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Synthesis, Structure, and Photophysical and Electrochemical Properties of a π-Stacked Polymer

Tamaki Nakano*,†,‡ and Tohru Yade‡

Contribution from PRESTO, Japan Science and Technology Corporation (JST), and Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), Takayama-cho 8916-5, Ikoma, Nara 630-0101, Japan

Received August 8, 2003; E-mail: nakano@ms.aist-nara.ac.jp

Abstract: Dibenzofulvene (DBF) was polymerized using anionic initiators to afford a vinyl polymer. Oligo-(DBF)s having from two to eight side-chain fluorene moieties bearing different chain-terminal groups were isolated by preparative size-exclusion chromatography. The structures of the isolated oligomers were revealed by single-crystal X-ray and ¹H NMR analyses. Both in solution and in crystal, the in-chain fluorene moieties stacked on top of each other, while the terminal conformation varied depending on the terminal group. These conformational characteristics were supported by molecular mechanics and dynamics calculations. The oligomers and polymers indicated hypochromism and red shift in UV absorption spectra and exclusive excimer emission in fluorescence spectra. In addition, reduced oxidation potentials were observed for the oligomers in electrochemical analyses, which suggests charge delocalization over the π-stacked electron systems. The photophysical and electrochemical effects increased with the chain length of the oligomers and leveled off around the chain length of an oligomer consisting of five fluorene units.

Introduction

The conformation of macromolecules often has significant influence on the properties and functions of polymeric materials. Polymers having a specific conformation, such as a helix, have been synthesized, and their functions have been explored in relation to their structures.[1] A type of unique conformation may be characterized by regularly stacked π-electron systems. Stable and regulated π-stacked structures in polymers are known for DNA,[2] poly(phenyleneethylnylene)s,[3] oligomers consisting of alternating donor and acceptor monomeric units,[4] and oligomers having perylene moieties in the main chain.[5] In the DNA, paired bases are regularly stacked inside the helical strand. In the poly-(phenyleneethynylene)s, phenylene groups in the main chain closely overlap due to helical folding of the polymer chain. In oligomers consisting of aromatic donor and acceptor units, the chain folds into a pleated conformation due to a donor—acceptor.

Vinyl polymers with side-chain aromatic groups could also have π-stacked conformations when they have stereoregular main chains. However, most examples of stereoregular synthesis of a side-chain aromatic vinyl polymer involve polystyrene[6] whose conformational dynamics are too fast in solution to maintain a specific conformation. Hence, synthesizing a vinyl polymer that has a stable, regulated π-stacked conformation is a challenging goal. Although a partial π-stacked conformation has been proposed for poly(N-vinylcarbazole),[7] the conformation is expected to exist only in relatively short monomeric sequences because the stereoregularity of the polymer is rather low.

In search of novel, functional polymers with specific conformations, we recently found that dibenzofulvene (DBF) affords a polymer with side-chain fluorene chromophores regularly stacked on top of each other, and we communicated the preliminary results.[8] Despite a structure similar to 1,1-diphenyl-ethylene that does not homopolymerize,[9] DBF readily polymerizes with anionic, cationic, and radical initiators. Because the polymer does not have stereocenters, only conformational isomers are possible as its stereochemical variations. A regular and stable π-stacked structure was indicated for poly(DBF) on

† PRESTO, JST.

‡ NAIST.

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Scheme 1. Anionic Polymerization of Dibenzofulvene (DBF)
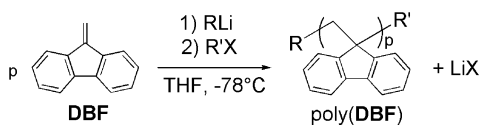
the basis of remarkable hypochromism in absorption spectra, exclusive excimer (dimer) emission in fluorescence spectra, and significant upfield shifts of aromatic proton signals in ^{1}H NMR spectra. The structure was supported by conformational calculations.

This Article describes the full details of the stereostructure of poly(DBF) prepared by anionic polymerization and its photophysical electrochemical properties. In this study, uniform oligomers of DBF with distinct chain lengths were isolated by size-exclusion chromatography (SEC), and the proposed π-stacked structure was unambiguously evidenced by single-crystal X-ray analyses of the uniform oligomers.[10] In addition, a π-stacked structure was also confirmed in solution by ^{1}H NMR analyses combined with theoretical chemical shift calculations. Further, the absorption and emission spectra and cyclic voltammograms were systematically measured for the uniform oligomers and polymers. Through these studies, the effect of the π-stacked structure on the photophysical and electrochemical properties was systematically investigated.

Stable π-stacked polymers may afford functional electronic materials because stacked π-electron systems can facilitate long-range charge transport, as reported for tetrathiafluvalenetetra-cyanoquinodimethane and tetramethyltetrasalenafluvalene crystals.[11] Such a charge transfer has been proposed also for DNA,[12a–d] although there is controversy as to whether it is real.[12e–h]

Synthesis and Isolation of Uniform Oligomers of Oligo(DBF)s

DBF was synthesized according to the literature with modifications.[13] Polymerization of DBF was initiated using an organolithium and was terminated using a protonating or an alkylating reagent (Scheme 1). The initiators were 9-fluorenyl-lithium (FlLi), *n*-BuLi, methyllithium (MeLi), and phenyllithium (PhLi), and the terminating reagents were methanol (MeOH), ethyl iodide (EtI), and benzyl bromide (PhCH$_2$Br). The conditions and results of the reactions with the expected polymer structures are summarized in Table 1.[14] In all cases, the DBF monomer was consumed in a high yield. In some cases, the

reaction products were partially insoluble in THF or chloroform. The THF-soluble and -insoluble parts indicated very similar IR signals, suggesting that the insoluble parts consist of higher-molecular-weight polymers whose chemical structures of repeating units are identical to those of the soluble parts. Higher-molecular-weight fractions may tend to become insoluble probably due to the crystallinity of the poly(DBF) chain.

The reactions afforded the products (oligomers and polymers) with five terminal-group combinations, **1**–**5**. The efficiency of introducing terminal groups was confirmed by a MALDI-mass spectrum. The observed mass numbers supported the expected polymer structures. The spectra for **1**, **2**, and **5** are shown in Figure 1 as examples. Although unintended protonation of the growing anion with protonic contamination could lead to a polymer having hydrogen at the termination end in entries 3, 5, and 6 aiming at structures **2**, **4**, and **5**, respectively, the corresponding spectra in Figure 1 showed no clear peaks based on oligomers having hydrogen at the termination end of the chain.

To obtain detailed information on the π-stacked conformation of the DBF polymer and its effect on photophysical and electrochemical properties, THF-soluble products were separated into oligomers that are uniform in terms of the number of fluorene units in a chain (**1**–**5** in Table 1; *n* = 2–8) and polymers (*n* ≥ 9, mixture) using a preparative-scale SEC apparatus. Chain lengths of the isolated oligomers were determined by MALDI-mass spectra. The purity of the separated oligomers **1** and **2**, which were used for the solution structure and property analyses, was checked by analytical scale SEC. The isolated oligomers contained a small amount of higher- and lower-molecular-weight fractions. The purity of oligomers **1** of *n* = 2–8 was in the range of 95–99%, and that of oligomers **2** of *n* = 2–8 was in the range of 92–99% (Supporting Information).

Crystal Structure Analyses

The oligomers isolated by SEC were subjected to crystallization for X-ray crystal structure analysis. Some of the oligomers led to single crystals suitable for X-ray analyses by recrystallization from a chloroform solution. Crystal structures were solved for **1** (*n* = 2 and 4), **2** (*n* = 2 and 6), **3** (*n* = 3), **4** (*n* = 4), and **5** (*n* = 2 and 5).[15] The crystal structures are shown in Figure 2, and the crystallographic data are summarized in Table 2. The single-crystal structures indicated two conformational characteristics: (1) the in-chain fluorene moieties of oligomers of *n* = 4–6 are in a π-stacked conformation with the corresponding main-chain carbon–carbon bonds having a slightly twisted trans–trans structure regardless of the terminal groups; and (2) the chain-terminal fluorene moieties are in a π-stacked conformation when the terminal group is ethyl or bulkier, while they are flipped when the terminal group is hydrogen. It is also noteworthy that the π-stacking is not in a perfectly face-to-face manner but the fluorene groups are slightly

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(15) The crystal structure of **4** (*n* = 4) has been presented: Nakano, T.; Yade, T.; Ishizawa, H.; Nakagawa, O.; Okamoto, Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43* (2), 609.

Table 1. Anionic Polymerization of Dibenzofulvene (DBF) in THF

entry	polymer structure[a]	DBF (mmol)	initiator (mmol)	terminator (mmol)	temp. (°C)	time (hr)	conv.[b] (%)	THF-soluble part	
								yield[c] (%)	Mn[d]
1	**1**	5.6	9-FlLi (1.1)	MeOH (4.0)	-78	24	>99	>99	860
2		4.6	9-FlLi (9.3)	MeOH (12.1)	0	1	>99	>99	350
3	**2**	10.0	MeLi (2.0)	CH_3CH_2I (25.0)	-78	48	84	98	760
4	**3**	11.2	*n*-BuLi (2.2)	MeOH (6.2)	-78	24	>99	81	790
5	**4**	2.8	*n*-BuLi (0.93)	$PhCH_2Br$ (8.4)	-78	24	>99	99	990[e]
6	**5**	10.0	PhLi (2.0)	$PhCH_2Br$ (16.8)	-78	48	84	63	950

[a] $n - 1$ and n denote of degree of polymerization for entries 1−2 and 3−6, respectively. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] THF-soluble part was a mixture of oligomers and unreacted monomer when the monomer conversion was not quantitative. The yield of this part was calculated excluding the weight of the unreacted monomer. [d] Determined by GPC using two OligoPore columns connected in series with oligo(DBF)s as the standard samples (eluent THF). [e] Determined by GPC using two TSKgel G1000H$_{HR}$ columns connected in series with oligo(DBF)s as the standard samples (eluent THF).

twisted; the twist takes place in one direction in a π-stacked structure consisting of three or more fluorene units leading to a helical structure. In addition, the stacked fluorene groups are not completely parallel to each other, which is probably due to steric repulsion. The twisted π-stacked structure is most clearly confirmed in **2** of $n = 6$, the longest molecule for which the crystal structure was solved. This oligomer has a π-stacked conformation throughout the chain and forms a long-pitched, single-handed helical structure where ca. nine monomeric units form one turn as a result of the twisted alignment of the fluorene groups. The conformationally enantiomeric right- and left-handed helices are paired in the solid state; that is, the crystal formed as a racemic crystal (see CIF files in Supporting Information). Induction of single-handed helicity is an intriguing subject and will be presented as a separate publication.

¹H NMR Spectra

¹H NMR spectra of the oligomers were measured to confirm the chemical structure and to obtain information on the solution conformation of oligomers **1** and **2** ($n = 2−8$) and polymers **1** ($Mn = 1700$, $n = 9.6$, mixture of $n \geq 9$) and **2** ($Mn = 1890$, $n = 10.4$, mixture of $n \geq 9$). Because poly(DBF) has no stereocenter in the main chain, the chemical shift information of a proton signal should only reflect the conformation of the oligomer in its vicinity.

The 1D spectra are shown in Figures 3 and 4, and the chemical shift values are summarized in Tables 3 and 4. The peak assignments were performed on the basis of H−H COSY

and NOESY spectra (Supporting Information).[16] The structures of **1** and **2** of $n = 8$ with the proton numbering system are shown in Chart 1 as generic specimens. The protons showing COSY correlation peaks are marked by blue arrows, and those showing NOESY correlations are marked by red arrows in Chart 1. The same proton−proton correlations were also observed for oligomers of $n = 2−7$.

As for oligomers **1**, the triplet peaks having an intensity of two protons were first assigned to the terminal methine protons, and the signals due to the methylene protons neighboring the methines were then found by the COSY experiment. In the case of oligomers **2**, the triplet peaks in the highest magnetic-field region were assigned to the terminal methyl protons, and the neighboring methylene signals were identified by the COSY experiment.

The peak assignments of the remaining main-chain methylene and aromatic protons were performed on the basis of the 1D spectral profiles and the NOESY spectra. In the 1D spectra, all oligomers indicated only one set of terminal peaks: triplet methine signals for **1** and ethyl signals consisting of a methyl triplet and methylene quartet for **2**. In addition, the number of observed peak sets for the methylene protons was only one-half the number of existing methylene groups for the oligomers of $n = 3$, 5, and 7 or [(number of existing methylenes) − 1]/2 + 1 for the oligomers of $n = 2$, 4, 6, and 8. This profile may

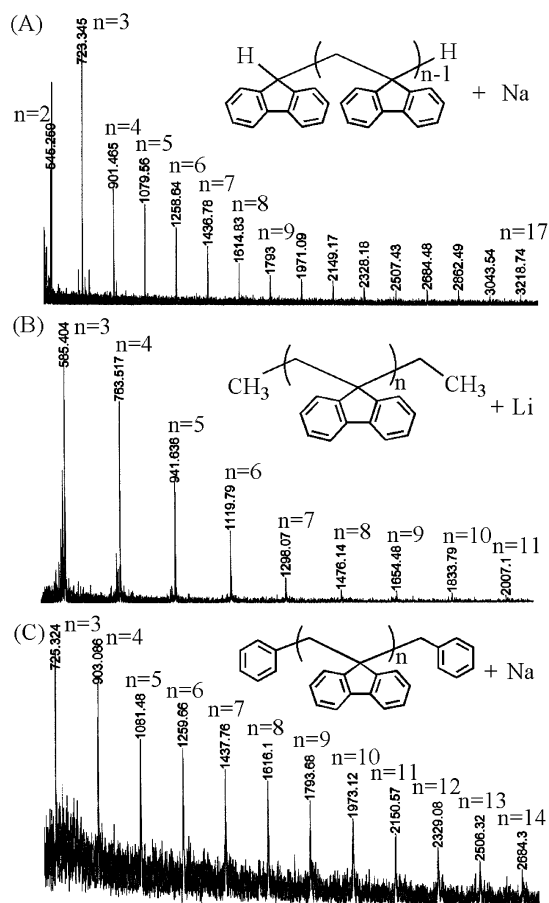(16) Sanders, J. K. M.; Hunter, B. *Modern NMR Spectroscopy*, 2nd ed.; Oxford University Press: New York, NY, 1993.

Figure 1. MALDI-TOF mass spectra of oligo(DBF)s **1** (Table 1, entry 1) (A), **2** (Table 1, entry 3) (B), and **5** (Table 1, entry 6) (C).

be explained in terms of a conformation symmetrical with respect to the central methylene (oligomers of $n = 2, 4, 6$, and 8) or the central fluorene group (oligomers of $n = 3, 5$, and 7), such as the crystal structures of **2** of $n = 6$ and **5** of $n = 5$ shown in Figure 2, if the conformation is stable in solution. A fast exchange between different conformations may also lead to a simple NMR profile. However, fast conformational dynamics in solution seem unreasonable because clear NOE correlations were observed that support a stable all-trans conformation as follows.

In the NOESY spectra of all oligomers analyzed here, all in-chain methylene protons indicated correlation peaks with one or two different methylene groups in addition to aromatic protons. This finding is best interpreted assuming an all-trans conformation as illustrated in Chart 1; only the neighboring groups in such a conformation will show correlation peaks in the NOESY spectra. Hence, the methylene protons were assigned as summarized in Tables 3 and 4 assuming an all-trans conformation, which is consistent with the regular numerical relations between the number of observed methylene signals and the exsiting methylene groups noted above.

The aromatic signals were assigned also using the 2D NMR information. The observed NOE signals were interpreted to correlate the protons at the 1- and 8-positions of the fluorene ring, denoted by H_{A-D1} in Chart 1, and the methylene groups in the vicinity. The position of each fluorene ring was assigned in this way. The peak assignments of the remaining aromatic protons were completed using the COSY information. NOE

correlations between protons of neighboring fluorene units in stacked conformation were also observed, although they are not shown in Chart 1 for clarity.

It is noteworthy that aromatic proton signals of all samples of **2** were within the range of 5.6−7.1 ppm. This is in stark contrast to the fact that poly(9,9-dimethyl-2-vinylfluorene)[17] which probably has a flexible conformation showed its aromatic protons signals in a much lower magnetic-field range (6−8 ppm). This supports the stable π-stacked conformation of **2** throughout the chain in solution.

The aromatic proton signals of **1** appeared in a wider chemical shift range as compared with those of **2**, suggesting that **1** may have a less regular π-stacked conformation. However, the samples of **1** of $n = 4$ and larger showed all aromatic signals, except for a doublet with a four-proton intensity at ca. 7.5 ppm, in the range of 5.6−7.2 ppm, similarly to all samples of **2**, indicating that most of **1** of $n = 4$ or larger has a regular π-stacked conformation similar to that of **2**. The exceptional four-proton intensity signals are due to the 4- and 5-positions of the terminal fluorene rings according to the peak assignments described above. This may indicate that the terminal fluorene rings of **1** are flipped as observed in the crystal structures of **1**.

The signals of **1** of $n = 2$ were similar to those of fluorene in the chemical shift range, implying that this oligomer does not have a π-stacked conformation. In the sample of **1** of $n = 3$, both flipped and stacked conformations may exist because the spectral profile in the aromatic region is just between those of the longer oligomer and the shorter one.

To obtain information on the stability of the conformation of the oligomers, temperature effects on the NMR spectra were examined for all oligomers in the range from −50 to +60 °C. Most peaks only monotonically shifted upfield or downfield with temperature, and the shift amount was within 0.2 ppm. The peak shift was reversible with temperature. These results suggest that the π-stacked conformation in solution proposed so far is stable and does not undergo a drastic conformational mutation in this temperature range.

It should be noted here that no clear NMR information indicating the helical twist in solution was obtained even at lower temperatures. The helical structure may be in an exchange between the right- and left-handed local twists that is faster than the NMR time scale under the experimental conditions of this study.

Chemical Shift Calculation

To rationally connect the NMR spectral information to the solution conformation of the oligomers, the chemical shifts of the main-chain methylene and terminal methine or ethyl protons were computationally estimated by density functional theory (DFT)[18] calculation for some optimized conformers of **1** of $n = 2$ and **2** of $n = 2$ and 4. The conformer structures optimized by the semiempirical PM5 method[19] are shown in Figure 5 with their heats of formation (H_f) (PM5) and theoretical chemical shifts obtained by the LORG method[20] using B88[21] exchange and LYP[22] correlation functionals. The H_f values of the

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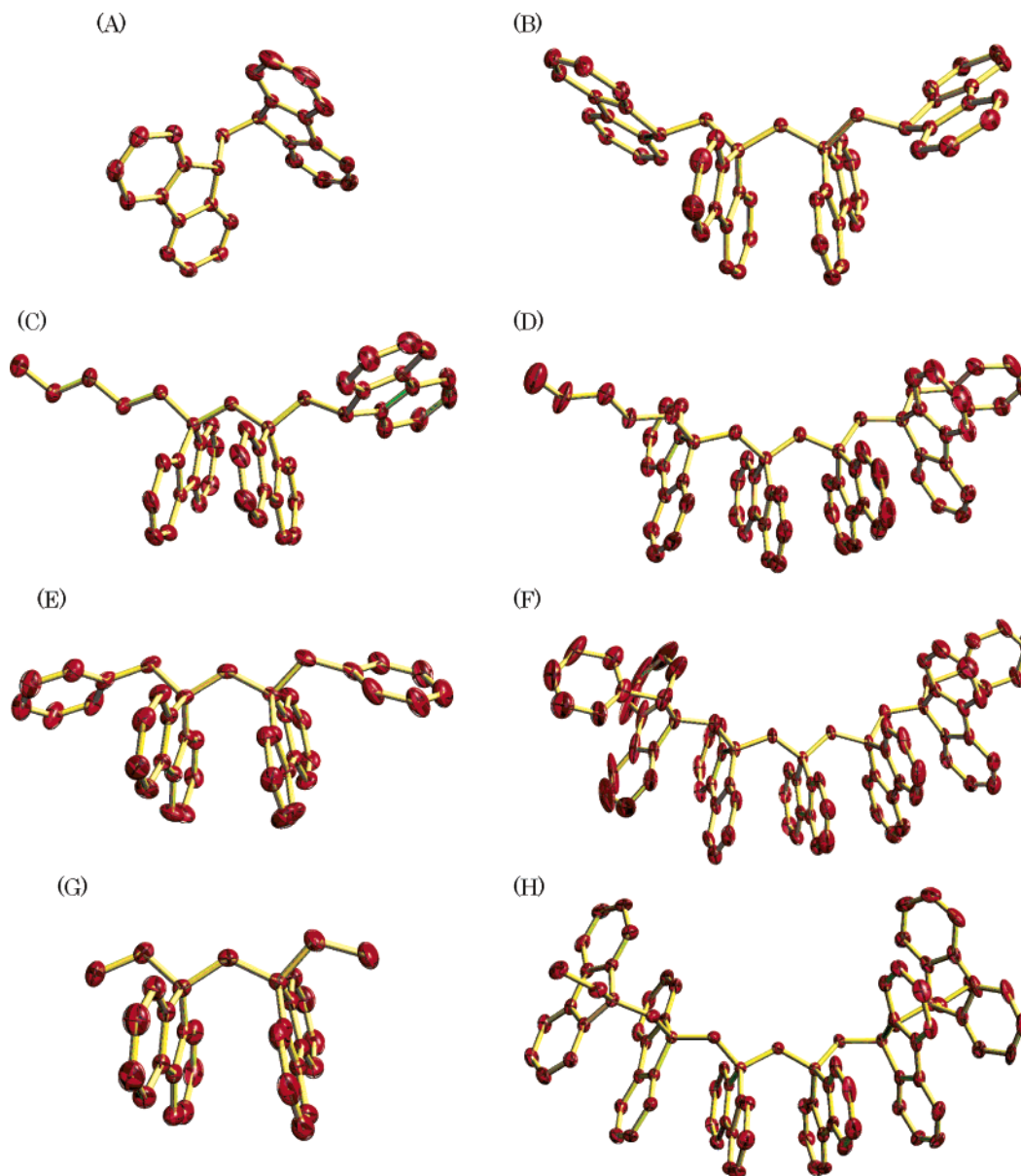(21) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

Figure 2. Crystal structures of oligo(DBF)s **1** (*n* = 2 (A) and *n* = 4 (B)), **3** (*n* = 3) (C), **4** (*n* = 4) (D), **5** (*n* = 2 (E) and *n* = 5 (F)), and **2** (*n* = 2 (G) and *n* = 6 (H)). Hydrogen atoms are omitted for clarity.

conformers having identical chemical structures were similar, indicating that all conformers shown in the figures could contribute to the experimental NMR spectra at similar probabilities.

Prior to application of the DFT method to the oligomers, the accuracy of the DFT chemical shift calculation was tested using fluorene, 9-methylfluorene, and superphane, which consist of methylene, methine, and an aromatic ring and are expected to have little conformational freedom. The experimental $-CH_2-$ shift for fluorene was 3.95 ppm (CDCl$_3$, 500 MHz, Me$_4$Si), and that for superphane was 2.98 ppm,[23] while the calculated shifts were 3.87 and 3.29 ppm for fluorene and superphane, respectively. The experimental $-CH_3$ and methine shifts for 9-methylfluorene were 1.53 and 3.95 ppm, respectively (CDCl$_3$, 500 MHz, Me$_4$Si), and the corresponding calculated values were 1.43

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and 4.03 ppm. These results mean that the theoretical calculation in this study may contain an error of 0.1−0.3 ppm.
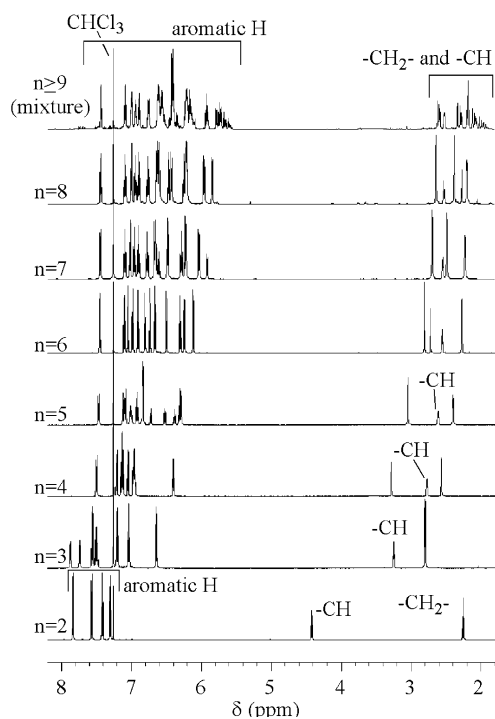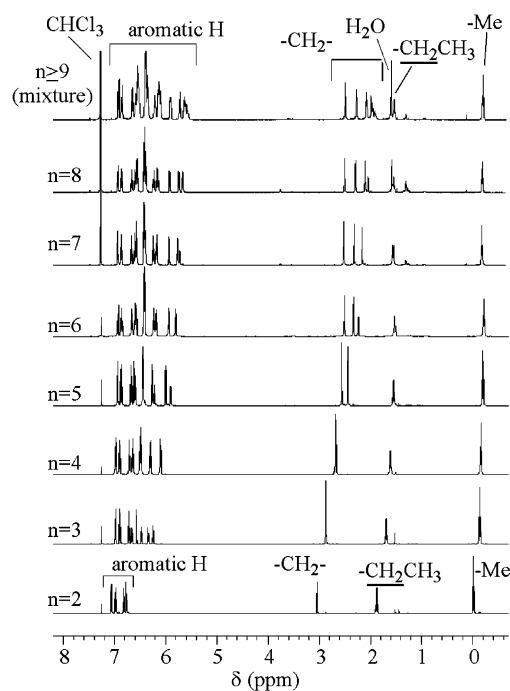
Conformers **1A$_2$**−**1C$_2$** were evaluated for **1** of *n* = 2. The calculated methylene shift of **1A$_2$** deviated from the experimental value by 1.6 ppm, and one of the calculated methine shifts of **1B$_2$** deviated from the experimental value by 2.0 ppm, suggesting that these are not the most plausible conformers. In contrast, the deviations of the calculated methylene and methine shifts of **1C$_2$** from the experimental values were only 0.4 and 0.1 ppm, respectively. These results suggest that **1C$_2$**, in which the two fluorenyl groups are flipped, is the most probable conformer although other conformers could also exist in conformational dynamics.

Conformers **2A$_2$**−**2C$_2$** for **2** of *n* = 2 were generated and subjected to shift calculations. The theoretical shifts of the central methylene protons of conformers **2A$_2$** and **2B$_2$** were rather close to the experimental shifts, while that of **2C$_2$** deviated from the observed value by 1.3 ppm. Therefore, **2C$_2$** may not

Table 2. Crystallographic Data of Oligo(DBF)s

property	1 (n = 2)	1 (n = 4)	2 (n = 2)	2 (n = 6)	3 (n = 3)	4 (n = 4)	5 (n = 2)	6 (n = 5)
molecular formula	$C_{27}H_{20}$	$C_{55}H_{40}$	$C_{31}H_{28}$	$C_{87}H_{68}$	$C_{46}H_{40}$	$C_{67}H_{56}$	$C_{41}H_{32}$	$C_{41}H_{32}$
fomula weight	344.45	700.92	400.56	1113.49	592.82	861.18	524.70	1059.40
temperature, K	296	296	296	296	296	296	296	296
wavelength, Å	71 069	71 069	71 069	71 069	71 069	71 069	71 069	71 069
crystal/color	colorless	colorless	colorless	colorless	colorlwss	colorless	colorless	colorless
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$
unit cell dimensions								
a, Å	9.9303(5)	16.3629(9)	12.534(2)	10.4024(5)	13.2214(3)	12.8765(4)	16.6849(5)	11.5072(5)
b, Å	8.5039(4)	15.273(1)	12.674(2)	19.7052(6)	13.3664(2)	15.4623(2)	12.2332(5)	22.102(1)
c, Å	22.030(1)	15.5365(7)	14.546(2)	29.916(1)	19.0154(1)	12.7814(2)	15.4247(5)	27.047(2)
α, deg	90	90	90	90	90	107.723(1)	90	90
β, deg	98.922(2)	103.475(4)	101.975(5)	92.6521(6)	92.523(1)	94.605(2)	110.5185(8)	89.836(1)
γ, deg	90	90	90	90	90	96.765(1)	90	90
volume, Å³	1837.8(1)	3775.9(3)	2260.4(5)	6125.7(4)	3357.19(7)	2388.91(9)	2948.6(2)	6879.1(5)
Z	4	4	4	4	4	2	4	4
D_{calcd}/g cm^{-3}	1.245	1.232	1.176	1.207	1.173	1.197	1.182	1.023
reflns collected	16 751	7865	8682	42 618	20 119	13 845	14 076	46 223
unique reflns	4192	4328	2543	12 813	7705	10 622	3388	14 864
R_1	0.042	0.042	0.055	0.066	0.053	0.075	0.058	0.143
wR_2	0.090	0.078	0.140	0.145	0.085	0.118	0.140	0.341
GOF	0.96	1.40	1.21	1.31	1.28	2.00	1.23	1.74

Figure 3. ¹H NMR spectra of oligo(DBF)s (**1**) (600 MHz, CDCl₃, room temperature).

Figure 4. ¹H NMR spectra of oligo(DBF)s (**2**) (500 MHz, CDCl₃, room temperature).

be reasonable. The predicted chemical shift for one of the terminal methylene groups of **2B₂** largely deviated from the experimental value, suggesting that **2A₂** having a π-stacked conformation is the most plausible. Although it is noticeable that the experimental terminal methyl shift of **2A₂** deviated from the predicted value by ca. 0.8 ppm, this may mean that the terminal ethyl groups rotate relatively fast and do not give an accurate shift in the calculation of a single conformer. Hence, flipped and stacked conformations were suggested by the NMR shift calculation for **1** of n = 2 and **2** of n = 2, respectively. As in crystal, an ethyl or a larger group may prevent the rotation of the terminal fluorene unit and force it into a stacked form.

For **2** of n = 4, four conformers, **2A₄**−**2D₄** were tested: **2A₄** is a model of a flawlessly stacked conformation, and **2B₄** and

2C₄ are models of stacked conformations with a "kink". Although the models with a kink were predicted to show a remarkable upfield shift of the main-chain methylene signals (δ 1−0.7 ppm) in the vicinity of the kink, no peak was observed in such a high magnetic field range in the experimental spectra. In addition, the calculated methylene shifts of **2A₄** were rather close to the experimental data. Therefore, **2A₄** is considered to be the most plausible conformation. In this case also, calculated shifts of the terminal methyl protons significantly deviated from the observed values, probably due to the relatively fast motion of the terminal ethyl group as noted above.

As described here, the chemical shift calculation appears to be an effective method of obtaining information on the oligomer conformation. Although longer oligomers and polymers were not subjected to chemical shift calculation, their experimental

Table 3. ^{1}H NMR Chemical Shifts (δ, ppm) of Oligo(DBF)s (**1**)[a]

n	2	3	4	5	6	7	8	≥9[b]
H_A	4.42 (t)	3.25 (t)	2.78 (t)	2.64 (t)	2.56 (t)	2.55 (t)	2.53 (t)	2.62−1.88 (methylene protons)
H_B	2.26 (d)	2.80 (d)	2.57 (d)	2.42 (d)	2.28 (d)	2.23 (d)	2.20 (d)	
H_C			3.28 (s)	3.06 (s)	2.82 (s)	2.70 (s)	2.64 (s)	
H_D					2.73 (s)	2.49 (s)	2.38 (s)	
H_E							2.27 (s)	
H_{A1}	7.57 (d)	6.64 (d)	6.41 (d)	6.31 (d)†	6.25 (d)	6.23 (d)	6.22 (d)†	5.55−7.44 (aromatic protons)
H_{A2}	7.30 (dd)	7.04 (dd)	6.96 (dd)†	6.93 (dd)	6.91 (dd)	6.91 (dd)	6.90 (dd)	
H_{A3}	7.42 (dd)	7.20 (dd)	7.14 (dd)*	7.13 (dd)	7.10 (dd)	7.10 (dd)	7.10 (dd)	
H_{A4}	7.84 (d)	7.56 (d)	7.50 (d)	7.48 (d)	7.46 (d)	7.45 (d)	7.44 (d)	
H_{B1}		7.74 (d)	7.05 (d)	6.85 (d)*	6.74 (d)	6.68 (d)	6.64 (d)	
H_{B2}		7.49 (dd)*	6.97 (dd)†	6.85 (m)*	6.81 (dd)	6.79 (dd)	6.77 (dd)	
H_{B3}		7.51 (dd)*	7.13 (dd)*	7.02 (m)	6.98 (dd)	6.97 (dd)	6.95 (dd)	
H_{B4}		7.88 (d)	7.22 (d)	7.10 (d)	7.06 (d)	7.03 (d)	7.01 (d)	
H_{C1}				6.33 (d)†	6.12 (d)	6.04 (d)	5.96 (d)	
H_{C2}				6.40 (dd)	6.31 (dd)	6.29 (dd)	6.25 (dd)†	
H_{C3}				6.74 (dd)	6.67 (dd)	6.66 (dd)	6.61 (dd)*	
H_{C4}				6.54 (d)	6.50 (d)	6.49 (d)*	6.43 (d)	
H_{D1}						5.93 (d)	5.85 (d)	
H_{D2}						6.24 (dd)	6.22 (dd)†	
H_{D3}						6.62 (dd)	6.61 (dd)*	
H_{D4}						6.50 (d)*	6.47 (d)	

[a] See Chart 1 for proton numbering. Spectra were recorded in CDCl$_3$ at room temperature (600 MHz). Residual CHCl$_3$ signal (7.26 ppm) was used as an internal reference. * and † indicate interchangeable assignments. [b] A polymer (Mn = 1700 (vs oligo(DBF)), $\bar{n}$ = 9.6, $n \geq 9$ mixture).

Table 4. ^{1}H NMR Chemical Shifts (δ, ppm) of Oligo(DBF)s (**2**)[a]

n	2	3	4	5	6	7	8	≥9[b]
Me−	−0.01 (t)	−0.14 (t)	−0.16 (t)	−0.20 (t)	−0.22 (t)	−0.23 (t)	−0.24 (t)	−0.25 (t)
H_A	1.88 (q)	1.69 (q)	1.61 (q)	1.55 (q)	1.53 (q)	1.51 (q)	1.50 (q)	1.49 (q)
H_B	3.05 (s)	2.87 (s)	2.68 (s)	2.56 (s)	2.51 (s)	2.48 (s)	2.47 (s)	2.46−1.86 (methylene protons)
H_C			2.67 (s)	2.45 (s)	2.34 (s)	2.28 (s)	2.25 (s)	
H_D					2.24 (s)	2.12 (s)	2.07 (s)	
H_E							2.00 (s)	
H_{A1}	6.77 (d)	6.58 (d)	6.50 (d)*	6.45 (d)*	6.42 (d)†	6.40 (d)†	6.39 (d)†	5.52−6.91 (aromatic protons)
H_{A2}	6.83 (dd)	6.72 (dd)	6.71 (dd)	6.68 (dd)	6.66 (dd)	6.65 (d)	6.64 (dd)	
H_{A3}	6.98 (dd)	6.90 (dd)	6.90 (dd)	6.87 (dd)	6.86 (dd)	6.85 (d)	6.85 (dd)	
H_{A4}	7.07 (d)	6.98 (d)	6.98 (d)	6.94 (d)	6.93 (d)	6.92 (d)	6.92 (d)	
H_{B1}		6.25 (d)	6.10 (d)	6.00 (d)	5.94 (d)	5.91 (d)	5.90 (d)	
H_{B2}		6.34 (dd)	6.30 (dd)	6.26 (dd)	6.24 (dd)	6.22 (dd)	6.21 (dd)	
H_{B3}		6.66 (dd)	6.65 (dd)	6.62 (dd)†	6.60 (dd)*	6.59 (dd)	6.58 (dd)	
H_{B4}		6.48 (d)	6.48 (d)*	6.45 (d)*	6.42 (d)†	6.41 (d)†	6.40 (d)†	
H_{C1}				5.90 (d)	5.81 (d)	5.75 (d)	5.72 (d)	
H_{C2}				6.22 (dd)	6.19 (dd)	6.16 (dd)‡	6.15 (dd)‡	
H_{C3}				6.60 (dd)†	6.58 (dd)*	6.56 (dd)*	6.55 (dd)*	
H_{C4}				6.45 (d)*	6.42 (d)†	6.40 (d)†	6.39 (d)†	
H_{D1}						5.70 (d)	5.65 (d)	
H_{D2}						6.15 (dd)‡	6.13 (dd)‡	
H_{D3}						6.56 (dd)*	6.54 (dd)*	
H_{D4}						6.38 (d)†	6.36 (d)	

[a] See Chart 1 for proton numbering. Spectra were recorded in CDCl$_3$ at room temperature (500 MHz). Residual CHCl$_3$ signal (7.26 ppm) was used as an internal reference. *, †, and ‡ indicate interchangeable assignments. [b] A polymer (Mn = 1890 (vs oligo(DBF)), $\bar{n}$ = 10.4, $n \geq 9$ mixture).

methylene shifts seem to converge into a value around 2 ppm, and no peaks of the methylene group were observed in a range higher than 1 ppm in the spectra. This suggests that the longer oligomers and polymers have a stable π-stacked conformation without a kink in the chain.

Conformational Calculation

Oligomer conformation was evaluated by force field and semiempirical molecular orbital calculations. Although the relatively generic Dreiding force field[24] was used for all conformational calculations in our preliminary studies,[8] MM3*,[25] MMFF94s,[26] and COMPASS[27] force fields with better energetic and structural precision and a semiempirical PM5 method were employed in this study.

First, Monte Carlo conformational searches with MM3* and MMFF94s force fields were performed on a DBF hexamer having ethyl groups at the chain terminals (**2**, n = 6) using a

(24) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, *94*, 8897−8909.
(25) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 1, 8551−8566.
(26) Halgren, T. A. *J. Comput. Chem.* **1999**, *20*, 730−748.
(27) Sun, H. *J. Phys. Chem.* **1998**, *102*, 7338−7364.

Chart 1. Structures of **1** and **2** of *n* = 8 with the Proton Numbering Systems[a]

1 of n = 8

2 of n = 8
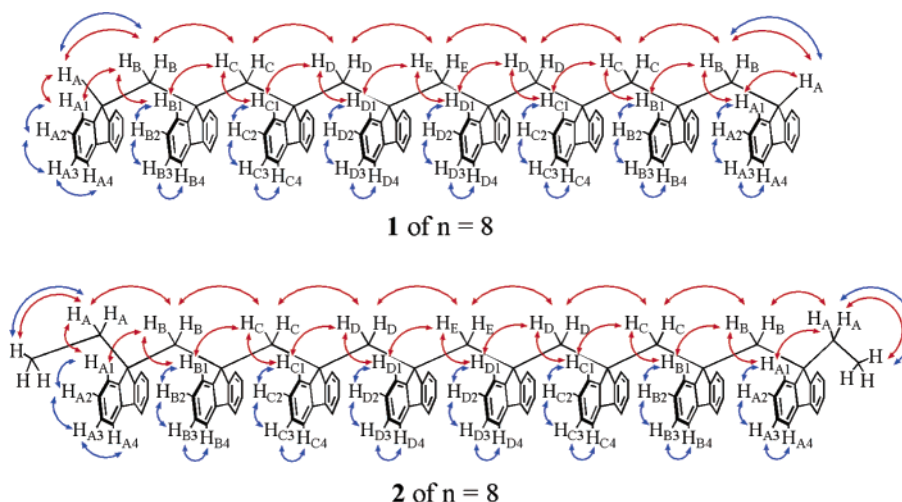
[a] COSY and NOESY correlations were marked by blue and red arrows, respectively. NOESY correlations between aromatic protons are omitted.
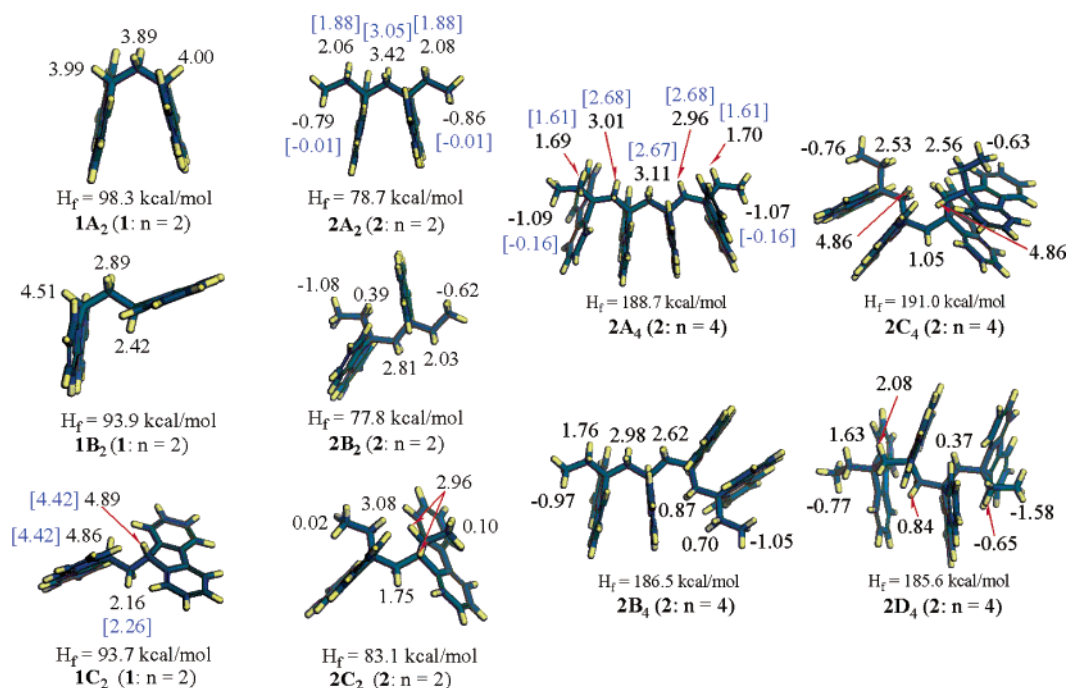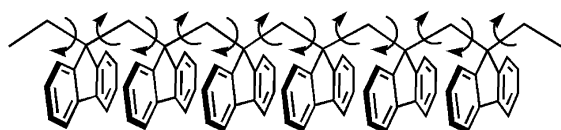

Figure 5. Conformers of **1** (*n* = 2) and **2** (*n* = 2 and *n* = 4) and calculated chemical shifts of methylene protons. The values in square brackets are the experimental chemical shifts.

Chart 2. Dihedral Angle Sets for the Monte Carlo Simulation of **2** of *n* = 6[a]

[a] Angle interval was 60°.

MacroModel[28] software package. Two distinctive structures were found to be the most stable conformations using MM3* and MMFF94s force fields out of 20 000 (MM3*) and 19 550 (MMFF94s) conformers, which were generated by changing the dihedral angles around the 12 main-chain bonds at an interval of 60°, as shown in Chart 2. These two most stable conformers were further minimized by the PM5 method to afford structures

2A₆ and **2B₆** shown in Figure 6. Structure **2A₆** was similar to the crystal structure (Figure 2), while structure **2B₆** had a partially trans-gauche-like structure. The two conformers indicated similar values of H_f by the PM5 method.

Next, the stability of conformations **2A₆** and **2B₆** was tested by molecular dynamics (MD) simulations using the COMPASS force field under NVT conditions with Berendsen's thermostat[29] (Figure 6, right-hand side). While conformation **2A₆** did not largely change in the MD simulation at 300 K for 10 ns to give structure **2A₆′**, conformation **2B₆** quickly changed into a mostly all-trans, π-stacked conformation with a kink (gauche−gauche

(28) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440−467.
(29) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684−3690.
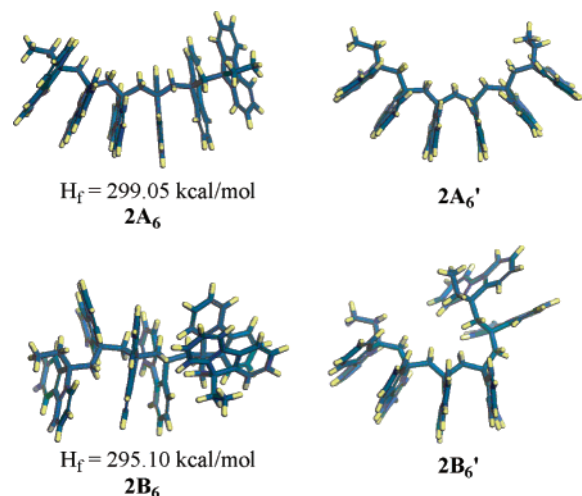
Figure 6. Conformers of **2** of *n* = 6 found most stable in the Monte Carlo simulation and optimized by the PM5 method, **2A₆** (force field, MM3*) and **2B₆** (force field, MMFF94s), and those after MD simulation, **2A₆′** (300 K, 10 ns) and **2B₆′** (300 K, 8.2 ns), starting from **2A₆** and **2B₆**, respectively.

main-chain conformation) (**2B₆′**) in the middle of the chain at 300 K within 0.1 ns, and structure **2B₆′** did not significantly change within 8 ns. These results suggest that a π-stacked conformation is preferred under dynamic conditions while several different conformers, including the π-stacked structure, may have similar steric energies under static conditions.

The conformational stability test was extended to a model of the polymer (**2**, *n* = 15). An all-trans model and an alternating trans-gauche model molecular-mechanically optimized using the COMPASS force field were subjected to MD simulations (NVT) (Supporting Information). The all-trans model remained in the π-stacked structure at 300 K in 15 ns, and the structure was only partially distorted even at 600 K. In contrast, the alternating trans-gauche model promptly changed into a preferentially all-trans, π-stacked conformation with a kink within 2 ns at 300 K.

These results suggest that the π-stacked conformation is most preferable for poly(DBF). Although some conformers with a kink in the main chain were observed in the calculations, most of the real molecules are considered to have a π-stacked structure throughout the chain, based on the discussions about the NMR spectra in the preceding section.

Absorption and Emission Profiles

The absorption and emission spectra of the oligomers (*n* = 2−8) and polymers (*n* ≥ 9) of **1** and **2** indicated characteristic profiles based on their structures. The absorption spectra are shown in Figure 7. Oligomer **1** of *n* = 2 bearing two fluorene groups indicated slight hyperchromicity relative to 9-methylfluorene, the model for the monomeric unit, which is obvious in the 240−280 nm region, while oligomers **1** of *n* = 3−8 and the polymer (*Mn* = 1700, *n* = 9.6, mixture of *n* ≥ 9) exhibited significant hypochromicity. In addition, all of the samples of **1** of *n* = 3 and larger showed a red shift of the absorption bands. As for oligomers **2**, all of the samples, including the one of *n* = 2, exhibited hypochromicity and a red shift.

Hypochromic effects have been reported for stacked base pairs in a double helical strand in DNA.[30] Therefore, the

(30) (a) Tinoco, I. *J. Am. Chem. Soc.* **1960**, *82*, 4785−4790. (b) Rohdes, W. *J. Am. Chem. Soc.* **1961**, *83*, 3609−3617.
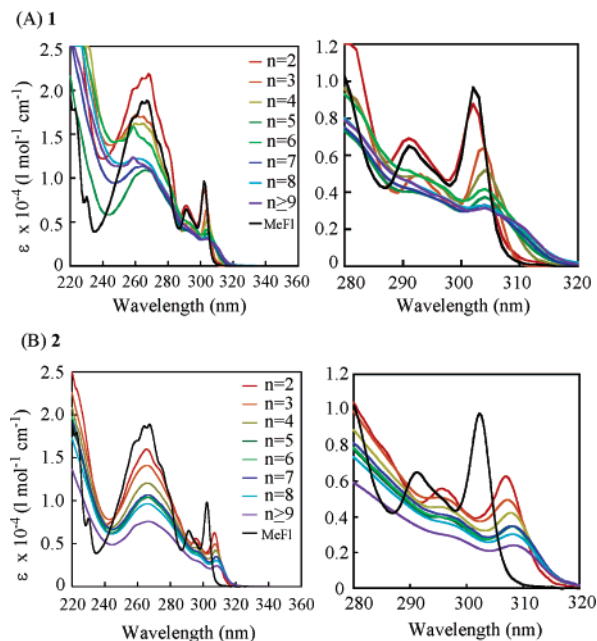
Figure 7. Absorption spectra of oligo(DBF)s **1** (A), **2** (B), and 9-methylfluorene (MeFl) in THF at room temperature.

hypochromicity described above is consistent with the above discussion that the oligomers and polymers studied here have a π-stacked conformation in solution. The degree of hypochromicity found for the oligomers and polymers in this study is larger than that for DNA. This may indicate that the π-electron systems are more densely packed in the present systems than those in DNA. The fact that **1** of *n* = 2 was hyperchromic[30a] while **2** of *n* = 2 was hypochromic supports the conclusion from the ¹H NMR studies that the former compound does not have a stacked conformation while the latter does.

The observed red shift of the absorption bands means that electronic interaction between neighboring fluorene units in the ground state lowered the excitation energy of the oligomers or polymers. In main-chain conjugated polymers, a longer chain length results in a significantly reduced band gap.[31,32] Electronic interaction between closely stacked but not covalently bonded aromatic groups may also make the band gap narrower from the present results, although the effect seems to be smaller as compared with that for main-chain conjugated polymers.[32]

To more quantitatively evaluate the red shift and the hypochromicity, the wavelength and molar extinction coefficient (ϵ) of the lowest-energy absorption peak were plotted against the chain length (*n*) of oligomers **2** (Figure 8).[33] The peak-top wavelength increased with the chain length and leveled off around *n* = 5 (Figure 8A). In addition, ϵ at the peak top decreased with *n* and leveled off also around *n* = 5 (Figure 8B). These results suggest that, in the ground state, the electronic interaction between the stacked fluorene groups may extend over as long as ca. five units. An exciton may be formed over ca. five successive monomeric units in a chain upon photoexcitation.

This may be interpreted as follows. The DBF oligomers and polymers have a π-stacked structure in solution as we concluded on the basis of the NMR data and theoretical simulations.

(31) Ellis, J. R. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, Chapter 13.
(32) Houk, K. N.; Lee, P. S.; Nendel, M. *J. Org. Chem.* **2001**, *66*, 5517−5521.
(33) Plots of wavelength and ϵ against 1/*n* led to λ = 308.5 nm and ϵ = 1894 L mol⁻¹ cm⁻¹ at an infinite *n* by extrapolation (Supporting Information).
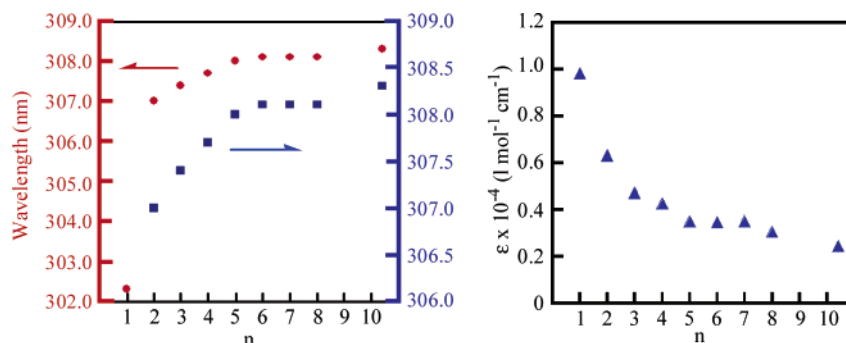
Figure 8. Wavelength versus n and molar extinction coefficient (ϵ) versus n plots for the longest wavelength absorption maxima of oligo(DBF)s **2**. Data at $n = 1$ are for 9-methylfluorene, and those at $n = 10.4$ are for a polymer ($Mn = 1890$ (vs oligo(DBF)), $\bar{n} = 10.4$).
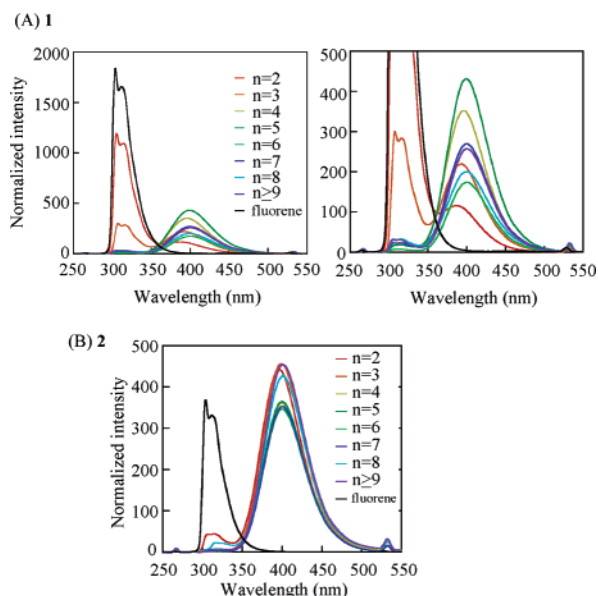

Figure 9. Emission spectra of oligo(DBF)s **1** (A), **2** (B), and fluorene in THF at room temperature ($\lambda_{ex} = 267$ nm). Intensity was normalized to a constant absorbance at 267 nm.

However, the π-stacked molecules should experience thermal vibration that does not largely distort the conformation. This may lead to heterogeneity of the stacked conformation; that is, the distance between the fluorene groups and main-chain torsion angle can slightly vary part by part in a chain, especially in a relatively short time range within which photoabsorption takes place. The roughly coincidental critical number of fluorene units suggests that ca. five fluorene units are always in one block of uniform stacked sequence even at a short time scale. In other words, the dynamic "persistence length" of a uniformly π-stacked sequence from the view of photoexcitation covers five monomeric units under the experimental conditions of this study.

An alternative interpretation may be that the electronic interaction of the stacked fluorene groups in the polymer side chain extends inherently up to ca. five units even for a long, completely uniform "frozen" π-stacked polymer. Absorption measurements at an extremely low temperature or in a solid-state matrix that may freeze molecular vibration might provide an answer. Computational studies on the electronic states of poly(DBF) may also be necessary. These aspects will be assessed in future studies.

Figure 9 shows the emission spectra of **1** and **2**. In the spectra of **1** (Figure 9A), those of $n \geq 4$ indicated predominant emission

bands around 400 nm, while that of $n = 2$ showed a shorter-wavelength emission band around 310 nm, which was similar in shape and wavelength to that of monomeric fluorene, and that of $n = 3$ indicated both bands around 310 and 400 nm. The bands around 400 nm are considered to arise from an excited dimer[34] in which excited energy delocalizes over two neighboring, stacked fluorene units because the band wavelength is rather close to those of the fluorene excimer[35] (367 nm, in toluene) and the excited side-chain dimer of poly(2-vinylfluo-rene)[36] (380 nm, in THF). In contrast to **1**, all samples of **2** indicated predominant dimer emission.

As discussed so far, the terminal fluorene moieties are flipped and are not stacked in samples of **1**. The terminal-flipped conformation explains the monomeric fluorene emission from **1** of $n = 2$ and 3. However, the sample of **1** with $n \geq 4$ showed only the dimer emission. This suggests that the energy transfer from the terminal, flipped fluorene moieties to dimer forming, in-chain stacked fluorene moieties quenches monomeric fluorene in the longer oligomers of **1**. The predominant dimer emission from all **2** samples is consistent with the fact that all oligomers of **2** have a π-stacked structure throughout the chain.

The emission wavelength of the dimer emission of **1** and **2** was slightly red-shifted as compared with that of the fluorene excimer[35] and the excited side-chain dimer in poly(2-vinylfluo-rene),[36] which may mean that the arrangement of two fluorene molecules in the excimer is different from that of two fluorene units in the oligomers. As can be seen in the crystal structure, the side-chain fluorene moieties are so densely packed along the chain that the main chain bends into a slightly arched shape. Such a close packing of two fluorene units probably enhances the electronic interaction between stacked π-electrons and, hence, reduces the delocalized excited energy level.

It is noteworthy that the emission profile of oligomer **1** of $n = 2$ is in sharp contrast to what is expected from "Hirayama's rule",[37] which predicts that a molecular array with two chromophores connected through three CH_2 groups favors excimer formation more than others with more or less CH_2 groups between the chromophores. Although in the structure of **1** of $n = 2$, two fluorenes are connected through three carbons, this

(34) "Excimer" emission could be an alternative term. However, "excimer" has been used to describe an excited species having stacked π-electron systems that does not have such a conformation as a predominant species in the ground state but changes conformation on excitation. The oligomers in this study have stacked structures in the ground state prior to photoexcitation; therefore, "dimer" emission is a more proper term.
(35) Horrocks, D. L.; Brown, W. G. *Chem. Phys. Lett.* **1970**, *5*, 117−119.
(36) Matsuda, M.; Watanabe, A. In *Recent Advances in Anionic Polymerization*; Hogen-Esch, T. E., Smid, J., Eds.; Elsevier: New York, 1987; p 73.
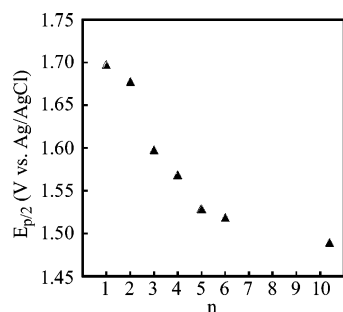(37) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163−3171.

Figure 10. Half wave potential versus *n* plot for **2**. Data at *n* = 1 are for fluorene, and those at *n* = 10.4 are for a polymer (Mn = 1890 (vs oligo-(DBF)), $\bar{n}$ = 10.4).

oligomer showed only monomer emission. The conformational dynamics of this sample seem to be slower than those of the compounds tested by Hirayama that form a stacked excimer before emission.

Electrochemical Profiles

Stacked π-electron systems may facilitate charge delocalization. To obtain information on how the stacked fluorene units may affect the electronic properties, cyclic voltammetry measurements were performed for oligomers **2**. The samples showed clear oxidation peaks around 1.5–1.7 V but no clear corresponding reduction peak in the reverse scans from 2 to 0 V (Supporting Information). In addition, the intensity of the oxidation peak gradually decreased in repeated runs, although the peak position was unchanged. These results suggest that the oxidized species may undergo some irreversible reaction on the electrode surface.

Figure 10 shows the dependence of oxidation potential ($E_{p/2}$) on the chain length. The oxidation potential decreased with chain length and was almost constant when an oligomer contains ca. five or more fluorene units.[38] This may mean that a hole is stabilized by delocalization over as many as ca. five stacked fluorene units. This critical number of fluorene units coincides with those for the changes in the absorption intensity and edge wavelength depending on the chain length. As discussed in the preceding section, this may be ascribed to the proposed dynamic "persistence length" of a uniformly π-stacked sequence consisting of five fluorene units or to the nature of charge delocalization through the π-stacked structure of poly(DBF) which may

inherently be limited to five fluorene units even if the chain has a longer, uniform "frozen" π-stacked structure. A low-temperature or solid-state study minimizing thermal vibration may give an answer.

Concluding Remarks

DBF oligomers and polymers were proven to have π-stacked structures with the main-chain carbon−carbon bondings being almost all in the all-trans conformation not only in the solid state but also in solution. The conformation is expected to be fairly stable by the MD simulation and the NMR experiments at different temperatures. The π-stacked structure led to remarkable hypochromicity in absorption and exclusive dimer emission and facilitated charge delocalization. Among several macromolecules characterized by a π-stacked structure, a highly regular, long-range π-stacked structure of the side-chain chromophores has been achieved only for DNA so far. Poly(DBF) is the first vinyl polymer with precisely regulated π-stacked side groups. This polymer may be recognized as a new macromolecular structural motif that may be useful in photophysical and photoelectronic (e.g., molecular wire)[39] applications.

Supporting Information Available: Experimental details, SEC curves of the oligomers, sample purity data, cyclic voltammograms, 2D NMR spectra, ϵ versus $1/n$, λ versus $1/n$, and $E_{p/2}$ versus $1/n$ plots for **2** (PDF), and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Plots of $E_{p/2}$ against $1/n$ led to a potential of 1.44 V (vs Ag/AgCl) at an infinite *n* by extrapolation (Supporting Information).

(39) We recently found that a poly(DBF) cast film shows a much higher hole mobility as compared with other vinyl polymers bearing aromatic side groups by time-of-flight experiments. This result will be published elsewhere.