Delocalization of Positive and Negative Charge Carriers on Oligo- and Poly-fluorenes Studied by Low-Temperature Matrix Isolation Technique

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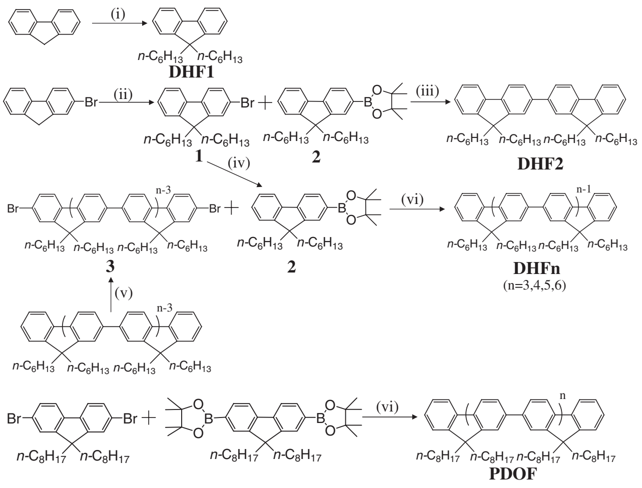
Oligofluorenes with well-defined chain length ($n = 1$–5) have been synthesized by step-by-step Suzuki coupling reaction as the basis sets of conjugated segments in polyfluorenes. Cation and anion radicals of oligofluorenes ($n > 2$) showed intense and clear three infrared absorptions attributed to transitions between SOMO state delocalized over fluorene moieties and valence (HOMOs) or conduction states (LUMOs) in the backbone. The transition energies of the IR band decreased linearly from 1.2 to 0.55 eV in the range of unit number while 1-D exciton transition energies showed apparent saturation at $n > 5$. This implied that delocalization degree of excess electrons or holes along fluorene chains would saturate at larger number of units than that of neutral excitons.

Conjugated polymers and oligomers have attracted great interest in recent years because of their potentials as organic light-emitting diodes (OLEDs), field-effect transistors, etc.[1] Oligofluoenes are more than the analogs of conjugated segments in the polyfluorene system providing the relationship between physical properties and structures, because the oligomers themselves have unique electronic and photonic properties arisen from their discrete structures.[2] Excitonic states on the fluorene derivatives have been intensively discussed in view of their feasibility to "pure" blue OLEDs, and demonstrated by device works.[3] One of the other key features of fluorene derivatives is their charge-transport properties to promote them as organic electronic materials.[4] Anion and cation radicals bearing one excess electron or hole corresponds precisely to the molecules conducting charge carriers, and the spectroscopy of the transient species gives direct evidences of the stabilization/delocalization mechanisms of charge carriers in the conjugated molecular orbitals.[5] Recent theoretical studies have suggested an important role of electron–phonon interaction (polaron/bipolaron) in the relaxation process of charge carriers on fluorene chains, and the models have been also supported experimentally by photomodulation,[6] absorption-detected magnetic resonance,[7] etc. In the present paper, anion and cation radicals of the oligo- and polyfluorenes are isolated in the low-temperature matrices without any counter ions by radiation chemical technique, and their transient absorption spectra are discussed in terms of the strength of polaron coupling interaction and/or the degree of charge-carrier delocalization.

Oligofluorenes (DHF*n*; *n*, number of fluorene units) and polyfluorene (PF)[8] were synthesized by step-by-step Suzuki cross-coupling reactions[9] as shown in the Scheme 1. All reactions were carried out under nitrogen atmosphere. All the compounds were dissolved in *n*-butyl chloride (BuCl) or methyltetrahydrofuran (MTHF) at (5–10) × 10^{-3} mol dm^{-3} conc. The solutions were put into suprasil quartz cells, and bubbled with dry Ar for 2 min. The γ-ray irradiation was carried out at 77 K, 4.0 kGy,[10,11] and UV–vis NIR spectroscopy was performed at wavelength: 250–2500 nm, temperature: 80–300 K.



Scheme 1. Reagents and conditions: (i) aq NaOH, [$C_6H_5N(CH_3)_3$] Cl, 1-bromohexane, DMSO, 60 °C, 1 day; (ii) aq NaOH, [$C_6H_5N(CH_3)_3$] Cl, 1-bromohexane, DMSO, RT, 5 h; (iii) Pd ($(PPh_3)_4$, K_2CO_3 aq, toluene, 80 °C, 20 h; (iv) bis(pinacolato)diboron, KCH_3CO_2, $PdCl_2$, 1,1′-bis(diphenylphosphino)ferrocene, DMF, 80 °C, 5 h; (v) Br, I, $NaHSO_3$, CH_2Cl_2, RT, 20 h; (vi) Pd($PPh_3)_4$, K_2CO_3 aq, toluene, 80 °C, 20 h.

Transition energies of UV–vis absorption (E_A) and fluorescence maxima (E_F) of the series of DHFs and PF are summarized in Table 1 with the band-edge energies (E_B) of the compounds determined by tracing the low-energy absorption profiles. The energies (E_A, E_F, and E_B) are obtained from the spectra of oligo- and polyfluorenes in steady-state condition. The π–π^* excitation gives neutral 1-D singlet exciton state, and the transition energies depends strongly on the chain length. The value of E_A observed as 3.5 eV for PF is almost identical to the value of DHF3–4, which suggests that the mean conjugation length in PF in MTHF solution at RT distributes predominantly at the range of 3–4 units. The E_B of PF (2.8 eV) is fairly even in the comparison with E_B of DHF5, because of the presence of highly developed conjugated segment in the backbone of PF. The energy shift of E_B with increasing chain length is well interpreted by the following model by Davydov,[13]

Table 1. Energies of UV–vis. absorption maxima (E_A), band edge (E_B), and fluorescence maxima (E_F) of the compounds[a]

Energy/eV	DHF1	DHF2	DHF3	DHF4	DHF5	PDOF
E_A	4.08	3.76	3.53	3.47	3.36	3.51
E_B	4.03	3.41	3.18	3.15	3.07	2.79
E_F	4.05	3.44	3.18	3.18	3.04	2.83

[a] The optical properties for the solutions of DHF1–5 in *n*-hexane and PDOF in THF at RT.

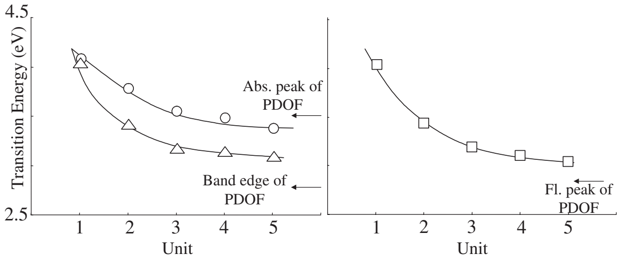


Figure 1. Absorption maximum, band edge, and fluorescence maximum energies of DHF 1–5 as a function of number of units contributing to the backbone conjugation. Circles, triangles, and squares are the energies of absorption maxima (E_A), band edge (E_B), and fluorescence maxima (E_F), respectively.

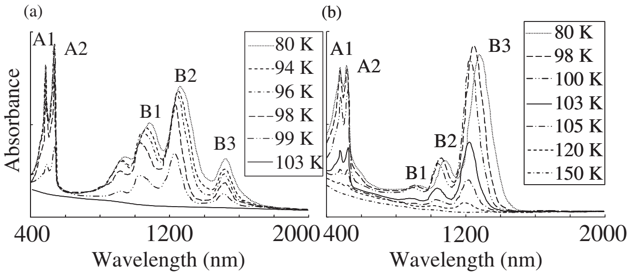


Figure 2. Absorption spectra of radical anions (a) and cations (b) of DHF2. The spectra were recorded at 80–150 K in MTHF at 10×10^{-3} mol dm^{-3} conc. (a) and BuCl at 5×10^{-3} mol dm^{-3} conc. (b) after γ-ray irradiation at 4.0 kGy.

$$E_B = E_{B1} - 2|M| \cos \frac{\pi}{n+1} \tag{1}$$

where E_{B1} is the value of E_B observed for DHF1, M is the interaction matrix, and n is the number of units in a chain, respectively. The dependence of the E_A, E_F, and E_B on the chain length is shown in Figure 1. The E_B dependence obeys approximately the Eq 1, and the extrapolation of the relationship to $E_B = 2.8$ eV gives the number of units as 9–10, contributing to the most extended conjugation in PF. This is compatible with the previous studies on the exciton delocalization in polyfluorenes.

Figure 2 shows the absorption spectra of anion and cation radicals of DHF2 observed at 80–150 K. Both spectra indicate 2 distinct peaks (A1 and A2) in vis (<600 nm) and 3 peaks (B1, B2, and B3) in IR region with shoulder peaks. The yield of negative or positive charges is calculated based on the dose of γ rays as less than 10^{-4} mol dm^{-3} at 80 K,[14] thus the formation of bipolaron can be neglected in the present case. The A1 and A2 bands are identical to the spectra of DHF1, and show no shift with an increase in the temperature. In contrast to the A band, the B bands are not observed for DHF1, and indicate considerable blue-shift with increasing temperature around 95 K (anion, MTHF) or 100 K (cation, BuCl). The A1 and A2 bands are ascribed to the local excitation bands of a monomer unit in a chain. Single charged polaron model gives good interpretation to the B bands: the transition from polaron state (SOMO) to LUMOs for anions, and from HOMOs to polaron state for cations, respectively.[15] Relatively high oscillator strength of B2 band in anions and B3 in cations is also supported by the highly degenerate LUMO + 1 (DHF$^{\bullet-}$) and HOMO (DHF$^{\bullet+}$), which are contributing predominantly to the optical transitions based on the optimized structures by HF/6-31G.[5]

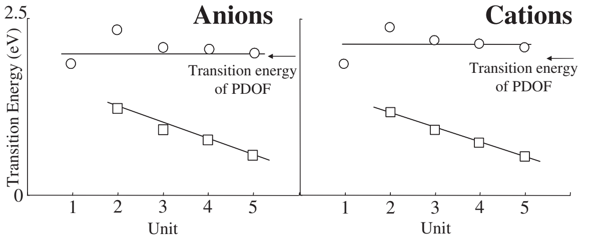


Figure 3. Dependence of transition energies of radical anions (in MTHF) and cations (in BuCl) on the number of units. Circles and squares are the energies of the lowest visible transitions (A1) and the highest infrared transition (B1) at 100 K, respectively.

The transition energy of B1 band is also in good agreement with the negative or positive polaron state observed by photomoduation spectroscopy technique.

The energy of the A2 and B2 bands at 100 K, where the blue-shift with increasing temperature is no longer observed, is plotted as a function of number of unit in Figure 3. The energy of the B1 band shows continuous red-shift with an increasing in the chain length. The red-shift is apparently different from the shift observed for E_A or E_B which shows clear saturation behavior even in the range of unit number. Especially the B1 band of PF$^{\bullet-}$ or PF$^{\bullet+}$ shifts toward longer wavelength region beyond the current observation range. This implies the presence of highly delocalized polaron state on the polymer backbone, and we conclude that the width of the polarons on a fluorene chain becomes longer than that of charge neutral exciton at RT.

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