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Photon-Mode Switching of Electrical Conductivity in a Photochromic Conducting Polymer

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Considerable interest has been focused on conducting polymers having extended π -conjugated electron systems on their main chain. Various physical, electrical and chemical properties of conducting polymers depend markedly on effective length of π -conjugated electron systems of alternative single and double bonds. Extended π -electron system with higher co-planarity can be an origin of relatively small band gap energy and high charge mobility and of relatively large electrical conductivity. Linear and non-linear optical polarizability of the conducting polymers are enhanced with the extended π -conjugated electron system. Dynamic control of effective conjugation length of conducting polymers has been achieved by thermal and chemical methods. For example, band gap energy and various properties of poly(3-alkylthiophene) have been modulated by the thermal treatment. However, to the best knowledge of the author, photon-mode switching of the π -conjugation length in conducting polymers and of electrical conductivity in dark state has never been achieved. Photochromic diarylethene has been also studied extensively for their unique properties such as thermally inactive and photochemically reversible ring-closure and ring opening photoisomerization reactivity. One of the most significant features of the diarylethene is reactivity in solid state such as polymer dispersed system, low molecular weight amorphous state and single crystalline state. Since the alternative π -conjugation system extends over the two thiophene rings in the diarylethene of the closed-ring isomer but not in the open-ring isomer, as shown in Figure 1, diarylethene unit can be a promising candidate for the photon-mode switching unit for the conducting polymers. Here, novel photon-mode switching effects of novel photochromic conducting polymer which exhibits reversible photochromic reactions of diarylethenes incorporated into the conjugated main chain are presented.

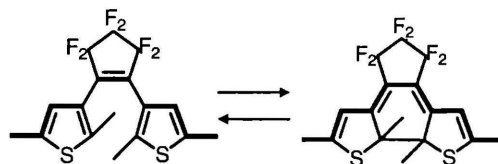


Figure 1 Photochromic reactions of diarylethene

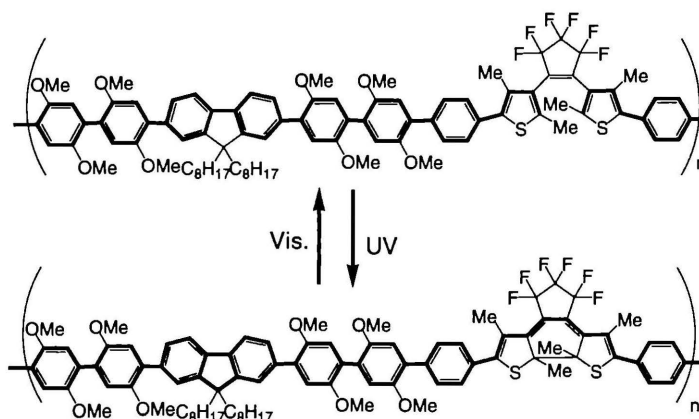


Figure 2 Molecular structure and photochromic reaction of polymer 1

Polymer 1 whose molecular structure is shown in Figure 2 was synthesized by Suzuki cross-coupling reaction of biphenyl diarylethene units and niphenyl fluorene units catalyzed by a Pd complex. The resulting yellowish polymer was soluble in conventional solvents and showed reversible photochromic reactions in both solution and film states under irradiation with UV light. The colored state was bleached with visible light and the coloration-bleaching cycles were performed for many times even in the solid films which were prepared by casting the chloroform solution. The photochromic reaction scheme illustrated in Figure 2 was confirmed by NMR spectral change before and after the UV light irradiation. Change in the integrated intensity of the NMR-CH₃ signals suggested that about 70% of diarylethene sites turned to the ring-closed form under continuous irradiation of UV light in solution phase.

Electrical conductivity was measured by conventional two probe method with ITO and Au electrodes. The colored film which was prepared by casting colored solution with about 70 % of conversion showed characteristic temperature dependence of the conductivity. After the measurement of the conductivity the film was bleached and conductivity was measured again. The conductivity after the photo-bleaching was markedly lower than the original colored state and showed much significant activation behavior. Although the origin of this conductivity switching effect is not clear at this stage, the present result is first demonstration of photochromic switching of conductivity of conjugated polymer system.