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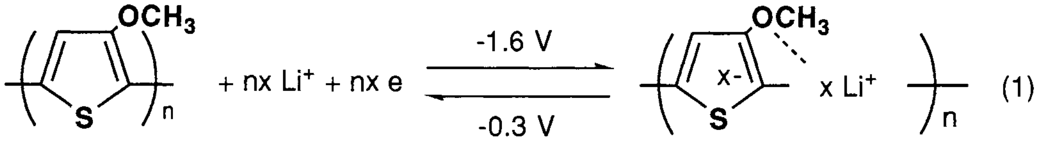
Poly (thiophene-2,5-diyl) Having Crown Ethereal Subunit. Preparation, Stable n-Doped State, and Light Emitting Diode

Yuichi MIYAZAKI and Takakazu YAMAMOTO*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

π-Conjugated polythiophene having crown ethereal subunit, PCT5, reacts with metallic Na to afford a Na-doped or n-doped semiconducting material, which shows good stability against O_2 in air presumably due to strong interaction between Na^+ and the crown ethereal subunit. An ITO | PCT5 | Al electric junction serves as a light emitting diode, which starts to emit light at 6 V.

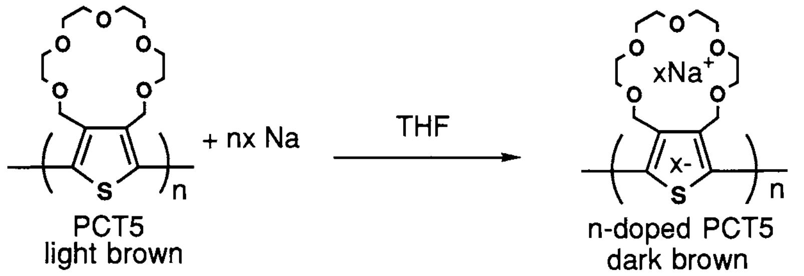
In contrast to good chemical stability of p-doped π-conjugated polymers against O_2 in air, n-doped π-conjugated polymers are usually very unstable to O_2 in air. In our previous study on the doping behavior of poly(thiophene-2,5-diyl)s (PTh's) having ethereal subunits, we noticed that they showed certain stability in their n-doped or cation-doped state against O_2 in air due to strong interaction of the cationic dopant with the ethereal group.1) For example, the n-doped state (dopant = Li^+) of PTh with 3-OCH_3 group formed by an electrochemical doping at -1.6 V *vs.* Ag/Ag^+ is stable up to -0.3 V *vs.* Ag/Ag^+ and the n-doped polymer maintains its n-doped color for several minutes under air.1)



(1)

These results suggest the n-doped state can be more stabilized by selecting an adequate substituent having a stronger interaction with the cation. Based on this view, we have prepared PTh having a crown ethereal subunit, and now report not only the stability of the n-doped state of the polymer but also its usability in the preparation of light emitting diode. Although crown ethers have been the subject of many papers, π-conjugated polymers with crown ethereal subunit has no precedent.

The reaction of the following light brown PTh having the crown ethereal subunit, poly(3,6,9,12,15-pentaoxa-19-thiabicyclo[15.3.0]-eicosa-1(20),17-diene-1(20),17-diyl) (PCT5)2) which is prepared by dehalogenation polycondensation3) of the corresponding dichloro monomer (18,20-dichloro-3,6,9,12,15-pentaoxa-19-thiabicyclo[15.3.0]-eicosa-1(20),17-diene) using zerovalent nickel complex and has high molecular weight (Mw=7.4×10^5) as well as high solubility in usual organic solvents, with metallic sodium in a tetrahydrofuran solution affords a precipitate of sodium-doped or n-doped dark brown polymer.



(2)

Figures 1a and 1b show the change of the IR spectrum on the doping. On the doping, the absorption band at 1100 cm^{-1} assigned to C-O-C stretching vibration is weakened and a new strong band appears at 1450 cm^{-1}, strongly suggesting that the crown ethereal ring interact with the sodium cation in the n-doped state. Treatment of the n-doped PCT5 with dil. HCl gives undoped PCT5 whose IR spectrum (Fig. 1d) is identical to that of original PCT5, revealing no cleavage of chemical bond of PCT5 takes place in the n-doping. The electrical conductivity of PCT5 (1.9×10^{-6} S cm^{-1}) increases to 1.7×10^{-4} S cm^{-1} on the n-doping; the conductivity is measured with a film prepared by compressing the powdery n-doped PCT5.

As described above, in cases of PTh and its usual derivatives, exposure of the n-doped sample to air causes rapid undoping of the n-doped state as easily confirmed by rapid color change. However, in the case of PCT5, its exposure to air [4] does not cause apparent color change even after 1 month. IR spectrum of the powdery n-doped PCT5 after exposure to air for 1 month (Fig. 1c) still shows the absorption band at 1450 cm^{-1} characteristic of the n-doped state, although the relative intensity of the peak is somewhat weakened.

Change in the electrical conductivity (σ) of the film sample of Na-doped PCT5 on the exposure to air for 1 month was observed, however, the change[5] is much smaller than that observed with usual n-doped polymers, which are converted into insulators on the exposure to air.

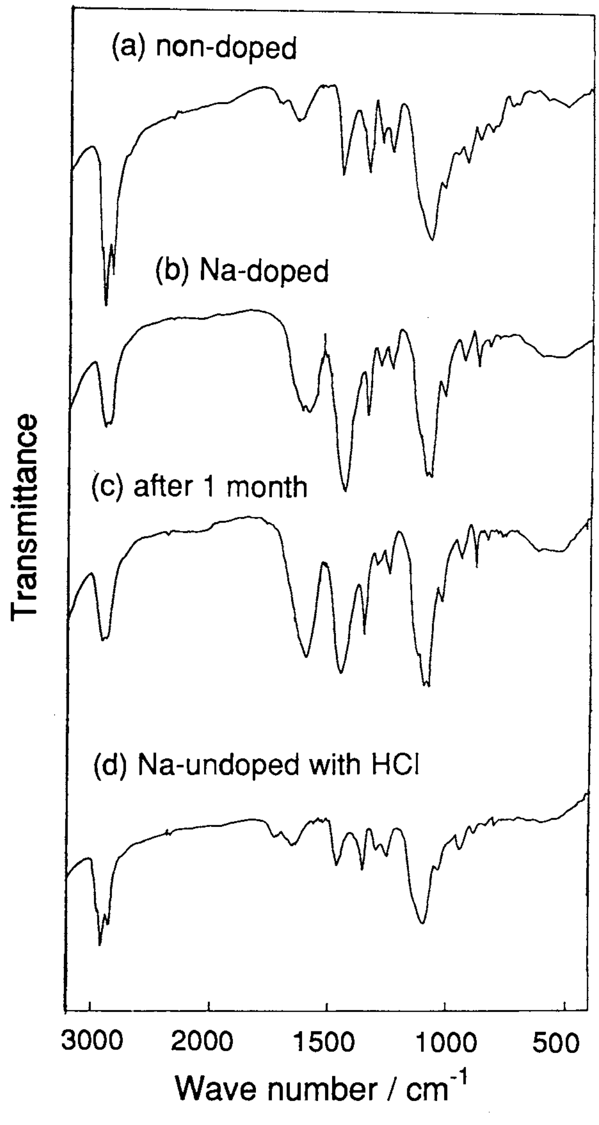


Fig. 1. IR spectra of (a) PCT5, (b) Na-doped PCT5 (just after the doping), (c) Na-doped PCT5 (after exposure to air for 1 month), and (d) undoped sample obtained by treatment of the Na-doped PCT5 with dil. HCl.

In accord with the high stability of the n-doped PCT5 against O_2 in air, electrochemically n-doped PCT5 at -2.6 V *vs.* Ag/Ag^+ is electrochemically stable and undoping occurrs at potential as high as 0 V *vs.* Ag/Ag^+ or 0.65 V *vs.* NHE, which is considerably higher than the n-undoping potential (-0.3 V *vs.* Ag/Ag^+) of PTh with the 3-OCH_3 group (Eq. 1). The n-undoping potential of 0.65 V *vs.* NHE is even higher than the reducing potential of O_2 in the presence of H_2O (e.g., $O_2 + 2H_2O + 4e = 4OH^-$, $E^0 = 0.40$ V *vs.* NHE[6]), thus explaining the stability of the n-doped state against O_2 in air.

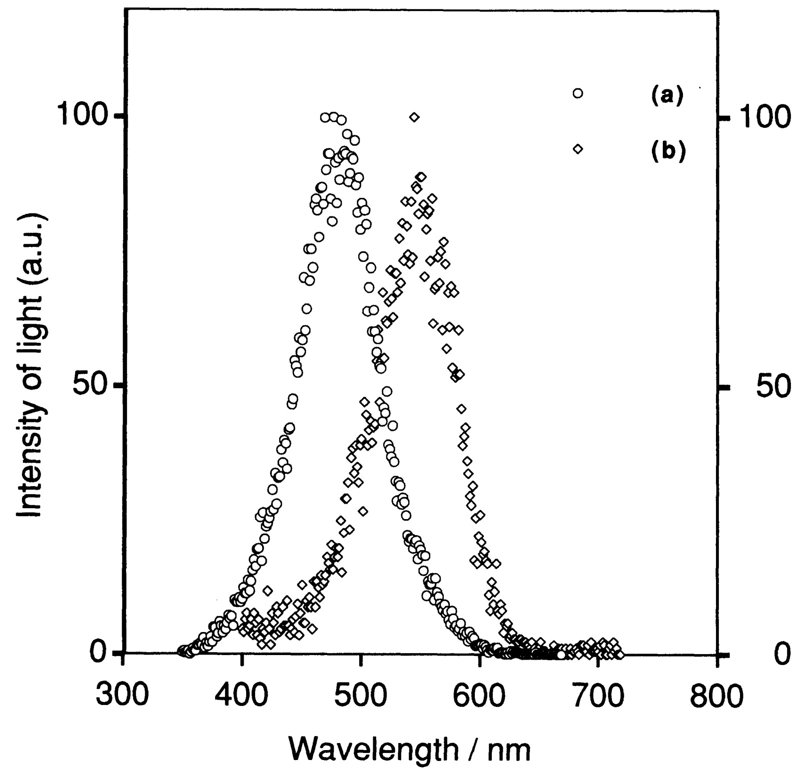
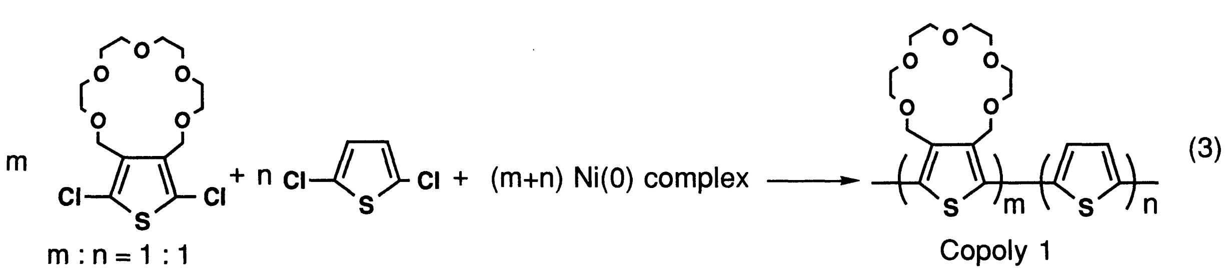


Fig. 2. Light emission profile for (a) ITO glass | PCT5 | Al and (b) ITO glass | Copoly 1 | Mg(Ag) diodes.

UV-vis. spectrum of PCT5 in $CHCl_3$ exhibits an absorption peak at 332 nm and an absorption edge at 440 nm. ITO (indium-tin-oxide) glass | PCT5 | Al electric junction, which is prepared as previously reported,[7] starts to emit light on application of about 6 V (direction of bias: ITO +; Al -), and Fig. 2 shows light emission profile from the electric junction (diode). The peak position of the light emission (470 nm) roughly agrees with the position of the absorption edge, suggesting the light emission takes place by transition of electron in the conduction band to the valence band. Logarithm of the intensity of the emitted light as well as that of electric current increase linearly with the applied voltage as usually observed with light emitting diodes. Copolymer prepared by the following equation



Ni(0) complex : 1 : 1 mixture of bis(1,5-cyclooctadiene)nickel and 2,2'-bipyridine

also has good solubility in organic solvents, and λ_{max} (395 nm) and absorption edge (528 nm) are shifted to longer wavelength compared with those of PCT5 presumably due to release of steric hindrance between the thiophene units having the big crown ethereal subunit by incorporation of the thiophene-2,5-diyl unit without the subunit. In accord with the shift of the absorption edge, the peak position of the emitted light from a diode using the copolymer, ITO glass | Copoly 1 | Mg(Ag), shifts to longer wavelength as shown by curve (b) in Fig. 2.

Because of the good stability of the n-doped state and the usability in the electric junction, PCT5 may have find some application.

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References

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2) Y. Miyazaki, T. Kanbara, K. Osakada, and T. Yamamoto, *Polym. Prepr. Jpn.*, **42**, 724 (1993).

3) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. -H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992).

4) The sample was placed in a desiccator, however, complete removal of moisture by evacuating air and replacement by dry air was not carried out.

5) 57% increase in resistivity corresponding to 36% decrease in conductivity was observed after 1 month for a specimen tested.

6) "Kagaku-benran, Kaitei 4th Edt., Kiso-hen," Maruzen, Tokyo (1993), p. II-467.

7) T. Yamamoto, H. Wakayama, T. Fukuda, and T. Kanbara, *J. Phys. Chem.*, **96**, 8677 (1992); T. Kanbara and T. Yamamoto, *Chem. Lett.*, **1993**, 1459. In the present case, PCT5 was spin-coated on the ITO glass.

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