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Long-Lived Charge-Separated Configuration of a Push−Pull Archetype of Disperse Red 1 End-Capped Poly[9,9-Bis(4-diphenylaminophenyl)fluorene]

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Studies of donor−acceptor systems capable of undergoing photoinduced electron transfer to mimic the primary events of the photosynthetic reaction center and also to develop molecular electronic devices are of current interest. For the construction of artificial molecular systems where both long-distance charge transport and formation of long-lived charge-separated (CS) states are required, there is increasing interest in utilizing conjugated polymers because of the sequential charge shift along the polymer chain.[1−4] The stabilization of the photoexcited electron−hole pair of the polymers can be achieved by blending the polymer with an acceptor molecule.

Along this line, we prepared bis(Disperse Red 1) end-capped poly[9,9-bis(4-diphenylaminophenyl)-2,7-fluorene] [abbreviated as $(DPAF)_n-(DR1)_2$] as a promising material for generating a long-lived CS state (Figure 1).[5] The $(DPAF)_n$ polymer was chosen because of its excellent hole injection, high mobility, and low ionization potential.[6] The triphenylamine (TPA) groups were expected to act as antioxidants for the polyfluorenes and inhibit their oxidation. By functionalizing $(DPAF)_n$ at both ends of the polymer chain with two units of electron-accepting, cyanoacetylated Disperse Red 1 (DR1), we successively obtained $(DPAF)_n-(DR1)_2$ polymer (Scheme S1 in the Supporting Information). The employed DR1 is useful in many optical-data-storage and optical-switching applications.[7] Quite recently, it was revealed that $(DPAF)_n-(DR1)_2$ can act as an electroactive component in memory devices.[5]

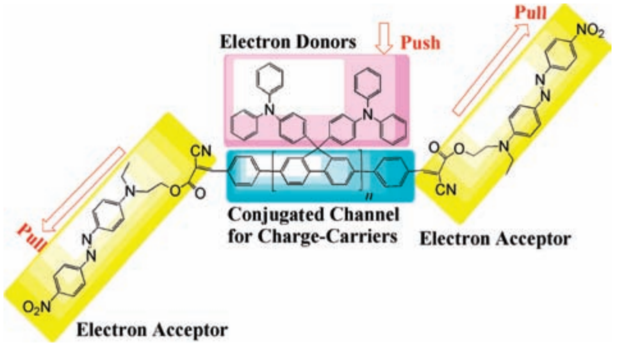

Figure 1. Molecular structure of $(DPAF)_n-(DR1)_2$.

An interesting question is whether the hole migration of the charged species along the polymer chain of $(DPAF)_n-(DR1)_2$ can result in the formation of the desired long-lived CS state. In this context, we herein report on the photoinduced intramolecular processes in $(DPAF)_n-(DR1)_2$, which we studied using time-resolved emission and absorption techniques. The photophysical and photochemical behaviors of $(DPAF)_n-(DR1)_2$ were first investigated using thermogravimetric analysis measurements, which showed that $(DPAF)_n-(DR1)_2$ exhibits high thermal stability up to 420 °C in nitrogen (Figure S1). As is well-known, high thermal stability is a critical factor in increasing the lifetimes of the solar energy harvesting system.[8] To gain insights into the electronic structure and examine the possibility of hole migration along the polymer chain, computational studies of $(DPAF)_4-(DR1)_2$ were performed using density functional theory at the B3LYP/6-31G level (Figure 2). The majority of the electron distribution of the HOMO was found to be located over the two TPA entities, while the electron distribution of the HOMO−1 and HOMO−2 were found to be over the TPA entities of the neighboring DPAF units. The orbital energies of the HOMO, HOMO−1 and HOMO−2 were found to be almost equal. On the other hand, the electron distributions of the LUMOs were found to be located mutually over the two DR1 entities. The calculated HOMO−LUMO gap was found to be 1.80 eV. On the basis of the MO calculations, one can say that the fluorene backbone acts as a conjugated channel for the charge carriers, the lateral TPA entities serve as the electron donors, and the DR1 terminals function as electron acceptors.

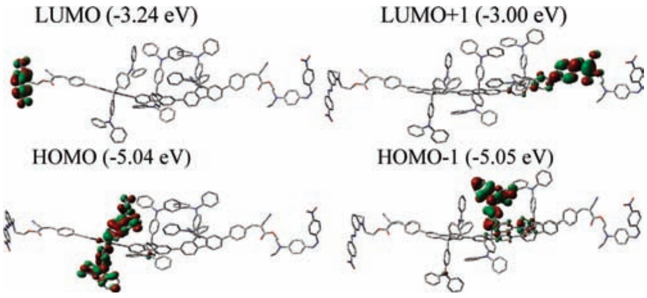

Figure 2. Calculated frontier HOMOs and LUMOs of $(DPAF)_4-(DR1)_2$.

The absorption spectra of $(DPAF)_n-(DR1)_2$ in benzonitrile (PhCN) exhibited peak maxima at 389 and 300 nm, corresponding to $(DPAF)_n$. The absorption band due to the $\pi-\pi^*$ transition in DR1 appeared at 453 nm in PhCN, which is 27 nm red-shifted relative to that in toluene (Figure S3). The emission bands of $^1(DPAF)_n^*-(DR1)_2$ in PhCN are found to be 417 and 440 nm, from which the energy of the singlet excited state was estimated as 2.90 eV (Figure S4). A significant fluorescence quenching of $^1(DPAF)_n^*$ was observed in PhCN (τ_f = 38 ps) compared with that in toluene (τ_f = 429 ps), reflecting the intramolecular deactivation of $^1(DPAF)_n^*$ by the attached DR1 entities. The rate contants (k_{CS}) and quantum yields (Φ_{CS}) of the charge separation were evaluated as 3.0×10^9 s^{-1} and 0.83, respectively, in toluene and 4.0×10^{10} s^{-1} and 0.98, respectively, in PhCN. The charge-separation process was supported from the viewpoint of the thermodynamics of the electron-transfer process. The electrochemical measurements on $(DPAF)_n-(DR1)_2$ (Figure S5) show the corresponding reduction potential (E_{red}) of the DR1 entities at −1.35 V vs Ag/AgNO$_3$. The oxidation potentials (E_{ox}) were determined to be 0.40 and 0.62 V

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vs Ag/AgNO$_3$. The first E_{ox} is cathodically shifted more than 270 mV lower than that of TPA, suggesting the greater hole injection in $(DPAF)_n$ than in TPA. The driving forces of the charge-recombination and charge-separation processes in PhCN were calculated as 1.75 and 1.15 eV, respectively. The negative ΔG_{CS} value suggests an exothermic charge-separation process via $^1(DPAF)_n^*$.

Experimental proof of the electron-transfer process of $(DPAF)_n-(DR1)_2$was obtained from nanosecond transient measurements. The transient spectra of the $(DPAF)_n$ reference in deaerated PhCN exhibited absorption bands in the visible region, with a maximum at 700 nm corresponding to the triplet state of $(DPAF)_n$ (Figure S6). By turning to $(DPAF)_n-(DR1)_2$ in deaerated PhCN (Figure 3a) and toluene (Figure S7), we were able to record a new broad absorption in the visible and NIR regions centered at 1370 nm, corresponding to the formation of the radical cation of $(DPAF)_n$, that overlaps the $^3(DPAF)_n^*$ band in the visible region. Since the absorption bands of $(DPAF)_n^{\bullet+}$ are different than that of the characteristic TPA monomer radical cation[9] and the MO calculations showed the delocalization of the HOMO over the two TPA entities, we can safely assign the NIR absorption bands to the TPA dimer radical cation.[10,11] Such assignment is supported by (i) the electrochemical oxidation of $(DPAF)_n$ at an applied potential of 1.0 V vs SCE (Figure S8), (ii) the addition of the one-electron oxidant $[Ru(bpy)_3]^{3+}$ to a solution of $(DPAF)_n$ (Figure S9), and (iii) the nanosecond transient spectra of mixed systems composed of $(DPAF)_n$ and C_{60} or C_{70} in PhCN (Figure S10). On the other hand, the electrochemical reduction of DR1 exhibited absorption at 370 nm and a weak absorption at 490 nm, which is similar to that of the reported radical anion of 4-methoxy-4′-nitroazobenzene.[12]

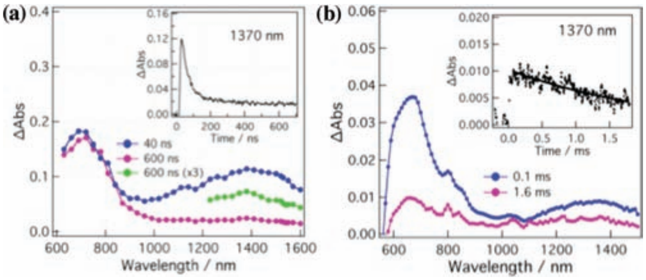
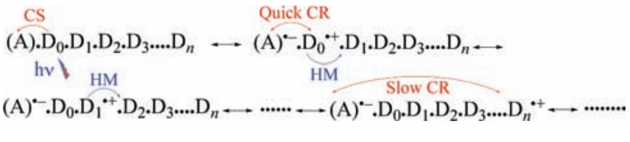


Figure 3. Nanosecond transient spectra obtained by 355 nm laser excitation of $(DPAF)_n-(DR1)_2$ in deaerated PhCN on (a) short and (b) long time scales. Insets: Time profiles at 1370 nm.

The decay profile of $(DPAF)_n^{\bullet+}$ at 1370 nm was employed as a probe to determine the rate constant of the charge recombination (k_{CR}). In toluene, the decay profile was fitted by a monoexponential decay. The k_{CR} value was evaluated as 6.3×10^7 s^{-1}, from which the lifetime of the CS state (τ_{CS}) was evaluated as 16 ns.

In PhCN, however, the profile of $(DPAF)_n^{\bullet+}$ showed a quick decay within 200 ns followed by a slow decay (Figure 3a, inset). The occurrence of the quick decay in PhCN can be rationalized as shown in Scheme 1. Upon photoexcitation, the charge-separation process from the excited DPAF to the attached DR1 moiety takes place efficiently. Charge recombination between $(DR1)_2^{\bullet-}$ and the nearest $(DPAF)_n^{\bullet+}$ may take place quickly, giving the initial quick decay with a rate constant of 2.0×10^7 s^{-1}, from which τ_{CS} was estimated as 48 ns. To shed light onto the origin of the slow decay of $(DPAF)_n^{\bullet+}$ in PhCN, we recorded the transient spectra on a longer time scale (Figure 3b). Interestingly, we could observe the absorption bands of $(DPAF)_n^{\bullet+}$ in the millisecond region. Such extremely slow decay of $(DPAF)_n^{\bullet+}$ (Figure 3b, inset) can be explained by the hole migration along the polymer chain (Scheme 1).[13] The long distance between the radical species attained by the hole migration results in the extremely slow charge recombination between $(DPAF)_n^{\bullet+}$ and $(DR1)_2^{\bullet-}$, with a rate constant of 4.5×10^2 s^{-1}. From the k_{CR} value, the lifetime of the CS state was calculated as 2.2 ms. In such a case, there may be multiexponential slow-decay components that depend on the distance between the radical species upon recombination. However, the slow movement of the polymer chain, which enables the electron and the hole to meet together, may determine the extremely long lifetime of the radical-ion pair. It is also interesting that the k_{CS}/k_{CR} ratio in PhCN is extremely high ($\approx 10^8$), suggesting the usefulness of the studied polymer as a light-harvesting system.

Scheme 1



In summary, the higher thermal stability (up to 420 °C), excellent hole-transporting ability, efficient charge-separation process, and long-lived CS state (2.2 ms) suggest the potential application of $(DPAF)_n-(DR1)_2$ in molecular-based electronic and optoelectronic devices.

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Supporting Information Available: Synthetic details, absorption and emission spectra, redox measurements, MO calculations, ESR spectrum, and nanosecond transient spectra of $(DPAF)_n-(DR1)_2$ and the $(DPAF)_n$ reference. This material is available free of charge via the Internet at http://pubs.acs.org.

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