Acid-doping to Tropone-containing Conjugated Polymer

Koji Takagi,* Kousuke Mori, Takatoshi Kinoshita, Hideo Kunisada, and Yasuo Yuki
Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555

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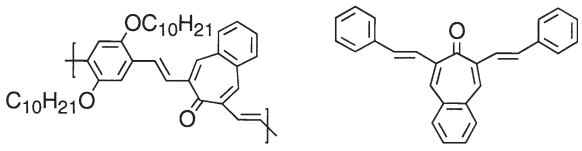
The acid-doping to the tropone-containing conjugated polymer (**TCP**) was demonstrated. The color of the chloroform solution of **TCP** changed from orange to dark red by the addition of trifluoroacetic acid, while no color change was observed in the experiment using the low molecular weight model compound. The fluorescence from **TCP** was completely quenched with the excess amount of a protic acid. The quasi-reversible protonation-deprotonation cycle was confirmed when triethylamine was dropped into the proton-doped **TCP**.

Conjugated polymers offer many possibilities in the optoelectronic application such as light-emitting diodes, thin-film transistors, and plastic lasers. They are also reliable candidates for the sensory materials because the sensing ability of the conjugated polymer can be enhanced by linking the receptor unit with the molecular wire.[1] The fluorescent sensor is one of the most desirable technique to detect chemicals because the guest binding event results in the increase, decrease, and the wavelength shift of the emission peak. The change in the absorption spectra, while sometimes less sensitive, has been also extensively used. The acid-base chemistry and the coordination chemistry play an important role in the sensor system. The introduction of the aromatic unit including the nitrogen atom into the conjugated polymer provides the sensory materials to probe acids and metal cations. Eichen reported the reversible protonation-deprotonation process of bipyridine-containing poly(*p*-phenylene vinylene) derivatives in the film state.[2] Okamoto, Jenekhe, and Bunz prepared the quinoline-embedded main-chain or side-chain conjugated polymers where the different behavior was observed by the protonation depending upon the polymer structure.[3] Recently, Monkman synthesized 1,4-phenylene-2,5-pyridine alternating copolymers to find out that the oxygen atom in the solubilizing alkoxy substituent on the benzene ring and the nitrogen atom on the pyridine ring cooperatively bind a proton to form the intramolecular hydrogen bond to provide the near-planar conformation, resulting in the red-shift of the absorption and the emission spectra.[4] Polyaniline emeraldine base also received the protonation on the imine nitrogen to afford the radical cation species.[5] Moreover, carbonyl groups are also known to function as the proton receptor unit although the synthesis and the photophysical properties of the conjugated polymer including the carbonyl group have been less investigated.[6] We have recently synthesized conjugated polymers containing benzotropone structure in the main chain.[7]

Tropone, seven-membered fully conjugated ketone, is predicted to be less aromatic and energetically very stable compound.[8] In this contribution, the control of photophysical (absorption and emission) properties of a tropone-containing conjugated polymer (**TCP** in Figure 1) is described since the absorption spectrum of tropone is known to be modulated by the protonation of the carbonyl group.[9]



TCP **MODEL**

Figure 1. Chemical structures of **TCP** and **MODEL**.

TCP and the model compound (**MODEL** in Figure 1) were synthesized as described previously by the Wittig (poly)condensation method. The isolated **TCP** readily dissolved into $CHCl_3$ and THF as well as toluene. The number-averaged molecular weight and the polydispersity of **TCP**, estimated by gel permeation chromatography (GPC) in THF using calibration curves made from standard polystyrene samples, were 4070 and 1.39, respectively, from which the degree of polymerization was found to range from six to seven. The polymer predominantly contained *trans*-vinylene structure as evidenced by the ^{1}H NMR spectrum. **MODEL** also consisted of the *trans*-vinylene structure.

By the addition of trifluoroacetic acid ($pK_a = 0.23$), the color of the chloroform solution of **TCP** gradually changed from orange to dark red. Because the chloroform solution was consistently transparent under the concentration of 10^{-5} M, the UV absorption spectra were measured in the presence of various amount of trifluoroacetic acid. Accordingly, the absorption intensity of the maximum peak at 418 nm observed in the virgin **TCP** decreased, and simultaneously the sharp peak at 300 nm appeared and the cutoff wavelength shifted toward the lower energy region (Figure 2). On the contrary, neither the visible color change nor the unambiguous change in the UV spectral pattern was observed in the similar experiment using **MODEL**. A stretching vibration signal of the carbonyl group in **TCP** was observed at 1602 cm^{-1} while that in **MODEL** was at 1610 cm^{-1}, from which one can suppose the more polarized and therefore the more basic character of the carbonyl system of tropone in **TCP**. The stronger proton adsorption ability of **TCP** compared with **MODEL** resulted in the dramatic change in the UV absorption spectra. The addition of the stronger protic acids such as methanesulfonic acid ($pK_a = -1.2$) brought about much remarkable spectral change at the relatively smaller [acid]/[tropone] ratio and conversely the weaker protic acids such as benzoic acid ($pK_a = 4.2$) did not trigger off any change. The virgin **TCP** emitted orange yellow light at 564 nm, whilst the emission wavelength blueshifted by ca. 20 nm and the intensity markedly decreased by the increment of the acid concentration leading to the complete quench of the fluorescence (Inset in Figure 2). Although the planarity of troponoid compounds is a matter of argument,[8] from our molecular orbital calculation about 2,7-dimethylbenzotropone (Figure 3),[10] the planarization of the seven-membered ring

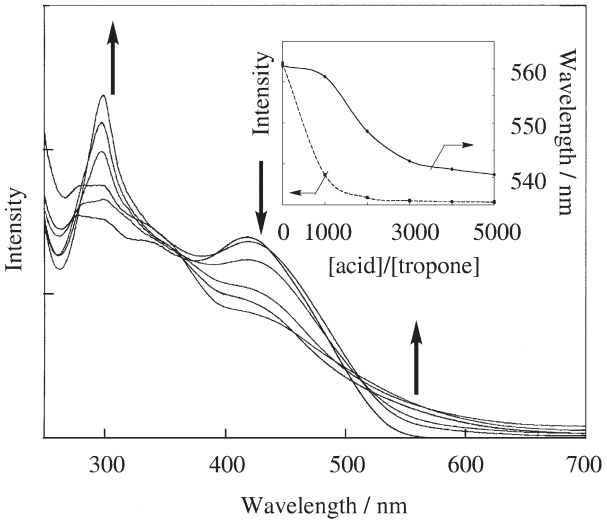


Figure 2. Changes in absorption spectra of chloroform solution of **TCP** (10^{-5} M) by addition of trifluoroacetic acid ($pK_a = 0.23$). Inset is changes in fluorescence intensity and wavelength as a function of acid concentration.

takes place caused by the protonation of the carbonyl group where the cation delocalizes on the tropone ring. Since the positive charge could travel over the conjugated polymer through the tropone segment, **TCP** becomes more planar and rigid to give rise to the aggregated structure so that the emission intensity should be decreased.

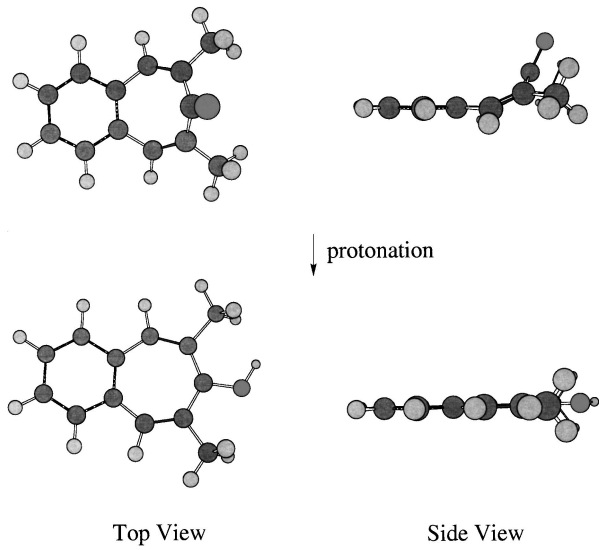


Figure 3. Stereoview of 2,7-dimethylbenzotropone and proton adduct thereof.

The addition of a Lewis base deprotonated the proton-doped **TCP**. Namely, to the fully protonated **TCP** with the excess amount of trifluoroacetic acid (5000 times relative to the tropone unit) was added triethylamine ($pK_b = 3.21$), which brought about the reverse change in the UV spectral pattern and the solution color also returned to clear orange (Figure 4). The difference in the UV spectra between the virgin polymer and the dedoped polymer may be due to the incomplete deprotonation by triethylamine having the weak basicity or the change in the polymer primary structure which must be concluded in the near future. Thus the protonation-deprotonation event is quasi-reversible to open the way to utilize **TCP** as the pH-responsive optical sensor.

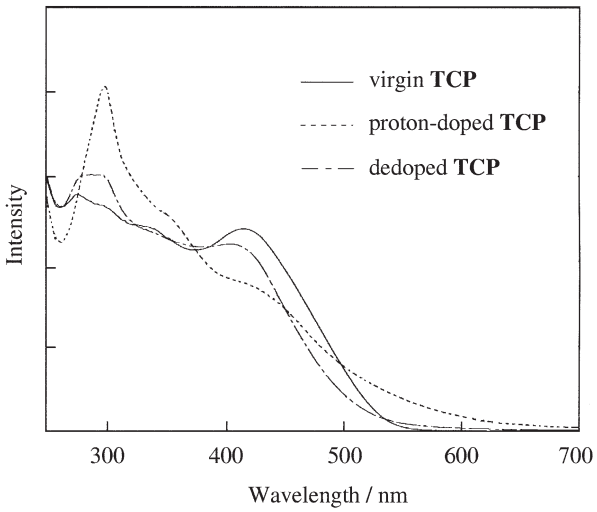


Figure 4. Changes in absorption spectra of chloroform solution of **TCP** (10^{-5} M) by addition of triethylamine ($pK_b = 3.21$).

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10 The ground state geometry of 2,7-dimethylbenzotropone was optimized by MOPAC with AM1 method on Chem3D Pro ver. 5.0.

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