ORIGINAL ARTICLE

Intramolecular CH/ π interaction of Poly(9,9-dialkylfluorene)s in solutions: interplay of the fluorene ring and alkyl side chains revealed by 2D ^1H – ^1H NOESY NMR and 1D ^1H -NMR experiments

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Herein, we demonstrate for the first time the existence of intramolecular CH/ π interactions within three chiral and one achiral poly(9,9-dialkylfluorene)s (S2MO, S37DMO, R37DMO and PF8) as well as a 9,9-di-*n*-octylfluorene molecule (F8) in chloroform- d_1 at 20 °C. The interaction is experimentally demonstrated by (1) intense cross-peaks between the ring and alkyl groups in two-dimensional ^1H – ^1H nuclear overhauser enhancement (NOE) correlated spectroscopy (NOESY) nuclear magnetic resonance (2D ^1H – ^1H NOESY NMR) and by (2) a marked upfield shift of several alkyl proton signals in one-dimensional ^1H nuclear magnetic resonance (1D ^1H -NMR) spectra. To support this idea theoretically, possible folded conformations were searched using Conflex7 (MMFF94s force field) for simple molecular models of S2MO, S37DMO and PF8, followed by optimizing the most probable conformation by second-order Møller–Plesett perturbation calculations (Gaussian 03, 6-311 G(d) basis set). This calculation revealed that the distances between the fluorene ring and the (*S*)-2-methyl and β -methylene protons of the alkyl groups (that is, ≈ 2.53 – 2.64 Å) was shorter than the closest van der Waals C–H/ring contact (2.90 Å). S2MO showed intense circular dichroism bands in the π – π^* region because of a stronger CH/ π interaction, whereas S37DMO and R37DMO exhibited no such detectable circular dichroism bands because of a weaker CH/ π interaction.

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INTRODUCTION

The weak attraction between an aliphatic C–H bond and a π -electron system is called the CH/ π interaction.^{1–4} The attraction energy is on the order of only 1 kcal mol^{–1}, whereas the thermal energy at 300 K is 0.6 kcal mol^{–1}. Several experimental and theoretical studies have supported the existence of inter- and intramolecular CH/ π interactions, which play key roles in conformational preference, crystal packing, host-guest complexation and self-organization processes.^{1–7} One can assume the existence of the intramolecular CH/ π (hereafter called intra-CH/ π) interaction of polymers containing a π -electron moiety in the main chain and the side chain. This possibility remains questionable because floppy main and side chains in a fluid solution must overcome the fluctuating thermal energy and enhance the low rotational barrier of the C–C bond on the order of 1 kcal mol^{–1}. Currently, for supramolecular polymer host-guest complexation, the existence of the intermolecular CH/ π interaction (hereafter called inter-CH/ π) in a highly condensed solution state is indicated by two-dimensional (2D) ^1H – ^1H nuclear Overhauser enhancement (NOE) correlated spectroscopy (NOESY) nuclear magnetic resonance (NMR),⁶ and the inter-CH/ π interaction

in the solid state is demonstrated by an advanced 2D phase-modulated Lee–Goldburg decoupling heteronuclear ^1H – ^{13}C correlation (PMLG-HETCOR) NMR technique with cross-polarization magic angle spinning (CPMAS).^{5,7}

In recent years, the synthesis, condensed-phase structure and photophysical properties of several stiff π -conjugated polymers with *n*-alkyl and branched alkyl side chains have been reported.^{8–25} The roles of the alkyl side chains are possibly (1) to endow better solubility to common organic solvents, (2) to reduce the crystallinity of solid films due to the introduction of highly branched alkyl chain and bulky aryl groups, (3) to enhance the liquid crystallinity by providing *n*-alkyl chains of the appropriate length and (4) to induce certain degrees of chiral and helical order in solutions and films because of the influence of chiral branched chains. The possibility of the intra-CH/ π interaction existing between main chain and alkyl side chains in these π -conjugated polymers under fluidic conditions, however, has not yet been fully clarified because of the rich conformational freedom of side chain and main chain and instrument limitations in structural analysis.

To answer the question of whether the intra-CH/ π interaction of π -conjugated polymers in solutions is detectable, we chose three chiral poly(dialkylfluorene)s (**S2MO**, **S37DMO** and **R37DMO**)^{19,22} and an achiral poly(di-*n*-octylfluorene) (**PF8**)¹⁵ (Figure 1). For comparison, we tested three achiral small molecules, di-*n*-octylfluorene (**F8**), *n*-butylbenzene (**BB**) and *n*-octane, as shown in Figure 1. The uniqueness of the dialkylfluorene ring is to fix the C₈–C_{ipso}–C₉–C _{α} dihedral angle and to restrict the rotational freedom of C_{ipso}–C₉, C₉–C _{α} , C _{α} –C _{β} and C _{β} –C _{γ} bonds. This inherent property facilitates the formation of the folded *gauche* geometry between the alkyl- π -ring linkage in **S2MO**, **S37DMO**, **R37DMO** and **PF8** in a fluid solution state at room temperature relative to what is observed in *n*-alkylbenzenes (Figure 1). Herein, we demonstrate for the first time that the intra-CH/ π interaction exists in these polyfluorenes (**PFs**) as well as in **F8** in chloroform-*d*₁ (CDCl₃), methylcyclohexane-*d*₁₄ (MCH-*d*₁₄), tetrahydrofuran-*d*₈ (THF-*d*₈) and toluene-*d*₈ (TOL-*d*₈), as revealed by ¹H–¹H NOESY and ¹H-NMR spectroscopy and circular dichroism (CD)/ultraviolet-visible (UV-vis) spectroscopy. NOESY NMR data indicate no detectable intra-CH/ π interaction of **BB** in CDCl₃.

To support this idea theoretically, possible folded conformations were searched using Conflex7 (MMFF94s force field)^{26,27} <http://www.conflex.us> for simple molecular models of **S2MO**, **S37DMO** and **PF8**, followed by optimizing the most probable conformation by second-order Møller–Plesett (MP2) perturbation calculations (Gaussian 03, 6-311 G(d) basis set)²⁸ (<http://www.gaussian.com>). This calculation revealed that the distances between the fluorene ring and the (S)-2-methyl and β -methylene protons of the alkyl groups (that is, ≈ 2.53 – 2.64 Å) are shorter than the closest van der Waals (vdW) C–H/ring contact (2.90 Å).

MATERIALS AND METHODS

Instruments

The CD and UV-vis spectra of the solutions were recorded on a JASCO (Tokyo, Japan) J-820 spectropolarimeter equipped with Peltier-controlled housing units using synthetic quartz-grade cuvettes with a 10 mm path length (100 nm min^{–1} scanning rate, 2 nm bandwidth, 1 s response time, 0.5 nm interval sampling and double accumulation) at 20 °C. The one-dimensional (1D) ¹H-NMR spectra were recorded on a JEOL JNM-ECP400 (400 MHz) spectrometer (JEOL, Tokyo, Japan) at 20 °C and, in some cases, at 25 °C, with 16 scans performed at a 45° pulse angle, a relaxation delay of 5.0 s and a repetition time of 7.1 s. The 2D ¹H–¹H NOESY NMR spectra were recorded on a JEOL JNM-ECX400 (400 MHz) spectrometer at 20 °C with 2048 scans and a mixing time of 0.5 s for polymer, through a mixing time of 1.0 s for small molecules, a relaxation delay of 1.5 s, a repetition time of 1.7 s and a scramble time of 1.0 ms.

Materials

The synthesis and characterization of **S2MO**, **S37DMO** and **R37DMO** have already been reported in our previous study.¹⁹ It should be noted that **R2MO**, which is an enantiomeric pair of **S2MO**, is not produced because (*R*)-2-methyloctanol is not commercially available as a starting material. Samples were stored in darkness and used without further treatment. Commercially available **PF8** (Sigma-Aldrich, Tokyo, Japan), **BB** (Sigma-Aldrich), **F8** Tokyo Chemical Industry (TCI, Tokyo, Japan) and *n*-octane (Sigma-Aldrich) were used for NMR and/or CD/UV-vis measurements. The weight-average molecular weight (*M*_w), number-average molecular weight (*M*_n) and polydispersity index (*PDI* = *M*_w/*M*_n) of the **PFs** evaluated by size-exclusion chromatography with polystyrene standards (PLGel 10 μ m Mixed-B (Agilent Japan, Tokyo, Japan), eluent THF, 40 °C) were as follows:¹⁹ **S2MO**: *M*_w = 5.66×10^4 and *PDI* = 3.09; **S37DMO**: *M*_w = 1.90×10^5 and *PDI* = 2.33; **R37DMO**: *M*_w = 1.79×10^5 and *PDI* = 3.01; and **PF8**, *M*_w = 8.77×10^4 and

Figure 1 Chemical structures of three chiral and one achiral poly(dialkylfluorene)s, and, for comparison, several dialkylfluorenes, *n*-butylbenzene and *n*-octane.

$PDI = 3.47$. Tetramethylsilane (Sigma-Aldrich) was used as an internal standard, and deuterated solvents ($CDCl_3$ (Cambridge Isotope Lab., Andover, MA, USA), $MCH-d_{14}$ (Sigma-Aldrich), $THF-d_8$ (Sigma-Aldrich) and toluene- d_8 (Sigma-Aldrich)) were used as the NMR solvents. The sample concentration of all NMR measurements was fixed to $1.0 \times 10^{-2} \text{ mol l}^{-1}$ ($\approx 0.4\%$ (w/v) for PFs) in deuterated solvents. Spectroscopic-grade chloroform (Dojindo, Kumamoto, Japan) was used for the CD/UV-vis measurements.

Calculation

Conflex7 (rev A) using an MMFF94s force field (Conflex, Japan) <http://www.conflex.us> generated possible conformers of fluorene molecules. A conformation search was performed according to not only energy dependence but also torsion angle. The total numbers of possible conformations of EPF, ES2MPF and ES3MPF were 37, 50 and 47, respectively. Among these, we focused on the specific conformers with the highest populations based on torsion angle of EPF (39.3%), ES2MPF (18.7%) and ES3MPF (17.7%) to apply MP2 calculations, using sequential STO-3 G, 3–21 G, 6–31 G and 6–311 G(d) basis sets with the Gaussian 03 (rev E) (Gaussian) package program.²⁸ (<http://www.gaussian.com>). Using an MP2 technique based on higher-level 6–31G and 6–311G(d) basis sets allowed us to provide reliable optimized conformers with CH/ π interactions.⁴ All calculations were run on an Apple MacPro (MacOS 10.5 for Gaussian 03 and 10.6 for Conflex7, Quad-core $\times$ 2, 2.8 GHz clock, 16 GB memory, 2 TB $\times$ 3 hard disk).

RESULTS AND DISCUSSION

In 1977, Nishio *et al.*²⁹ proposed the intra-CH/ π interaction to account for an unexpected conformation in which the closest contact is between bulky alkyl and phenyl groups in solid crystals, as observed by X-ray crystallographic analysis. In 1980, Smalley *et al.*^{30,31} discovered the coexistence of *gauche*- and *trans*-conformations with almost equal intensity by analyzing π - π^* absorption and fluorescence excitation spectra in a series of supersonic jet-cooled *n*-alkylbenzenes (alkyl number: 3–6) in a collision-free gas phase. In the *gauche*-*n*-alkylbenzenes, the C_α - C_β bond of the *n*-alkyl chain (see Figure 1) partially covered one side of the phenyl ring, whereas the *n*-alkyl chain in the *trans*-form extended away from the phenyl ring to avoid a van der Waals (vdW) contact between alkyl and phenyl groups.³⁰ This uniqueness arises from the rotational freedom of the C_α - C_β bond of *n*-alkylbenzenes. Later theoretical and experimental studies demonstrated that the intra-CH/ π interaction allows for the aromatic ring and the alkyl side chain to move into close proximity.^{32–37} This finding led to the adoption of the folded *gauche*-geometry of *n*-alkylbenzenes and several benzene analogs carrying freely rotatable alkyl moieties in the vapor phase. A subsequent analysis of BB revealed the existence of two *gauche*-forms under the jet-cooled conditions.³⁵ More elegantly, the advanced 1D ^1H -NMR NOE effect successfully allowed for the detection of the intra-CH/ π interaction as a folded *gauche*-conformation in several mono-substituted benzene derivatives carrying aliphatic groups in chloroform- d_1 and dimethylsulfoxide- d_6 at 30°C .³⁶ These studies prompted us to study the possible existence of the intra-CH/ π interaction in S2MO, S37DMO, R37DMO and PF8 and, for comparison, F8, BB and *n*-octane in chloroform- d_1 at 20°C .

π -Ring systems bearing achiral side chains

^1H -NMR spectra. Figures 2a–c compare the α -methylene regions in the ^1H -NMR spectra of BB, F8 and PF8 in $CDCl_3$ at 20°C . The full ^1H -NMR spectra of BB, F8, PF8 and *n*-octane are provided in Supplementary Figure S1. Two α -methylene protons of BB have a triplet signal, whereas four α -methylene protons of F8 apparently consist of doublet and triplet signals, and PF8 has one broad signal with a couple of additional signals. The α -methylene protons of BB

Figure 2 The ^1H nuclear magnetic resonance (^1H -NMR) spectra of the α -methylene region for (a) *n*-butylbenzene (BB), (b) di-*n*-octylfluorene (F8) and (c) poly(di-*n*-octylfluorene (PF8) in chloroform- d_1 ($CDCl_3$) at 20°C .

resonate at ≈ 2.6 p.p.m., whereas the α -methylene protons of F8 and PF8 are shifted upfield to ≈ 1.9 – 2.1 p.p.m. This upfield shift is induced by the ring-current shielding effect of benzene and fluorene rings. This induces the intra-CH/ π interaction because of the restricted rotational freedom of C_9 - C_α - C_β - C_γ dihedral angle and the fixed C_{ipso} - C_9 - C_α bond angle. Thus, two α -methylenes of PF8 are in largely restricted rotational motion, as indicated by the largely broadened proton signals. Similarly, doublet and triplet signals for α -methylene protons in hexa-*n*-propylbenzene and *n*-propylbenzene have been reported.³⁸

The BB pattern is ascribed to a magnetically equivalent, freely rotating A_2X_2 spin system of α - and β -methylenes, whereas the F8 and PF8 pattern indicates the magnetically nonequivalent $AA'BB'/C_3$ spin system because of restricted rotational motion. The C_{ipso} - C_α - C_β - C_γ bond of BB adopts a statistical population of *anti*:*gauche* = 1:2,³⁸ whereas the apparent doublet–triplet signals of C_9 - C_α - C_β - C_γ in F8 arise from the unaveraged $^3J_{trans}$ and $^3J_{gauche}$ couplings in the CH_α - CH_β fragment. Two α - and β -methylenes of PF8 are possibly in restricted rotational states to a greater degree. This leads to the idea that the C_{ipso} - C_9 - C_α - C_β bonds of F8 could facilitate the intra-CH/ π interaction between the fluorene ring and α -, β - and γ -methylene protons in *n*-alkyl side groups (PF8), as illustrated in Figure 1. This hypothesis may naturally be extended to the possibility of the intra-CH/ π interaction existing between the fluorene ring and methyl protons located at the β - and γ -positions of the chiral alkyl groups (S2MO, S37DMO and R37DMO).

The upfield shift in the β -methylene proton signals of F8 and PF8 is more remarkable than the shift in the signals of BB. The upfield shift originates from the ring-current-induced shielding effect according to the classical Johnson–Bovey (J-B) model,^{39–41} and allows interrogation of the relative position of alkyl and aromatic rings in experimental conditions. Indeed, the J-B model applies to the unusual upfield shift of freely rotating alkyl moieties in μ -trialkylsiloxy silicon phthalocyanines, although the CH/ π interaction between the phthalocyanine ring and trialkylsiloxy groups is not postulated in this case.⁴⁰ The J-B model thus allows for interrogation of the possible CH/ π interaction of aromatic derivatives bearing alkyl side groups in a fluid solution.

Figures 3a–c compare the β -methylene region in the ^1H -NMR spectra of BB, F8 and PF8 in $CDCl_3$ at 20°C . Two β -methylene protons of BB have multiplet signals at ≈ 1.5 – 1.6 p.p.m., whereas four β -methylene protons of F8 broaden and resonate at ≈ 0.6 p.p.m., with the upfield shift attained at ≈ 1.0 p.p.m. Four β -methylene protons of PF8 resonate at ≈ 0.7 – 0.8 p.p.m. as broadened signals, highlighted by

Figure 3 The ^1H nuclear magnetic resonance (^1H -NMR) spectra of the β -methylene region for (a) *n*-butylbenzene (**BB**), (b) di-*n*-octylfluorene (**F8**) and (c) poly(di-*n*-octylfluorene (**PF8**) in chloroform- d_1 (CDCl_3) at 20°C .

arrows that completely overlap six methyl protons of the *n*-octyl side groups, which can be seen as well-resolved triplet signals centered at 0.75 p.p.m. These upfield shifts in β -methylene protons should support the existence of the intra-CH/ π -interaction in **F8** and **PF8** in CDCl_3 at 20°C .

Although located at remote positions from the fluorene ring, the mobile terminal methyl proton signals of **F8** and **PF8** weakly shifted toward the upfield because of the ring-current effect, as shown in Supplementary Figure S1. The methyl protons of *n*-octane resonate at 0.88 p.p.m., whereas those of **F8** and **PF8** resonate at 0.81 and 0.75 p.p.m., respectively. The subtle upfield shifts of **F8** (0.07 p.p.m.) and **PF8** (0.13 p.p.m.) are because of a weak ring-current-induced shielding effect. Conversely, methyl protons of **BB** resonate at 0.93 p.p.m. and show a downfield shift of 0.04 p.p.m. because of a ring-current-induced deshielding effect.

Similarly, as shown in Supplementary Figure S1, the weak upfield shifts in the mobile methylene proton signals of aromatic **F8** and **PF8** that are due to the ring-current effect, although at remote positions from the fluorene ring, can be observed. The most intense methylene protons of *n*-octane resonate at 1.26 p.p.m., whereas those of **F8** and **PF8** resonate at 1.03 and 1.07 p.p.m., respectively. Compared with the shift of *n*-octane, the upfield shifts of **F8** and **PF8** are 0.23 and 0.19 p.p.m., respectively. Conversely, the mobile two methylenes of **BB** resonate at approximately 1.35 and show downfield shift of ≈ 0.1 p.p.m. and ≈ 0.3 p.p.m., respectively.

These subtle upfield shifts in the methyl and methylene protons of **F8** and **PF8** should mainly originate from the weak ring-current shielding effect of fluorene, not from a direct intra-CH/ π interaction. We thus assume that the methyl and methylene protons of **F8** and **PF8** are remotely located at the top and/or bottom positions of the fluorene ring, possibly reflecting the intra-CH/ π interaction between β - and/or γ -methylene protons and the fluorene ring. Indeed, because of the detection of cross-peaks between the fluorene ring and several methylene protons within **PF8** in fluid solutions by the NOESY NMR spectrum, the intra-CH/ π interaction may exist, as discussed in the following section.

^1H - ^1H NOESY NMR spectra

^1H - ^1H NOESY NMR spectroscopy⁴² of **F8** and **PF8** in solution allows for the detection of the hypothetical intra-CH/ π interaction between alkyl groups and fluorene rings and between different alkyl groups, arising from the restricted rotational freedom of the $\text{C}_9\text{--C}_\alpha\text{--C}_\beta\text{--C}_\gamma$ and fixed $\text{C}_{\text{ipso}}\text{--C}_9\text{--C}_\alpha$ bond angle, to be more directly tested.

Figures 4a and b show the NOESY NMR spectra of **F8** and **PF8** in CDCl_3 at 20°C . For comparison, the original NOESY NMR spectra of **F8** and **PF8** in CDCl_3 at 20°C are presented in Supplementary Figure S2, and the original spectrum of **BB** in CDCl_3 is presented in Supplementary Figure S3. The cross-peaks between the *n*-butyl groups and the benzene ring of **BB** cannot clearly be seen because of a very weak interaction between the alkyl groups and the ring in CDCl_3 at 20°C , indicating no detectable intra-CH/ π interaction in **BB**, as discussed above.

From Figure 4a, two major cross-peaks, highlighted by arrows in the NOESY NMR spectrum of **F8**, can clearly be seen. This suggests that the α - and β -methylene protons of *n*-octyl groups are in close contact with the fluorene ring protons in the 1,2,3,6,7,8-positions. Similarly, the three major cross-peaks due to α -, β - and γ -methylene protons suggest close contact between these species.

On the other hand, from Figure 4b, the NOESY NMR spectrum of **PF8** shows several major cross-peaks, highlighted by arrows. Major cross-peaks between broadened α -methylene protons at ≈ 2.1 p.p.m. and fluorene ring protons in the 1,3,6,8-positions are evident. Additionally, weak cross-peaks between the α -methylene protons and the β -methylene protons at ≈ 0.8 p.p.m. can be seen, whereas cross-peaks between the α -methylene protons and broadened γ -methylene protons at ≈ 1.1 p.p.m. are observed. This result is consistent with the idea that the attractive intra-CH/ π interaction of **PF8** and **F8** exists in CDCl_3 at 20°C , leading to a folded *gauche*-like geometry of *n*-octyl chains in contact with the fluorene ring, as demonstrated by the considerable upfield shift of the β -methylene proton signals because of the ring-current effect based on the J-B model.^{39,40}

Stereocenter dependency of polyfluorenes with chiral alkyl side groups at 9,9-positions

^1H -NMR spectra. In a previous paper, we compared the stereocenter dependency of the CD magnitude using **S2MO**, **S37DMO** and **R37DMO**.¹⁹ The stereocenter of **S2MO** is located at the β -position of the side group, whereas the stereocenters of **S37DMO** and **R37DMO** are in the remote γ -position. This subtle difference in the stereocenter of 9,9-alkyl groups largely affects the magnitude of Cotton CD signals in solutions. Although **S2MO** in THF shows considerably intense CD signals at room and elevated temperatures, **S37DMO** and **R37DMO** in THF do not show any detectable CD signals at 50°C and exhibit intense CD signals at -80°C .¹⁹ However, the reason for this stereocenter dependency remains an unresolved issue to date. Keeping in mind the intra-CH/ π interaction of **PF8** and **F8** discussed above, we revisited **S2MO**, **S37DMO** and **R37DMO** with the help of advanced ^1H - ^1H NOESY and ^1H -NMR spectroscopy and CD/UV-vis spectroscopy with high sensitivity.

Figures 5a and b and Supplementary Figure S4 present the ^1H -NMR spectra of **S2MO**, **S37DMO** and **R37DMO** in CDCl_3 at 20°C . Four α -methylene protons of **S2MO** are split into two broader signals of an equal intensity at 2.00 and 2.28 p.p.m., indicating magnetically nonequivalent and diastereotopic protons. This feature is in contrast to a broad signal located at 2.13 p.p.m. that is due to magnetically equivalent α -methylene protons of **S37DMO** and **R37DMO**.

Figure 4 Contour plots from the 2D ^1H - ^1H NOESY NMR spectra of (a) **F8** and (b) **PF8** in chloroform- d_1 (CDCl_3) at 20°C showing the inter-residual cross-peaks that contact between the fluorene ring protons and the α - and β -methylene protons of the *n*-octyl groups.

Figure 5 Aliphatic regions from the ^1H nuclear magnetic resonance (^1H -NMR) spectra of (a) **S2MO** and (b) **S37DMO** in chloroform- d_1 (CDCl_3) at 20 $^\circ\text{C}$.

A more notable difference between the (S)-2-methyl proton signals in **S2MO** and the (S)-3-methyl proton signals in **S37DMO** (and **R37DMO**) can be seen. The (S)-2-methyl protons generating a doublet signal due to H- C_β methine protons resonate at 0.37 and 0.36 p.p.m., along with several additional signals in the upfield region of ≈ 0.3 p.p.m. In contrast, the (S)-3-methyl protons generating a doublet signal due to H- C_γ methine protons resonate at 0.75 and 0.77 p.p.m., along with the sharper triplet signals of terminal mobile termini methyl protons in the downfield region of ≈ 0.8 p.p.m. The upfield shift because of the (S)-2-methyl protons is much greater than that of the (S)-3-methyl protons. This behavior suggests that the marked upfield shift of the (S)-2-methyl protons of **S2MO** originates from an intense intra-CH/ π interaction, whereas the upfield shift of the (S)-3-methyl protons of **S37DMO** originates solely from a ring-current shielding effect and/or a weaker chiral intra-CH/ π interaction because of the long distance between the (S)-3-methyl proton and a fluorene ring. However, it is unclear whether the γ -/ δ -methylene and β -methine protons of **S2MO** and β -/ δ -methylene and γ -methine protons of **S37DMO** contact a fluorene ring because of the high complexity of ^1H -NMR spectra.

For comparison, Supplementary Figures S5a–m displays the aliphatic region in the ^1H -NMR spectra of **S2MO**, **S37DMO**, **R37DMO** and **PF8** in CDCl_3 , $\text{MCH-}d_{14}$, $\text{THF-}d_8$ and $\text{TOL-}d_8$, respectively. Similar upfield shifts of the β -methylene and (S)-2-/ (S)-3-methyl proton signals induced by the fluorene ring current can be seen, indicating the existence of a similar intra-CH/ π interaction in these deuterated solvents at 20 $^\circ\text{C}$.

^1H - ^1H NOESY NMR spectra. Additionally, the NOESY technique⁴² more directly allows for the detection of the chiral intra-CH/ π interaction arising from the closest contacts between chiral alkyl groups and fluorene rings, reflecting the fixed $\text{C}_8\text{-C}_{\text{ipso}}\text{-C}_9\text{-C}_\alpha$ dihedral angle and the restricted rotational freedom of $\text{C}_9\text{-C}_\alpha\text{-C}_\beta\text{-C}_\gamma$ bonds. Figures 6a and b show the NOESY NMR spectra of **S2MO** and **S37DMO** in CDCl_3 at 20 $^\circ\text{C}$. For comparison, the spectrum of

R37DMO, which is similar to that of **S37DMO**, is presented in Supplementary Figure S6.

It is evident from Figure 6a that at least five cross-peaks between the fluorene ring and (S)-2-methyloctyl groups exist. The split α -methylene protons at 2.00 and 2.28 p.p.m. strongly interact with the 1,3,6,8-ring protons of fluorene at ≈ 7.6 p.p.m. and weakly interact with the 4,5-ring protons at ≈ 7.7 p.p.m. It is also clear that both the (S)-2-methyl protons at ≈ 0.3 p.p.m. and γ -methylene protons at ≈ 0.7 – 0.8 p.p.m. also strongly interact with the 1,3,6,8-ring protons and weakly interact with the 4,5-ring protons. The β -methylene protons are difficult to identify because of a high degree of overlap of several proton signals. The (S)-2-methyl proton at ≈ 0.3 p.p.m. of **S2MO** may be shifted upfield by ≈ 0.45 – 0.47 p.p.m. relative to the (S)-3-methyl protons of **S37DMO** at 0.75–0.77 p.p.m. Surprisingly, the γ -methylene protons, which may also split into two signals, resonating at ≈ 0.9 and 1.1 p.p.m., appear to strongly interact with the 1,3,6,8-ring protons and weakly interact with the 4,5-ring protons. The γ -methylene protons, as well as the α -methylene protons, may thus become magnetically nonequivalent and diastereotopic. These five cross-peaks support the existence of an intense intra-CH/ π interaction between the fluorene ring and (S)-2-methyloctyl groups.

As shown in Figure 6b, at least four cross-peaks between the fluorene ring and (S)-3,7-dimethyloctyl groups also exist. The broader α -methylene protons at ≈ 2.13 p.p.m. weakly interact with the 1,3,6,8-ring protons. The (S)-3-methyl protons at 0.75 p.p.m. and 0.77 p.p.m., although difficult to definitively identify, interact with the 1,3,6,8-ring protons and weakly interact with the 4,5-ring protons. The β -methylene protons at ≈ 0.7 p.p.m. interact with the 1,3,6,8-ring protons. These four cross-peaks support the existence of an intra-CH/ π interaction between the fluorene ring and several C-H protons of the (S)-3,7-dimethyloctyl groups.

S2MO, **S37DMO** and **R37DMO** commonly provide the cross-peaks between the several alkyl and ring protons in the contour plots. However, the subtle difference in the stereocenter of the chiral side chains greatly affects the magnitude of the Cotton CD bands in the π - π^* region in chloroform at 20 $^\circ\text{C}$, as shown in the following section.

Figure 6 Contour plots from the two-dimensional ^1H - ^1H nuclear overhauser enhancement (NOE) correlated spectroscopy (NOESY) nuclear magnetic resonance (2D ^1H - ^1H NOESY NMR) spectra of (a) **S2MO** and (b) **S37DMO** in chloroform- d_1 (CDCl_3) at 20°C showing the inter-residual cross-peaks that contact between the fluorene ring protons and the α -, β -, γ -methylene protons and between the fluorene ring protons and the (S)-2-/(S)-3-methyl protons of chiral alkyl groups.

CD-/UV-vis spectra in chloroform. Figures 7a and b display the CD and UV-vis spectra of **S2MO**, **S37DMO** and **PF8** in CHCl_3 at 20 °C. For comparison, Supplementary Figure S7 presents the CD and UV-vis spectra of **R37DMO** in CHCl_3 at 20 °C. **S2MO** shows large positive Cotton CD bands at 380 and 310 nm that correspond to the π - π^* transition and, possibly, adopt the 5_2 helical conformation with preferential *right*- or *left*-handed screw-sense.^{14–19,22} However, regardless of the chiral alkyl substitution at the 9,9-position, **S37DMO** and **R37DMO** do not show any detectable Cotton CD bands at 380 and 310 nm, reconfirming our previously reported results in dilute THF.¹⁹

Thus, the β -position at the stereocenter of the chiral side chain is required to induce optical activity in the floppy PF main chain in a fluid solution, whereas the γ -branched chiral side chains do not provide any detectable chiroptical induction effects. As revealed by the cross-peaks in the NOESY NMR spectra and the large upfield shift signals from the ^1H -NMR spectra of **S2MO**, the intense intra-CH/ π interaction between the fluorene ring and (S)-2-methyloctyl group should induce a certain helical conformation with a preferential screw direction. The appearance and disappearance of optical activity in PF bearing chiral substituents in a fluid solution can be explained by the fact that the α -methylene protons of the side chains are magnetically nonequivalent and surrounded by a diastereotopic environment.

S37DMO, **R37DMO** and **PF8** in CHCl_3 at 20 °C are in CD-silent stiff helical conformational states with an equal probability of

producing a right- or left-handed helix because the λ_{max} values are almost identical to each other.¹⁹ The persistence length (q) of **S37DMO** in THF at 20 °C has been determined to be 9.5 nm.²² This q -value, responsible for the efficiency in chiral amplification, is similar to that of other PFs bearing alkyl side chains: $q = 8.5$ nm for **PF8** in THF (40 °C)²³ and $q = 7$ nm for PF carrying 2-ethylhexyl groups in toluene at 20 °C.²⁴ These PFs are as stiff as some aromatic polyamides and cellulose derivatives and stiffer than typical randomly coiled flexible polystyrene ($q = 1$ nm), but they are more flexible than typical stiff poly(*n*-hexylisocyanate) ($q = 42$ nm) in *n*-hexane at 25 °C.⁴³ However, CD-silent **S37DMO** and **R37DMO** in CHCl_3 at 20 °C may possibly yield optically active PF particles during aggregation with the help of poorer alcoholic solvents. Results supporting this notion are likely to be reported in the future.

Computational simulation

MP2 calculations using Gaussian 03 (6-311G(d) basis set)²⁸ <http://www.gaussian.com> and Conflex7 (MMFF94s force field)^{26,27} <http://www.conflex.us> also support the existence of the intra-CH/ π interaction between (S)-2-methyl/ β -methylene protons and the fluorene ring in **S2MO** and **PF8**. First, Figures 8a–c show the possible folded *gauche*-like conformers of (a) 9-ethyl-9-*n*-pentyfluorene (**EPF**), (b) 9-ethyl-9-(S)-2-methylpentyfluorene (**ES2MPF**) and (c) 9-ethyl-9-(S)-3-methylpentyfluorene (**ES3MPF**) (Figure 1), respectively, generated using Conflex7. **EPF**, **ES2MPF** and **ES3MPF** are simplified molecular models of **PF8**, **S2MO** and **S37DMO**, respectively.

Regarding **EPF**, conformer (a) depicts intra-CH/ π interactions with a distance of 2.64 Å between β -methylene protons and *ipso*-carbons. This distance is shorter than the closest vdW contact distance of 2.90 Å by ≈ 0.26 Å.^{44,45} In this case, the β -methylene protons and 1,3,4-carbons of the fluorene ring attract each other by a weak Coulombic interaction because the Mulliken charges of β -methylene protons and ring carbons are oppositely charged, +0.228 and $-0.238/-0.215/-0.227$, respectively. This picture is also applicable when accounting for the achiral intra-CH/ π interaction between the β -methylene protons and fluorene ring of **PF8** and **F8**.

As for **ES2MPF**, conformer (b) shows two possible chiral intra-CH/ π interactions at ≈ 2.54 Å between the (S)-2-methyl proton and *ipso*-carbons of the ring and at ≈ 2.53 Å between the β -methine proton and *ipso*-carbon. These distances are shorter than the closest vdW contact distance of 2.90 Å by ≈ 0.36 Å and ≈ 0.37 Å, respectively.^{44,45} The (S)-2-methyl proton is slightly more favorable than the β -methine proton because the Mulliken charges of the (S)-2-methyl and the β -methine protons are +0.258 and +0.237, respectively, whereas those of the 1,3,4-ring carbons are $-0.228/-0.205/-0.247$. The same idea is applicable to the chiral intra-CH/ π interaction between the (S)-2-methyl protons and the fluorene ring of **S2MO**.

We noted that conformer (c) of **ES3MPF** shows two possible intra-CH/ π interactions at ≈ 2.57 Å and ≈ 2.67 Å between the β -methylene protons and *ipso*-carbons. These distances are shorter than the closest vdW contact distance of 2.90 Å by ≈ 0.33 Å and ≈ 0.23 Å, respectively.^{44,45} A distance of ≈ 2.88 Å between the terminus methyl proton and the *ipso*-carbons of the ring may be because of vdW contact, leading to an upfield shift due to the ring-current effect. Note that the distance between the (S)-3-methyl protons and the *ipso*-carbon is unexpectedly long (4.55 Å). However, the (S)-3-methyl and β -methylene protons can be attracted by 1,3,4-carbons because the Mulliken charges of the (S)-3-methyl and β -methylene protons are +0.207 and +0.232/+0.248, respectively, and those of the 1,3,4-ring carbons are $-0.240/-0.215/-0.225$. These results may lead to considerably reduced chiral intra-CH/ π interactions between (S)-3-

Figure 7 The circular dichroism (CD) and ultraviolet-visible (UV-vis) spectra of (a) **S2MO** and **S37DMO** and (b) **PF8** in CHCl_3 at 20 °C.

Figure 8 Folded *gauche*-like intramolecular CH/ π interactions of optimized (a) EPF, (b) ES2MPF and (c) ES3MPF conformers with Mulliken charges on several alkyl protons and fluorene ring carbons.

methyl protons and the fluorene ring, thus accounting for the intra-CH/ π interactions of **S37DMO** and **R37DMO**.

Crystallographic analysis of a fluorene dimer bearing four *n*-propyl groups at the 9,9,9',9'-positions⁴⁶ (**F3-dimer** in Figure 1) provides clearer evidence of the folded *gauche*-like geometry of the fluorene ring covered with β -methylene protons in the solid, possibly due to the existence of the intra-CH/ π interaction. A similar folded *gauche*-like geometry for the fluorene ring covered with β -methylene protons can be seen in a solid crystal of fluorene molecules with 2,7-thiophene substituents bearing two *n*-octyl groups at the 9,9-positions,⁴⁷ which is an analog of **F8**. These crystallographic data^{46,47} clearly indicate that several fluorenes capped with β -methylene protons in their molecular crystals may be common and that the folded *gauche*-like geometry is one of the most favorable geometries, possibly because of the existence of the intra-CH/ π interaction.^{1–5}

This tendency agrees well with the magnitudes of the upfield shifts seen in the NMR spectra of **F8**, **PF8**, **S2MO** and **S37DMO** mentioned above. The shortest intra-CH/ π distance of **ES2MPF**, inducing an intense ring-current effect, is believed to afford the ≈ 0.6 p.p.m. upfield shift of the (S)-2-methyl protons of **S2MO**; moreover, the shortest intra-CH/ π distance of **EPF**, which also induces an intense ring-current effect, affords the ≈ 1.0 p.p.m. upfield shift of **PF8** and the ≈ 0.6 – 0.7 p.p.m. upfield shift of **F8**. However, the longer intra-CH/ π distance of **ES3MPF** might only effect an ≈ 0.18 p.p.m. upfield shift of the (S)-3-methyl protons of **S37DMO**.

Perspectives

We have deduced the origin of the intense photoluminescence of **PF** derivatives bearing alkyl side chains in aggregate and solid films.^{12–19,48–51} Although most π -conjugated molecules and polymers dissolved in a dilute solution are highly emissive,^{8–21,48–54} their solid films and aggregates in solution often form nonemissive, face-to-face π – π stacking structures. Among several π -conjugated molecules and polymers,^{8–25,48–51} **PF** derivatives and their copolymers are exceptionally emissive in the form of solid films and aggregates with a high quantum efficiency (Φ_F) of ≈ 0.9 . Based on ¹H-NMR studies and the theoretical calculations discussed above, the existence of alkyl side chains at the 9,9-position is the key to efficiently cover one side and/or both sides of the fluorene ring due to the *gauche*-like geometry of the *forced* intra-CH/ π interaction. This self-wrapping by *n*- and/or branched alkyl groups prevents the formation of face-to-face, intermolecular fluorene ring π – π stacks in solid films and aggregates.^{48–53} The introduction of the *forced gauche*-like intra-CH/ π

interaction into other π -conjugated aromatic polymers and molecules should provide a new way of preventing unfavorable face-to-face π – π stacks.

When the *forced* chiral intra-CH/ π interaction using chiral α -/ β -/ γ -branched chains is applied to π -conjugated aromatic systems, the resulting materials may emit strong circularly polarized light because of *J*-type slipped helical π – π stacks in the solid film and aggregate states. If the *forced* achiral intra-CH/ π interaction with achiral α -/ β -/ γ -branched and *n*-alkyl chains and/or bulky aromatic substituents is applied, the resulting films and aggregates would be highly emissive with loss of the optical activity.

Recently, Yamaguchi *et al.*⁵⁴ designed 3-boryl-2,2'-bithiophene derivatives exhibiting an intense emission with very high Φ_F values of 0.30–0.87 in the solid state by introducing a bulky dimesitylboryl substituent to a bithiophene skeleton. The ORTEP (Oak Ridge Thermal Ellipsoid Plot) drawing of the bithiophene crystal suggested the existence of forced intra-CH/ π interactions between the methyl group and the benzene ring within two mesityls and between two methyl groups of the mesityl and bithiophene ring.⁵⁴ We assume that the forced intra-CH/ π interactions in the bithiophenes are responsible for the high Φ_F .

CONCLUSION

We tested the possibility of intra-CH/ π interactions existing in **S2MO**, **S37DMO**, **R37DMO** and **PF8** and, for comparison, **F8**, **BB** and *n*-octane under fluidic conditions at 20 °C by 2D ¹H–¹H NOESY and ¹H-NMR. Regarding **S2MO**, **S37DMO**, **R37DMO**, **PF8** and **F8**, the 2D NMR revealed several cross-peaks between the fluorene ring and alkyl side chains, revealing the intra-CH/ π interaction between the fluorene ring and α -/ β -/ γ -methylene and (S)-2-/(S)-3-/(R)-3-methyl protons in the alkyl side chains, regardless of chiral and achiral alkyl groups and regardless of polymer and molecular structures. In the 1D NMR spectra, marked upfield shifts of several proton signals because of the alkyl groups of **S2MO**, **S37DMO**, **R37DMO**, **PF8** and **F8**, relative to the spectra of **BB** and *n*-octane, were consistent with these cross-peaks in the 2D NMR spectra. Among these chiral **PFs**, only **S2MO** showed intense cross-peaks in its 2D NMR spectra and large upfield shifts in the signals of (S)-2-methyl protons in its 1D NMR spectra. **S2MO** provided magnetically nonequivalent, diastereotopic α -methylene protons with doublet signals. CD spectroscopic data reconfirmed the notion that the β -position at the stereocenter of the side chain, (S)-2-methyloctyl group, is required to induce optical activity in the **PF** main chain in a fluid solution, whereas the

γ -branched (S)-3,7-dimethyloctyl and (R)-3,7-dimethyloctyl did not induce any detectable CD signals under the same conditions. This tendency is consistent with the magnitudes of the cross-peaks in the 2D NMR spectra and the upfield shifts in the 1D NMR spectra. Theoretical calculations performed using Confelx7 and Gaussian 03 at the MP2 level (6-311G(d) basis set) also supported these upfield shifts in the NMR spectra, indicating that the folded *gauche*-like geometry is because of the attractive intra-CH/ π interactions.

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