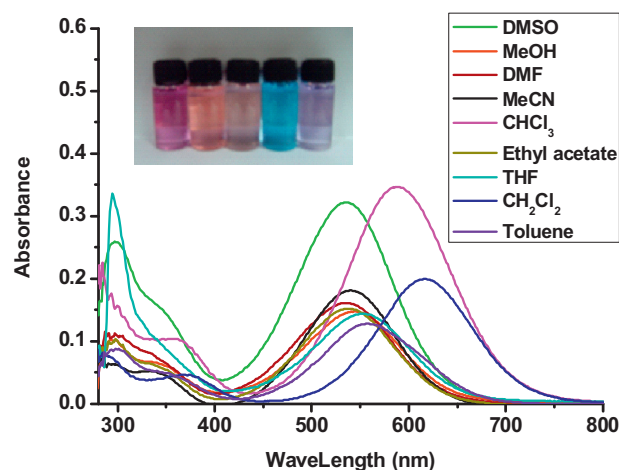


Fig. 1. Normalized one-photon absorption of **PM-1** in various solvents. Inset: solvatochromic properties of **PM-1** in various solvents (from left to right): (a) DMSO, (b) MeOH, (c) THF, (d) dichloromethane, and (e) toluene.

a series of mono-, bis- and trisvinyl-pyridinium triphenylamines (**TP-py** compounds) by this approach [6]. However, we found that compound **1** could not be converted to methyl pyridinium salt by methyl iodide, which could be attributed to the presence of two electron-withdrawing methoxycarbonyl groups known to deactivate the pyridine ring-nitrogen [23]. Methylation was then accomplished by the application of methyl trifluoromethanesulfonate [24].

One challenging problem to be addressed in many biological applications is water solubility. The **TP-py** compounds display high water solubilities, since 0.5 to 1 mM aqueous stock solutions could be prepared without any observation of the formation of precipitates [6]. We note that **PM-1** possesses, in contrast to the **TP-py** compounds, higher water solubility, which are apparently due to the two methoxycarbonyl groups in pyridine ring [2,25]. This high water solubility is clearly a strong advantage for biological applications.

3.2. ICT absorption and solvatochromism

PM-1 exhibits two absorption bands in THF, appearing at 294 nm and at 553 nm, respectively. The former is ascribed to the absorption of the triphenylamine moiety and the later can be assigned as an intramolecular charge-transfer (ICT) band (Fig. 1). The ICT bands of **PM-1** in various solvents are shown in Table 1. For convenience, the solvents are arranged in order of increasing polarity using a widespread empirical scale of solvent polarity $E_T(30)$ [26].

Table 1
ICT band peaks and two-photon absorption cross sections of **PM-1**.

Solvent	$E_T(30)$	PM-1	
		λ_{max} (nm)	σ^a (GM)
CCl_4	32.4	558	
Toluene	33.9	559	
Chlorobenzene	36.8	586	
THF	37.4	553	681
Ethyl acetate	38.1	538	
CHCl_3	39.1	588	
CH_2Cl_2	40.7	617	
Acetone	42.2	539	
DMF	43.2	534	
DMSO	45.1	535	
Acetonitrile	45.6	539	

^a Two-photon absorption cross section value.

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