Photoluminescence Wavelength Control of Fluorene Derivatives through H-bonding and Protonation

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A fluorene monomer, which comprised 4-pyridylcyanovinyl groups (FL-CNPy), was synthesized, and the photoluminescence (PL) properties of FL-CNPy combined with various (di)acids were evaluated. Due to hydrogen (H)-bonding or protonation between the pyridine end groups and acids, the PL emission maxima varied from 460 to 557 nm according to the acidity (pK_a) and type of (di)acid. Additionally, adjusting the ratio of FL-CNPy/(di)acid tuned the PL emission wavelength without modifying the materials.

Controlling the electrooptical properties of photoluminescent materials is an important issue in organic light-emitting diodes (OLEDs) as well as lighting and chemical sensor applications.[1–3] Various types of monomeric and polymeric π-conjugated materials, including quinoline and fluorene derivatives, have been synthesized owing to their high photoluminescence (PL) and high thermal stability. In these materials, the photo- and electroluminescent properties can be adjusted by introducing π-conjugated linkages, which alter the electronic state of the material.[4–6] When a light-emitting π-conjugated core contains basic nitrogen atoms, the electrooptical properties can be varied through protonation or hydrogen (H)-bonding using proton-donating materials.[7–11] This technique allows the electrooptical properties to be controlled without synthetic modification. Lin et al. have reported the H-bonded supramolecular liquid crystalline structures of phenylene–vinylene oligomers with pyridine end groups combined with a few types of aromatic acids, and found the PL emission property is influenced by the acidity (pK_a) of the acids.[7–9] Monkman et al. have studied the effects of protonation accompanied by internal H-bonding on the spectroscopic and structural properties of phenylene–pyridylene copolymers using strong acids of methanesulfonic acid and camphorsulfonic acid (CSA).[10] Moreover, the protonation-induced continuous tunability in the optical properties of a π-conjugated heterocyclic oligomer composed of quinoline and pylene units using CSA has also been reported.[11] These studies imply that adjusting the acidity of the proton-donating material can tune the electro-physical properties of nitrogen-containing photoluminescent materials. However, controlling the optical properties of fluorene derivatives by means of H-bondings and protonation using various types of acids with different pK_a's has not been explored.

In this letter, a new fluorene derivative, dihexylfluorene terminated with 4-pyridylcyanovinyl groups (FL-CNPy), was synthesized and the photophysical properties of thin films doped with various (di)acids and CSA were investigated to clarify the influence of the pK_a and the structure of the acids on the absorption and PL emission.

Figure 1 shows the chemical structure of FL-CNPy, (di)acids, and CSA used in this study. These acids exhibit various pK_a values, which influence the characteristics of H-bondings. Thin films were prepared from a THF or chloroform solution of FL-CNPy, (di)acid, and poly(methyl methacrylate) (PMMA). The PMMA matrix was used to avoid the molecular aggregation, which alters the photophysical properties of the material. Detailed synthetic procedures for FL-CNPy and film preparation are described in the Supporting Information.[12]

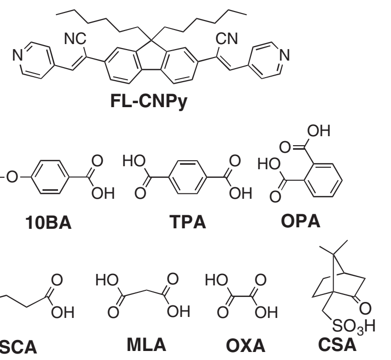

Figure 1. Chemical structure of materials used in this study.

The UV–vis absorption and PL properties in the THF solution of FL-CNPy and (di)acid mixture were similar to that without the (di)acids because the pyridine end groups and (di)acids do not interact, as summarized in Table 1. On the other hand, both the UV–vis absorption and PL properties for the films [FL-CNPy/(di)acid = 1/2 (mol/mol) dispersed in PMMA] varied with the (di)acids. Figures 2a and 2b show the UV–vis and PL spectra of thin films of FL-CNPy doped with (di)acids and their photograph of the emission, respectively. Both the absorption and PL emission maxima shifted to longer wavelengths when the pK_a of the (di)acid was decreased. Although the pK_a of SCA is greater than 10BA, the PL emission maximum was longer than 10BA. The structural and electrical differences between aromatic and aliphatic acids, and number of carboxylic

Table 1. pK_{a1} of (di)acids and spectroscopic data of FL-CNPy/(di)acid in solution and film state

(Di)acid	pK_{a1}	Solution[a]		Film[b]	
		λ_{max}/nm	λ_{PLmax}/nm[c]	λ_{max}/nm	λ_{PLmax}/nm[c]
None	—	378	452	378	460
10BA	3.9	379	451	385	491
SCA	4.2	380	451	384	508
TPA	3.5	378	452	387	510
OPA	2.9	378	452	393	540
MLA	2.9	376	451	389	543
OXA	1.2	379	451	425	557
CSA	—	—[d]	—[d]	418	555

[a]In THF solution. [b]On quartz substrate. [c]Excited at 365 nm. [d]Insoluble.

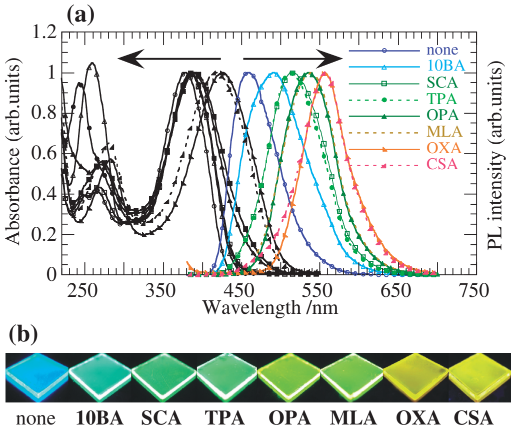

Figure 2. (a) UV–vis absorption and PL spectra of FL-CNPy/(di)acid (1/2 mol/mol) films on quartz substrate. Black lines: UV–vis spectra, colored lines: PL spectra. (b) Photographs of FL-CNPy/(di)acid films when irradiating with 365 nm light.

acids (pK_{a1} and pK_{a2}) should affect the electrooptical state of the H-bonded light-emitting core.

For films doped with 10BA, SCA, TPA, OPA, and MLA, the red shifts in the absorption maxima were 6–15 nm, whereas films with OXA and CSA displayed much greater shifts (40–47 nm) (Table 1). It was reported that protonation caused a large red shift in absorption of phenylene–pyridylene copolymers with strong acids due to protonation.[10] Because OXA and CSA exhibited large acidites, the nitrogen atom of the pyridine end groups was protonated. In contrast, large red shifts (31–97 nm) in the PL emission, which depended on the acidity of (di)acids, were observed for all the doped films. It was interesting that the red shifts in the PL emission of films doped with 10BA, SCA, TPA, OPA, and MLA were large (≈83 nm), although the red shifts in the absorption of these films were small (≈15 nm). The difference in the electronic state between the H-bonded and the protonated FL-CNPy films caused these differences in the absorption and PL properties.

The H-bonding of thin films doped with 10BA, SCA, TPA, OPA, and MLA were confirmed by FTIR spectroscopy as new absorption bands around 1860–1940 and 2500–2600 cm^{-1} (H-bonded O–H stretching)[13–15] were detected (see Supporting Information). Additionally, new small absorption at 1635 cm^{-1} was observed for film doped with OPA and MLA. This band was also observed in films doped with OXA and CSA, although the vibrations around 1860–1940 cm^{-1} were not observed. In these cases, new absorption bands around 2120–2150 and 2500–2600 cm^{-1}, which were assigned to the protonated N–H stretching, were detected. Furthermore, the absorption intensity at 1635 cm^{-1} increased in the order of OPA, MLA, OXA, and CSA. Because the absorption at 1635 cm^{-1} was observed when FL-CNPy was mixed with dilute HCl solution, this absorption was also assigned to be protonated N–H stretching. Therefore, partial protonation should occur when the pK_a was small, according to the equilibrium 1.[15] Moreover, the PL wavelength was controlled by adjusting the ratio of FL-CNPy/diacids. Figure 3a shows the PL spectra of FL-CNPy/OPA films when the content of OPA was varied. This controllability was achieved when TPA was used although the maximum PL wavelength depended on the pK_a as plotted in Figure 3b.

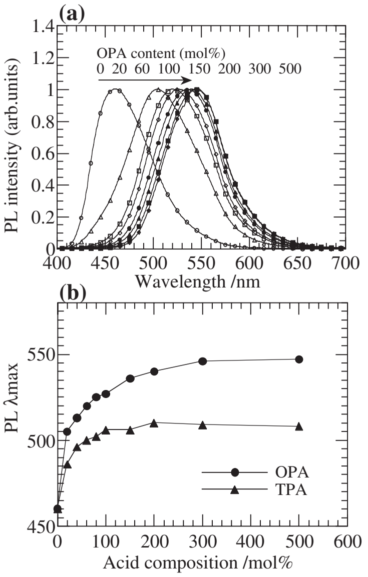

Figure 3. (a) PL spectra of FL-CNPy/OPA/PMMA films on quartz substrates with various OPA content. (b) PL emission maxima of FL-CNPy/OPA/PMMA and FL-CNPy/TPA/PMMA films as a function of acid composition.

$$\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{A{-}H\cdots B} \rightleftharpoons (\mathrm{A\cdots H\cdots B}) \rightleftharpoons \mathrm{A\cdots H{-}B} \rightleftharpoons \mathrm{A^{-}H^{+}{-}B} \quad (1)$$

Further studies on the influence of type and content of the polymer matrix on the photophysical properties and fabrication of electroluminescent devices are currently in progress.

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