Charge Delocalization over Stacked π-Electron Systems

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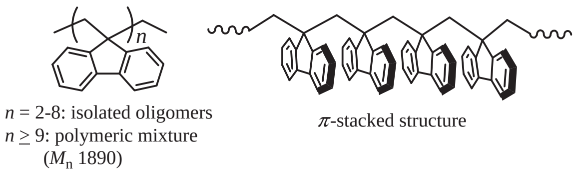
Cation radicals of oligomers and polymers of dibenzofulvene having a π-stacked conformation showed broad absorption bands based on charge resonance in near IR region, which red-shifted with increasing degree of polymerization, indicating that charge delocalization takes place through multiple, stacked fluorene moieties.

Polymers and oligomers that may transport injected charges are gathering attention as potential molecular wire.[1] In this regard, various main-chain conjugating polymers have been designed. Apart from such long-range through-bond conjugating molecules, charge transport through stacked π-electronic systems has been proposed as represented by the discussion on conduction behavior of DNAs.[2] We recently reported the synthesis and properties of poly(dibenzofulvene) (poly(DBF)) having a stable π-stacked structure with the main-chain C–C bondings being all-trans and the side-chain fluorene chromophores being tightly stacked on top of each other.[3,4] Based on the findings that this polymer shows a high hole mobility in a bulk film form[5] and a reduced oxidation potential in electrochemical analysis,[4] it has been proposed that the stacked π-electron systems of poly(DBF) may be an effective molecular wire. However, no direct information has been obtained on whether poly(DBF) delocalizes and transports charges.

Here, we report the chemical oxidation of DBF oligomers having two to eight monomeric units isolated by size-exclusion chromatography (SEC) and a polymeric mixture ($n \geq 9$, M_n 1890) and the observation of charge resonance (CR)[6] in multiple, stacked fluorene groups by near infra-red (NIR) absorption[7] spectroscopy. CR is directly connected to charge delocalization. Although there are several clear examples of CR band detection involving two aromatic molecules,[8–14] no systematic study has been reported on CR in regularly stacked, multiple aromtic groups in a molecule.

The oligomers and the polymeric mixture having different degrees of polymerization (n in Scheme 1, left) were obtained by SEC separation from the anionic polymerization products of DBF prepared using MeLi as an initiator and EtI as a terminating reagent in tetrahydrofuran at −78 °C.[4] The oligomers and the polymer were dissolved in dry CH_2Cl_2, and $SbCl_5$ in CH_2Cl_2 was added to the solution.[15] The mixed solution showed a blue-green color, indicating the generation of radical cation.



Scheme 1. Chemical structures of DBF oligomers and polymers and illustration of π-stacked conformation.

Figure 1 indicates the NIR absorption spectra of the oxidized oligo- and poly(DBF) samples and that of oxidized fluorene as a model of monomeric unit. In the spectrum of oxidized fluorene, a clear band was observed at 635 nm due to cation radical.[9] The spectra of the oxidized π-stacked DBF oligomers and polymer indicated broad absorption bands due to CR in the near IR region in addition to the peak at 660–680 nm due to cation radical. Using the polymer sample ($n \geq 9$, mixture), it was confirmed that the peak position of the near-IR band was not significantly affected by the sample concentration ([DBF unit] = 1.5×10^{-4} M, 5.9×10^{-5} M; see Supporting Information[16]), indicating that this band is ascribed to intramolecular CR interaction and not to intermolecular effects. Also, because the peak intensities of the cation radical bands of the oligomers and polymer are similar to that of fluorene, the presence of a diradical–dication species would be neglected.

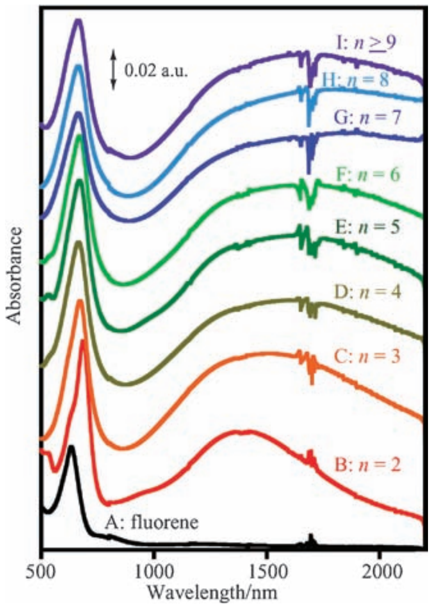


Figure 1. NIR absorption spectra of fluorene (A), DBF oligomers of $n = 2$–8 (B)–(H), and a polymeric mixture ($n \geq 9$, M_n 1890) (I) treated with $SbCl_5$ in CH_2Cl_2 at room temperature. Solvent spectra were subtracted. Absorbance was normalized to a constant concentration of oligomer at [oligomer] = 1.0×10^{-5} M. Measurement conditions: [DBF unit or fluorene] = 0.59–1.6×10^{-4} M; [$SbCl_5$] = 0.66–1.3×10^{-3} M.

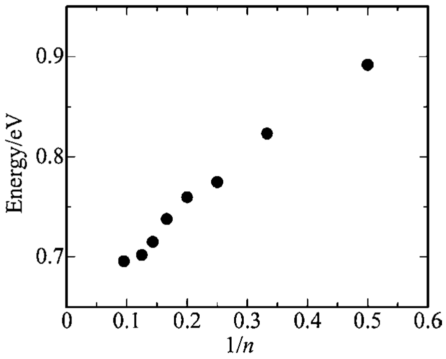


Figure 2. CR band peak-top energy plotted against oligomer chain length ($1/n$). The peak-top positions of the CR band for $n = 5$ and 6 were estimated using the first derivatives of the spectra[16] and those for the other species were directly determined from the spectra shown in Figure 1.

While the peak position of cation radical was not significantly affected by the oligomer size, the CR band position clearly red-shifted as the number of stacked aromatic groups increased in a molecule. As shown in Figure 2, the CR band energy decreased as the chain length increased. These results suggest that the charge is delocalized over multiple, stacked fluorene moieties of the DBF oligomers and polymers. The effect of chain length on CR band wavelength has also been reported for *N*-vinylcarbazole oligomers and polymers.[17] However, because poly(*N*-vinylcarbazole) has a flexible conformation, the effect of chain length on CR band wavelength cannot be directly connected to the number of successive monomeric units (chromophores) through which CR takes place.

For comparison, an atactic poly(2-vinylfluorene) (M_n 9560, M_w/M_n 2.59) having a flexible conformation prepared by radical polymerization using AIBN in benzene at 60 °C was also treated with $SbCl_5$. This sample indicated the cationic radical band at 650 nm and the CR band at 1330 nm.[16] The CR band was at a significantly shorter wavelength position compared with that of DBF dimer ($n = 2$). CR in poly(2-vinylfluorene) possibly takes place over two chromophores in proximity. Probably, the two chromophores are not in a stable stacked conformation. The CR bands in the longer wavelength range may be a characteristic of tightly stacked chromophores. The stable π-stacked conformation with the almost all-trans conformation of the main chain of the oligo- and poly(DBF) appears to be important in achieving a long-range charge delocalization as observed in this study.

CR was also studied by ESR spectroscopy.[16] Fluorene, the oligo(DBF)s consisting of two and six monomeric units ($n = 2$ and 6), and the polymer ($n \geq 9$, M_n 1890) oxidized with $SbCl_5$ indicated clear ESR signals. While g value (2.002) for the signals did not depend on chain length, band width clearly did: 0.648 mT (fluorene), 0.657 mT ($n = 2$), 0.602 mT ($n = 6$), and 0.601 mT ($n \geq 9$, M_n 1890). Although band width was sensitive to sample concentration and tended to be broader at lower concentrations, this relation between chain length and bandwidth tendency was also observed at different sample concentrations. These results mean that spin–spin relaxation is slower in a longer π-stacked sequence. Although the mechanism how spin–spin relaxation is retarded by CR is not clear at this point, a shorter relaxation time may be characteristic for charge delocalization through a longer π-stacked sequence.

In summary, using the oligo- and poly(DBF) samples having a stable π-stacked conformation, we demonstrated that such a structure effectively facilitates CR, and the charge delocalizes in multiple, stacked chromophores in a molecule. This strongly suggests that π-stacked poly(DBF) and its derivatives may transport charges under proper conditions as a molecular wire. Further study is under way to reveal more details of CR in the π-stacked poly(DBF) and its derivatives including the dynamic profiles.

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