Editor's Choice

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Tuning Photoluminescent Wavelength of Water-Soluble Oligothiophene/Polymer Complex Film by Proton Bonding

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We synthesized a new oligothiophene derivative with pyridine end groups and investigated their optical properties. Upon adding an aqueous polystyrene sulfonic acid solution, it forms homogeneous polymer complex films with protonated structure. Furthermore, reversible color change in photoluminescence in response to a base due to reversible protonation of pyridyl end groups in oligothiophene was demonstrated, which can be applied to acid sensors.

Recently, controlling the electron status of π-conjugated materials to optimize optoelectrical properties by external stimuli has been intensively investigated. In particular, using hydrogen bonding (H-bonding) or protonation at basic atoms in π-conjugated linkages has attracted attention because it reversibly varies dynamic features, morphology, and processing characteristics as well as electrooptical properties of the materials without synthetic modification.[1,2] This technique has been applied in photovoltanic devices for tuning such optical properties as absorption (Abs.) and photoluminescent (PL) spectra with improvement of dispersity. Lin and co-workers used liquid-crystalline phenylene–pyridilene derivatives, and developed supramolecular structure from them and tuned the optical properties by using such various acidic compounds as acid-modified gold nanoparticles,[3] monofunctional acid, and bifunctional acid.[4]

In the previous work, we explored tunability of the PL wavelength of fluorene (FL) derivatives composed of pyridylcyanovinyl groups by doping various acids. The maxima wavelength of PL varied according to acidity of the dopants, which causes H-bonding or protonation.[5] Furthermore, we succeeded in simultaneous light-driven patterning of molecular alignment and photoluminescent behavior of FL derivatives by using hydrogen-bonded photocrosslinkable liquid-crystalline polymer films as an alignment layer.[6] In this work, we used oligothiophene with pyridiyl ring alternatively to achieve longer-wavelength emission with simple structure. Oligothiophenes are promising π-conjugated materials for organic semiconductors, photovoltanic devices, as well as photoluminescent devices though tunability of optoelectrical properties by acidity have not yet been much explored because of poor solubility in water.[7,8] We synthesized terthiophene containing pyridine rings with a methyl side branch at both molecular termini (3Th-MP, Figure 1) to enhance solubility and explored their photoluminescent behavior.

The synthetic route of the compounds and experimental details are written in Supporting Information (SI).[9]

First, we explored change in optical properties of 3Th-MP by adding various acids. We found that 3Th-MP can dissolve in chloroform and tetrahydrofuran (THF) due to improvement of solubility by introducing methyl side branches at pyridyl rings.

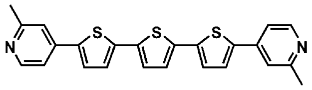

Figure 1. Chemical structure of oligothiophene used in this study.

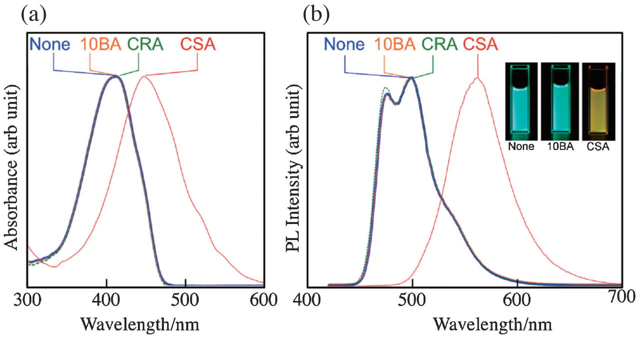

Figure 2. UV–vis absorption (Abs., (a)) and photoluminescent spectra upon exposure to 405-nm light (PL, (b)) of 3Th-MP/acid complexes (3Th-MP/acid = 1/4(mol/mol)) dissolved in THF. The inset in (b) shows photographs of the complex solution upon exposure to 365-nm light.

Figure 2 shows Abs. and PL spectra of 3Th-MP in THF solution containing various acids. It was clearly observed that maximum wavelength shifted from 400 to 430 nm in Abs. and from 500 to 560 nm in PL spectrum on adding a strong acid (10-camphorsulfonic acid (CSA)) while both spectra showed no change on adding other weak acids: 4-decyloxybenzoic acid (10BA) and crotonic acid (CRA). In addition, the chemical shift of ^{1}H NMR of around pyridyl rings was observed in 3Th-MP/CSA complex in comparison to other weak acids (see SI[9]). The inset in Figure 2b displays photographs of THF solution of 3Th-MP and 3Th-MP/CSA complex exhibiting greenish and yellowish photoluminescence upon exposure to 365-nm light. The maximum shift of PL was a little longer though the shift range was smaller than our previous report of FL derivatives.[5] These results indicate that 3Th-MP easily forms a protonated structure with stable, soluble, and long-wavelength emissive structure by adding strong acids[6] while no gradient change occurred in maximum wavelength due to formation of H-bonding as we previously reported. Next, aqueous polystyrene sulfonic acid (PSS) solution was used to prepare protonated 3Th-MP. Figure 3a shows PL spectra of the aqueous complex solution containing 3Th-MP with different concentration. A peak at

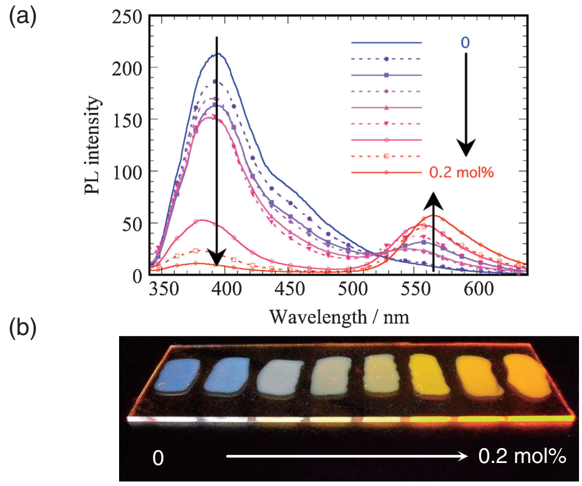

Figure 3. Change in PL spectra of aqueous solution (a) and photographs of 3Th-MP/PSS complex film (b) containing 3Th-MP at different ratio. The films in (b) were irradiated with 365-nm light.

367 nm originating from PSS decreased while a broad absorption around 560 nm increased with an increase in 3Th-MP content. The PSS peak also disappeared on adding ammonium solution, suggesting that the decrease in PL spectra of PSS resulted from energy transfer from PSS to 3Th-MP and diacidification. Furthermore, it can form a homogeneous and transparent film without aggregation of chromophore when the complex solution is cast onto a glass substrate. The films prepared with the complex solution exhibited photoluminescence upon exposure to 365-nm light with relevant emission wavelength (Figure 3b). It changed from blue to orange through whitish emission with increase in thiophene content. In addition, the melting point of 3Th-MP (240 °C) was erased upon binding to PSS, and no obvious peak was observed before the decomposition temperature of PSS (<270 °C, see SI[9] suggesting that 3Th-MP dispersed in PSS homogeneously and that thermal stability was enhanced by protonation).

Figure 4 displays FT-IR spectra of PSS, 3Th-MP, and the complexes to evaluate formation of a proton bonding between PSS and 3Th-MP. PSS and the complex films were powdered to compare to 3Th-MP powder. 3Th-MP shows strong peaks at 1594 and 1548 cm^{-1} assigned to a typical vibration of C=N and C=C at a free pyridine ring, respectively. In contrast to pure 3Th-MP, these peaks disappeared upon biding to a large amount of PSS (3Th-MP/PSS = 1/20 (mol/mol)) while new peaks at 1517, 1440, and 1348 cm^{-1} appeared which were not detected in pure PSS. These peaks are indicative of formation of protonated pyridyl ring in 3Th-MP at both molecular terminals. Furthermore, these peaks increased when the feed ratio of chromophore reached 20 mol %; however, the peaks of pure 3Th-MP appeared again when the content of 3Th-MP increased in 33 mol %. The protonated oligothiophene easily reverted to its original structure in the film under basic condition. Figure 5 shows photographs of 3Th-MP/PSS complex film under air and ammonia upon exposure to 365-nm light. The complex contained 0.24 mol % 3Th-MP to clarify the change in color. When the film was kept under basic atmosphere, the emission immediately changed greenish from orange, while it reverted to the original color when kept under air, and the change can be repeated over three times. Dissolving the complex films in water changed the color when the solution became basic (see SI[9]). This suggests that the color change in the complex films is due to the deprotonation of 3Th-MP under the basic atmosphere.

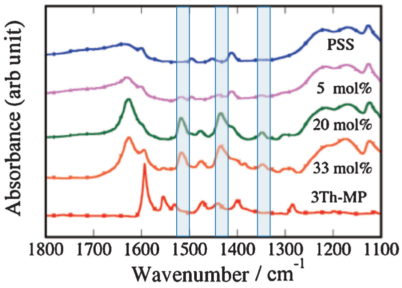

Figure 4. IR spectra of 3Th-MP combined with PSS in a different ratio. The highlights indicate absorbance around 1517, 1440, and 1348 cm^{-1} of the samples.

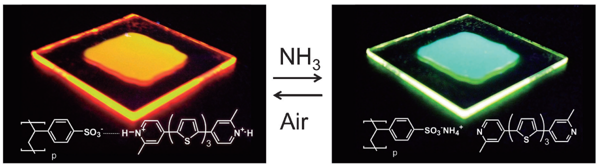

Figure 5. Photographs of the complex film containing 0.24 mol % 3Th-MP irradiated with 365-nm light under air (left) and ammonia (right). The inset of the photograph indicates plausible relevant structure.

In summary, we investigated photoluminescent behavior of PSS/3Th-MP complexes by absorption, FT-IR, and PL spectroscopy. They can dissolve in water, and their absorption and photoluminescent spectra can be tuned by acid resulting from reversible diprotonation of pyridyl rings in 3Th-MP. This can be applied to fluorescent acid sensors. Furthermore, water-soluble conductive polymer complex can be applied by spray-coating as well as spin-coating[10] at low temperature to prepare a thin film due to high processability. The effect of protonation and binding in PSS on conductance are now under investigation.

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