

Fluorescent Switch Behavior of 1, 2-Bis(4-pyridyl) Ethylene Controlled by pH in Aqueous Solution

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Abstract With the decrease of pH value from 8.45 to -1.0, the UV-Vis absorption and fluorescent spectra of 1,2-bis(4-pyridyl) ethylene(BPE) took on the same changing trend at four different successive pH stages: 8.45–7.20, 7.20–5.62, 5.62–2.60, and 2.60–1.0, namely, no change, decrease, increase, and decrease again. Among these, in a range of 7.20–5.62, the fluorescence wavelength blueshifted from 418 to 359 nm, but the UV-Vis absorption wavelength, in contrast, redshifted from 285 to 298 nm. The fluorescence intensity of BPE had a drop even to quench upon a decline in the pH value from 2.60 to -1.0 probably owing to its cation- π interaction to reduce the π electron cloud density of BPE. Two dissociation constants, pK_{a1} (4.30 \pm 0.01) and pK_{a2} (5.65 \pm 0.04), were obtained based on fluorescence data. The changes of fluorescence spectra indicate that BPE has “off-on-off” switch behavior. The fluorescent spectra of BPE were nearly independent on the presence of α - and β -cyclodextrins.

Keywords 1,2-Bis(4-pyridyl) ethylene; Fluorescent switch; pH fluorescence probe; Cation- π interaction

1 Introduction

1,2-Bis(4-pyridyl) ethylene(BPE) exhibits good photophysical property and is used frequently in constructing supramolecular entities as a basic molecular stock. It can be used as metal ion ligand to construct varieties of complexes^[1–3] and as bridging ligand to prepare metal ion coordination polymers^[4–9] on account of its structural symmetry, some of which can emit novel fluorescence^[9,10], as well as be utilized as halogen bonding(XB) acceptor to play an important role in XB crystal engineering^[11–15]. BPE is hydrophobic and easily included into cyclodextrin(CD) cavity to form rotaxanes^[16,17]. Ethylenyl of BPE can be *cis*- or *trans*-isomerized under the radiation of UV and visible light, respectively; its photoisomerization is a molecular key in unlocking the self-locking molecules of ferrocene derivatives containing amidocyanogen and zinc porphyrin groups^[18]. Having combined hydrophobicity with photoisomerization, BPE and its derivatives can be used to prepare photoisomerization functional materials^[1,5,19–22] and molecular devices. UV light can induce the double bond to isomerize to drive CD to shuttle between two hydrophobic sites, and the molecular shuttler driven by light is thus

formed^[23,24]. In addition, the metal-ligand charge transfer(MLCT) complexes of BPE with metal ions perform excellent optical properties. For instance, molecular squares coordination polymer of BPE featuring octahedral Rh corners formed by self-assembly whose maximal wavelength of absorption spectrum of MLCT is 358 nm, is different from other analogical complexes; the excited state of the complex of BPE decayed exclusively *via* nonradiative pathways^[9]. The complex prepared from BPE, 5-hydroxyisophthalic acid, and zinc ion can emit novel fluorescence^[10].

In recent years, molecular probe has become one of the most interesting investigative hotspots. Fluorescent pH probes are widely applied in medicine and bio- or analytical chemistry. The working mechanism of fluorescent pH probes can be divided into two categories according to the basic process of photophysics as follows: photoinduced electron transfer(PET) and photoinduced charge transfer(PCT)^[25]. These two kinds of interaction mechanisms were realized generally by protonation^[26,27], hydrogen bond^[28,29], and instable chemical bond^[30] as the transitional state formed between proton and fluorescent dye. We herein investigate in detail the spectral

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characters of BPE fluorescent pH probes and obtain two dissociation constants fitted by the Sigmoidal method at different ionic strengths according to the change of fluorescent intensity with pH. The spectral changes indicate that BPE has "off-on-off" switch behavior upon a decline in pH value from 7.45 to -1.0, and thus, BPE can be used as a functional molecule and be applied in molecular devices.

2 Experimental

2.1 Reagents

BPE was purchased from Fluka(purity>98%, America) and used as received. Ethanol of analytical-purity grade was obtained from Beijing Chemical Reagent Factory. Water was doubly distilled in a sub-boiled quartz apparatus. β -CD(purity>99%), was the product of the Guangdong Yunan Cyclodextrins Factory and was used without further purification. All other reagents were of analytical-reagent grade.

2.2 Instruments

All auto-corrected fluorescence spectra were recorded on a Varian Cary Eclipse(Varian Co., America), which was equipped with a pulsed xenon lamp. The UV-Vis absorption spectrum was obtained on a GBC cintra 10e(GBC Co., Australia) UV-Vis spectro-

photometer. The pH value was monitored by a Model PHS-3C pH Meter(Shanghai Precision & Scientific Instrument Co. LTD, China). All experiments were carried out at room temperature.

2.3 Procedures

An aqueous solution of 50 mL of 4.0×10^{-5} mol/L BPE was prepared by adding 2 mL of BPE stock solution into an 80 mL beaker; the systematic target ionic strength(I) was regulated with potassium chloride, and then placed on the constant temperature magnetic stirrer to stir. The pH value was monitored with a real-time pH meter and regulated with a 10.0 mol/L HCl or 5.0 mol/L NaOH solution when the pH value was above 2.0. As for pH value lower than 2.0, each pH value by addition of concentrated HCl. Fluorescence and UV-Vis absorption spectra were measured at intervals of *ca.* 0.2 pH unit.

3 Results and Discussion

3.1 UV-Vis Absorption Spectra

Fig.1 shows the change of UV-Vis absorption spectra of BPE in aqueous solution with pH. As seen in Fig.1, the maximal absorption wavelengths of neutral and protonated forms of BPE are 285 and 298 nm, respectively.

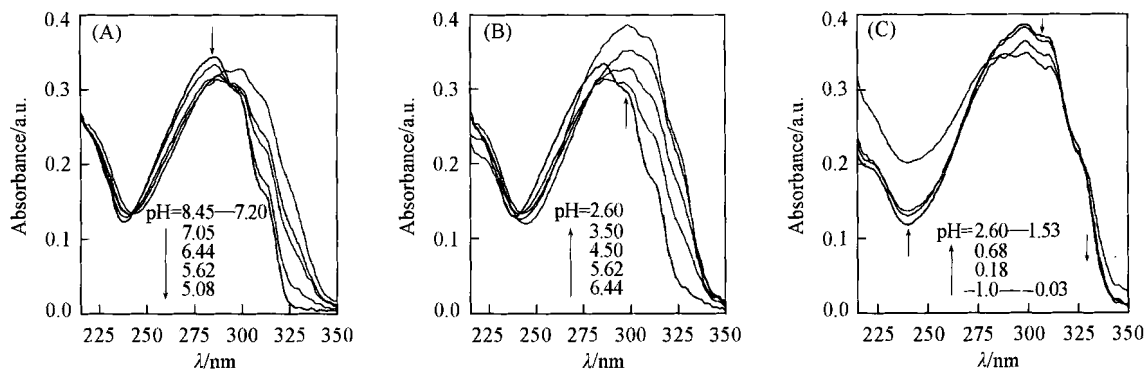


Fig.1 UV-Vis spectral change of BPE with pH

In Fig.1(A), the UV-Vis absorption wavelengths have no change upon a drop in pH value from 8.45 to 7.20 at 285 nm(corresponding to the state 1 in Fig.2). When the pH was continuously reduced to 6.44, one end of BPE started to be protonated, while the other remained at free state, and the UV-Vis absorption intensity decreased slightly(corresponding to the step from 1 to 2 in Fig.2). The protonated end of BPE was totally protonated upon a fall in pH value from 6.44 *via* 5.87 to 5.62, and the UV-Vis absorption peak redshifted to 298 nm. At this moment, the BPE realized

the transition from the neutral to the semi-protonation(corresponding to state 2 in Fig.2). Then, the free end of BPE molecule started to be protonated(corresponding to the step from 2 to 3 in Fig.2). In Fig.1(B), the newly protonated end of BPE was continually protonated completely, and the UV-Vis absorption intensity increased gradually because of the augment of the number of totally protonated BPE(corresponding to state 3 in Fig.2). In Fig.1(C), the UV-Vis absorption intensity at 298 nm showed a decrease upon a decline in pH value from 2.60 to -1.0,

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