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Self-Condensed Nanoparticles of Oligofluorenes with Water-Soluble Side Chains

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Conjugated polymers and oligomers have attracted great interest in recent years due to their potential applications as organic light emitting diodes (OLEDs), field effect transistors, and luminescence sensors.[1] Water-soluble polyfluorenes with amphiphilic side chains have also been the subject of much interest due to their ability to form complexes with dyes and biomacromolecules, including DNA, which results in dramatic changes in their optical properties.[2,3] The specific spectral shifts resulting from this form the basis of a sensitive probing technique for oligonucleotides. Self-assembly properties have also been demonstrated by polyfluorenes in several studies, with the resulting structures showing characteristic optical properties.[4−6] Excitonic states of fluorene derivatives have been intensively studied in view of their possible application in "pure" blue OLEDs, which has been demonstrated in various devices.[7] Their emission spectra have often been observed to contain weak "green" emissions in the solid state, whose origin is thought to be "keto-defects" in the fluorene units, as well as inter- and intramolecular exciton states.[4,6]

Oligofluorenes are more than simply analogues of conjugated segments in the polyfluorene backbone; the oligomers themselves possess unique electronic and photonic properties arising from their discrete structures.[8] Amphiphilic oligofluorenes are good candidates for investigation of intermolecular interactions between fluorene units because their molecular aggregation can be controlled by external polar−nonpolar solvent fields. In the present paper, we report the synthesis of an amphiphilic trifluorene (Am-F3) with *n*-hexyl and hydroxyethoxymethyl side chains, as well as a hydrophobic analogue, perhexyl trifluorene (DHF3). Their optical properties are discussed in terms of molecular configuration in various solvent systems.[9]

Am-F3 and DHF3 were synthesized by a Suzuki cross-coupling reaction, as shown in Scheme 1.[10] Melting point of DHF3 was determined at 370 K (ΔH = 54 J/g), and Am-F3 showed only isotropization temperature[11] at 399 K (ΔH_{iso} = 2.8 J/g). For investigation of molecular aggregates, a dilute solution of Am-F3 in THF at 5.0×10^{-4} mol dm^{-3} was poured into water, and a quartz substrate was dipped in the resulting solution. Atomic force microscopy (AFM SPI-4000, Seiko Instruments) was used for direct observation of nanoparticles transferred onto the substrate.

The UV−vis absorption spectra of Am-F3 and DHF3 in various solvent mixtures are shown in Figure 1. The transition energy of UV−vis absorption (E_A) for DHF3 was E_A = 3.50 eV in solvent mixtures of all polarities, but the spectra of Am-F3 showed a gradual red shift with increasing solvent polarity, with E_A decreasing from 3.62 to 3.49 eV. It has previously been suggested that a neutral 1-D singlet exciton state results from $\pi-\pi^*$ excitation in steady-state conditions;[8b,9b,11] this model suggests that the E_A value and the oscillator strength of the band correlate with the effective conjugation length along the oligofluorene backbone and the planarity of the fluorene units. The calculated dipole moment of Am-F3 (2.47 D) is 10 times larger than that of DHF3 (0.25 D), which is lower than the averaged dipole moments of all solvent systems used in the present study. This is the cause of the gradual red shift observed for Am-F3 by solvent−molecule dipole interaction. The oscillator strength of Am-F3 molecules, calculated by numerical integration in the range of 2−4 eV, increases with solvent polarity, reaching a value almost identical to that of DHF3 in THF−H_2O solution. This supports the contention that the total number of fluorene units contributing to conjugation is equivalent in DHF3 and Am-F3, with Am-F3 taking the planar form in the THF−H_2O mixture.

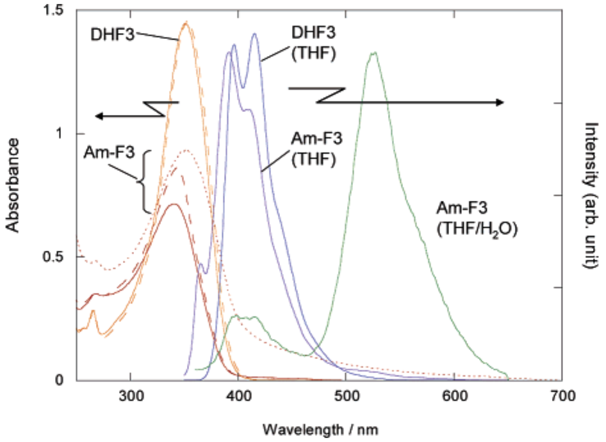

Figure 1. UV−vis absorption and fluorescence spectra of Am-F3 and DHF3. Absorption spectra were recorded for solutions with a concentration of 4.0×10^{-5} mol dm^{-3} in THF containing 20% MeOH (solid line), MeOH containing 20% THF (dashed line), and H_2O containing 8% THF (dotted line). Fluorescence spectra (blue and green lines) were recorded for solutions at a concentration of 8.5×10^{-5} mol dm^{-3} in THF or H_2O containing 8% THF.

The fluorescence spectra of Am-F3 and DHF3 are also shown in Figure 1. The fluorescence peaks of Am-F3 in THF appeared at 350−500 nm, with DHF3 showing a similar spectrum. In contrast, when Am-F3 in THF (or acetone) was added to a strongly polar solution, such as H_2O, the blue emission around 400 nm was dramatically quenched. In addition, the 400 nm band was shifted 7 nm toward the longer wavelengths, and another strong emission band appeared around 540 nm. The relative intensity of the blue and green emission bands showed no change in Am-F3 solutions varying in concentration from 5.0×10^{-7} to 1.0×10^{-4} mol dm^{-3}, with fairly clear green emissions observed even in the most dilute of these solutions. Emission quantum yield (ϕ) was determined as $\phi = 0.75$ for DHF3 in THF, 0.55 for Am-F3 in THF, and 0.3 for Am-F3 in THF−H_2O, respectively. This suggests that the effect of free intermolecular excimer formation via diffusion processes in the solution system is negligible; thus, the green emission was attributed to the excitation of steady-state molecular aggregates.[11−13] This is also supported by the low-energy optical transition (<3 eV) of the Am-F3 absorption spectrum in THF−H_2O, reflecting the

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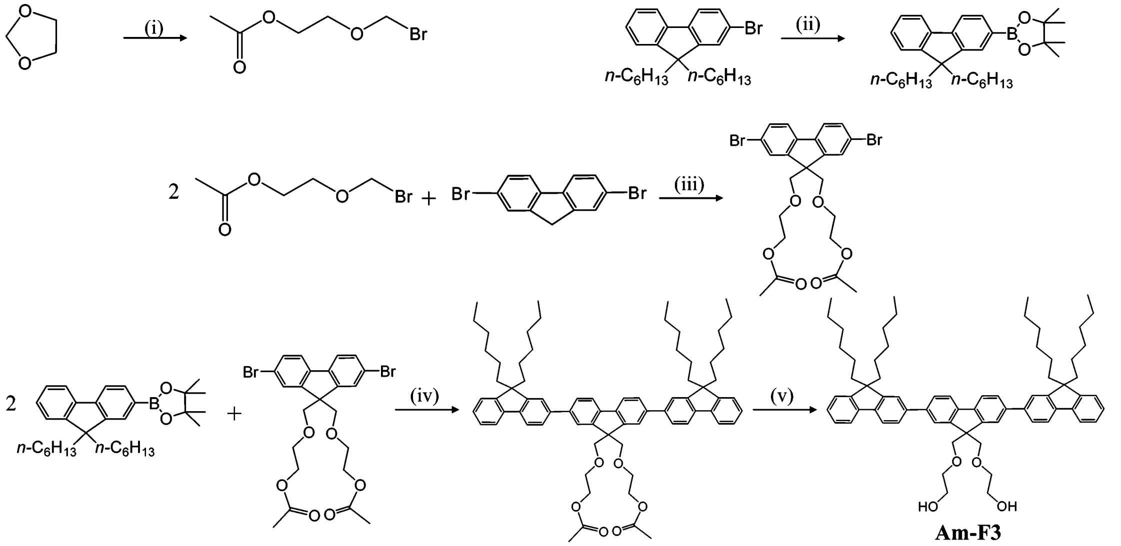
Scheme 1. Synthetic Process for Am-F3[a]



[a] Reagents and conditions: (i) acetyl bromide, 1,3-dioxolane, DMF, 80 °C, 5 h; (ii) 2-bis(pinacolatoborol-2-yl)-9,9′-dihexylfluorene, KCH_3CO_2, $PdCl_2$, 1,1′-bis(diphenylphosphino)ferrocene, DMF, 80 °C, 5 h; (iii) $[C_6H_5N(CH_3)_3]Cl$, aqueous NaOH, 1-bromomethoxyethyl acetate, DMSO, 60 °C, 27 h; (iv) $Pd(PPh_3)_4$, 2 M K_2CO_3 (aq), NaOH, toluene, 80 °C, 27 h; (v) NaOH, THF, 50 °C, 10 min.

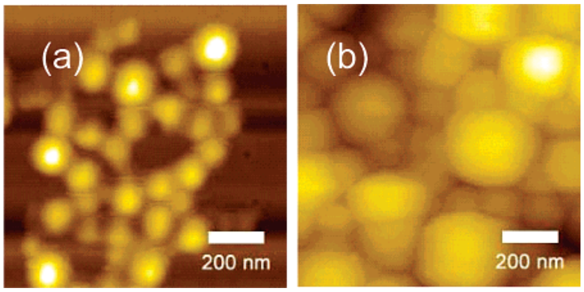


Figure 2. AFM micrographs of the nanoparticles transferred onto a quartz substrate from Am-F3 solutions: (a) MeOH with 20% THF at 1.1×10^{-5} mol dm^{-3} concentration, and (b) H_2O with 8% THF at 8.5×10^{-5} mol dm^{-3} concentration.

highly developed π-conjugation of the molecular aggregates.[14] Redissolution of the aggregates into THF resulted in recovery of the pure blue emission, which suggests a minor contribution to the green emission by keto-defects.[4,6,15]

Figure 2 shows AFM micrographs of molecular aggregates of Am-F3 after transfer from THF−H_2O solution onto a quartz substrate. The nanoparticles with radii of 20−100 nm were observed clearly on the substrate. The average radius could be controlled by changing the concentration of the solution and/or the solvent ratio, which suggests that self-condensation of the molecules occurs in the solvent mixture, with the resulting nanoparticles remaining suspended in solution. Largely identical fluorescence spectra with the peak at 545 nm were recorded for the film samples after the transfer process. Thus we conclude that the green emission of Am-F3 in THF−H_2O may be attributed to excimer emission via excitation of aggregated dimer structures in the nanoparticles. Although there have been reports of observation of green emissions from polyfluorene derivatives due to formation of complexes with DNA and dyes,[2,3] this is the only reported case of clear green emissions from "pure" fluorene derivatives. The present study also suggests the possibility of spectral tuning of emissions from oligofluorene aggregates.

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Supporting Information Available: Experimental procedure, complete ref 9, and spectral data for compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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