

FLUORESCENCE AND RED SHIFT OF THE PHOTOPHYSICAL PROPERTIES FROM PROTONATED SMALL MOLECULE

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Abstract

In this work, the fluorescence (FL) and bathochromic of the photophysical properties from protonated small molecule in cast film state have been investigated. To realize these purposes, the material of 4',4''''-(1,4-phenylene bis (2,2':6',2''-terpyridine) (Phtpy) as a small molecule and camphorsulfonic acid (CSA) as an acid for protonation was selected. For Phtpy, its maxima absorption is 300 nm and no FL color emission. After CSA solution was added in chloroform solution of Phtpy, the absorption spectrum of protonated Phtpy is broaden to longer wavelength with two new peaks appear at around 350 and 370 nm. Upon direct excitation at wavelength of 300 nm, the range of FL spectrum of original and protonated Phtpy is from 320 to 580 nm and from 370 to 580 with their maxima FL intensities at 360 and 460 nm. Interestingly, protonated Phtpy emits blue FL color emission. In addition, energy gap of protonated Phtpy is smaller than that of pristine Phtpy. Finally, the FL and remarkable red shift of absorption and FL spectra of protonated Phtpy will pave the way to develop sensor and other photonic devices with high performances in the ultraviolet region.

Keywords: *FL color, red shift, photophysical properties, small molecule, protonation*

INTRODUCTION

Fluorescent organic polymers such as conjugated polymer and other polymers have significantly potential interest for their widespread application in optoelectronic, microelectronics and sensor [1,2] and other photonic devices such as micro laser, organic light emitting diode (OLED), [3,4] polymer solar cells (PSC), [5] organic field effect transistor (OFET), [6,7], temperature sensing and luminescent solar concentrators.[8] In general, conjugated polymer and other large polymers have high absorption and fluorescence (FL) intensity, emit from ultraviolet to near infrared area,[9] non-toxic,[10] low cost and mechanical flexibility,[11] and they can be deposited as uniform thin film by drop-cast or spin coating from their solutions.[9] In contrast to small molecules, their absorption spectra are located in the ultraviolet region (190-300 nm) so that fluorescence of several small molecules cannot be investigated by irradiation with UV lamp at 365 nm. One of the methods to shift the photophysical properties including absorption and FL of organic polymers is protonation process using several kinds of acid[12–15] such as CSA[12,14] an p-toluene sulfonic acid (PTS), methane sulfonic acid (MSA) and hydrochloric acid (HCl)[16].

In principle, every organic polymer whose basic nitrogen atoms offers the possibility of protonation to the lone electron pair of nitrogen for modification their optical properties.[12,17] The addition of acid to the organic polymer solution can change color and shift photophysical properties of organic polymer to blue shift[15] or red shift,[12,13] which is indicated by the appearance of a new peak in absorption and FL spectra of protonated organic polymer[16,18].

So far, several protonated organic polymers in thin films have been applied in OLED and other applications.[12,13,17] Ngara, et.al.[19] have investigated the red shift of absorption and FL of poly[(9,9'-dioctyl-9H-fluoren-2,7-yl)-5,5'-(2,2':6',2''-terpyridine) (F8tpy) by protonation using CSA in both thin film and microsphere. [19] F8tpy is a large molecule and emits blue color emission[19,20] when it is irradiated by UV lamp at 365 nm. In this work, The FL color and red shift of absorption and FL spectra of a small molecule by protonation process were investigated. In order to realize this target, the material of 4',4''''-(1,4-phenylene bis (2,2':6',2''-terpyridine) (Phtpy) as a small molecule and CSA as an acid were selected. The Phtpy contains six nitrogen atoms (Figure 1) that can

be expected to bind hydrogen atom from CSA for so that protonated Phtpy can be realized (Figure 1). The CSA was selected because it has sufficiently strong acidity in solid acid and can be thermally evaporated without decomposition. [13] The molecule structure of Phtpy and CSA was shown in Figure 1. By addition of CSA in the Phtpy solution, the protonated Phtpy (Phtpy-CSA) emit blue color emission and the red shift of its absorption and FL spectra takes place in comparison with absorption and FL spectra of pristine Phtpy. The fluorescence and remarkable red shift of absorption and PL spectra of protonated Phtpy will pave the way to develop sensor and other photonic devices with high performances in the ultraviolet region.

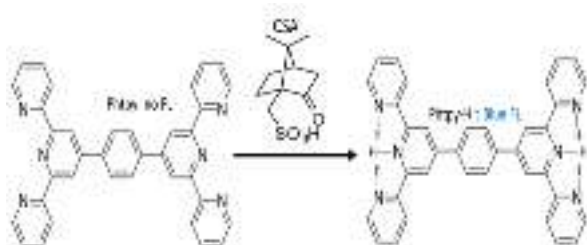


Figure 1. Molecular structure of Phtpy and CSA

EXPERIMENTAL SECTION

Materials and Measurements

The Phtpy, CSA and other materials were purchased from Aldrich Co Ltd. and used without further purification. The absorption and emission spectra of pristine and protonated Phtpy in cast films were measured using JASCO model UV-570 spectrophotometer and model FP-6200 spectrofluorometer, respectively. Fluorescent color of original and protonated Phtpy were investigated by irradiation with UV lamp at 365 nm.

Preparation of pristine and protonated Phtpy solution and thin film

Phtpy solution (1 mg. mL⁻¹, CHCl₃, 50 μL) was drop-casted on a clean quartz substrate and air-dried. For preparation of protonated Phtpy, Phtpy (1 mg. mL⁻¹, CHCl₃, 0.2 mL) was blended with CSA (1 mg. mL⁻¹, CHCl₃, 0.2 mL) and stirring for 5 minutes. Then, 50 μL

from this resultant solution were drop-casted on a clean quartz substrate and air-dried.

Measurement of absorption and emission spectra from pristine and protonated Phtpy

Absorption and emission spectra of the pristine and protonated Phtpy in cast films at room temperature were measured by JASCO model UV-570 spectrophotometer and model FP-6200 spectrofluorometer, respectively.

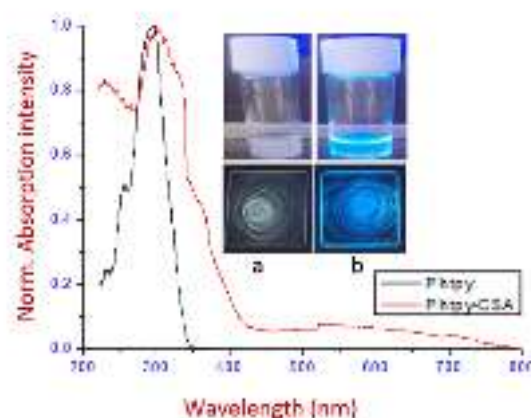


Figure 2. Absorption spectra of pristine (black) and protonated (red) Phtpy. Inset: Fluorescent color in both solution and cast films of pristine (a) and protonated (b) Phtpy

Result and discussion Absorption and FL spectra of pristine and protonated Phtpy

The absorption spectrum of pristine and protonated Phtpy in cast films was demonstrated in Figure 2. According to the Figure 2, the maxima absorption of original Phtpy is at around 300 nm. While the absorption spectrum of protonated Phtpy is broaden to longer wavelength and two new peaks appear at around 350 and 370 nm. This result indicated that red shift of the absorption spectrum of protonated Phtpy took place. Inset in Figure 2 displays fluorescent color emission of protonated Phtpy (Figure 2, inset: b) in both solution and cast films by irradiation with UV lamp at 365 nm. While pristine Phtpy has no color emission in both solution and cast films (Figure 2, inset: a). Fluorescent blue color of protonated Phtpy is consisted with the range of its absorption spectrum from 200 to

420 nm. Figure 3 exhibits the FL spectrum of pure and protonated Phtpy. By direct excitation of wavelength at 300 nm, the range of FL spectrum of pristine Phtpy is from 320 to 580 nm with its maximum FL intensity at 360nm.

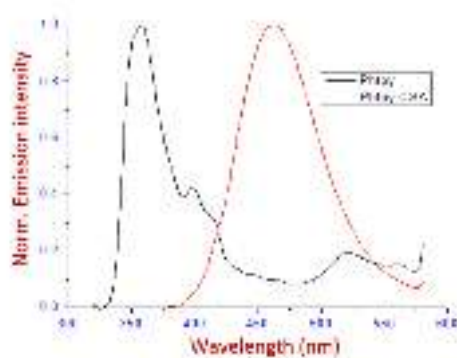


Figure 3. FL spectra of pristine (black) and protonated (red) Phtpy with excitation wavelength at 300 nm

For protonated Phtpy with direct excitation of wavelength at 300 nm, the range of its FL spectrum is from 370 to 580 nm with its maxima FL intensity of 460 nm. Interestingly, by direct excitation of wavelength at 350 nm, the range of FL spectrum is from 370 to 625 nm and its maxima FL intensity is at around 460 nm (Figure 4). These results demonstrate that FL peak of protonated Phtpy does not change even though excitation wavelength is different. It means that FL spectrum of a material does not depend on excitation wavelength.[21] The blue color emission and the red shift of absorption and FL spectra from protonated Phtpy are induced by protonation using CSA with stokes shift at around 1.59 eV. The protonation of Phtpy induces the decreasing of energy gap (E_g)[22] from Phtpy. In this protonation, nitrogen atoms from Phtpy bind hydrogen atom from CSA so that protonated Phtpy can be derived as displayed in Figure 1.

The protonation of Phtpy using CSA can be described as follows: when solutions of Phtpy and CSA solution were blended, hydrions from CSA attach to nitrogen atoms[15] in tpy moiety to form protonated Phtpy (Figure 1) and leaving sulphite (SO_3)²⁻ ion as the counterions. As a result, the protonated Phtpy emits blue color emission (Figure 2, inset: b) and red shift of its

absorption and FL spectra takes place. In addition, the E_g value of protonated Phtpy is smaller than that of pristine Phtpy. According to Figure 2, the calculated energy gap of pristine and protonated Phtpy is 3.54 and 2.95 eV, respectively.

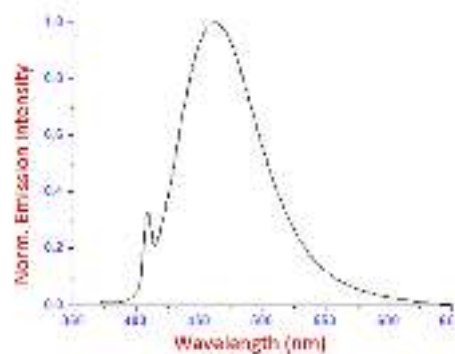


Figure 4. FL spectra of protonated Phtpy with excitation wavelength at 350 nm.

CONCLUSION

By simple mixture between Phtpy and CSA solutions, protonated Phtpy can be realized. Originally, pristine Phtpy has no color emission. By addition of CSA in the Phtpy solution in chloroform solvent, the protonated Phtpy emits blue color emission. By direct excitation at 300 for pristine and protonated Phtpy, their maxima FL intensities are located at 360 and 460 nm, respectively with stokes shift at around 1.59 eV. In addition, the absorption spectrum of protonated Phtpy is broaden and two new peaks appear at around 350 and 370 nm. These results indicated that red shift of the absorption and FL spectra of protonated Phtpy took place. The fluorescence and the remarkable red shift of absorption and FL spectra of protonated Phtpy have a great potential for application in sensor and other photonic devices with high performances in the ultraviolet region.

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