

Communication

Synthesis of a Highly Luminescent Three-Dimensional Pyrene Dye Based on the Spirobifluorene Skeleton

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Abstract: We have synthesized a highly luminescent ($\log \epsilon > 5.0$, $\Phi > 0.9$) pyrene dye based on a spirobifluorene skeleton [2,2',7,7'-tetrakis(7-*tert*-butyl-1-pyrenyl)-9,9'-spirobi[9H-fluorene; **4-PySBF**]. The use of spirobifluorene prevents fluorescence quenching by intramolecular energy transfer and/or electron transfer among the chromophores in the excited state. The emission spectra of **4-PySBF** exhibited a red shift of 20 nm in comparison to a model compound [9,9'-dioctyl-2,7-bis(7-*tert*-butyl-1-pyrenyl)-9H-fluorene; **2-PyF**], but its UV-Vis spectrum remained unchanged.

Keywords: Spirobifluorene; pyrene; fluorescence; π -conjugation; dye

Introduction

Recently, blue emitting dyes with high efficiency ($\Phi \approx 1.0$, $\log \epsilon > 4.5$) [1] have been attracting considerable attention because of their applicability to molecular electronic materials such as organic field effect transistors (OFETs) and organic light-emitting diodes (OLEDs). Many studies have been conducted on strategies for synthesizing a highly efficient dye. For example, rod- [1,2] and star-shaped [3-6] hydrocarbons that expand π -conjugation to two dimensions can be used to control the emission color of a dye with high efficiency.

Spirobifluorene derivatives are considered the most promising candidates for organic optoelectronics [7-11]. The rigidity of spiro-compounds affords them high thermal stability. In addition, their solubility is higher than that of corresponding compounds without a spiro moiety,

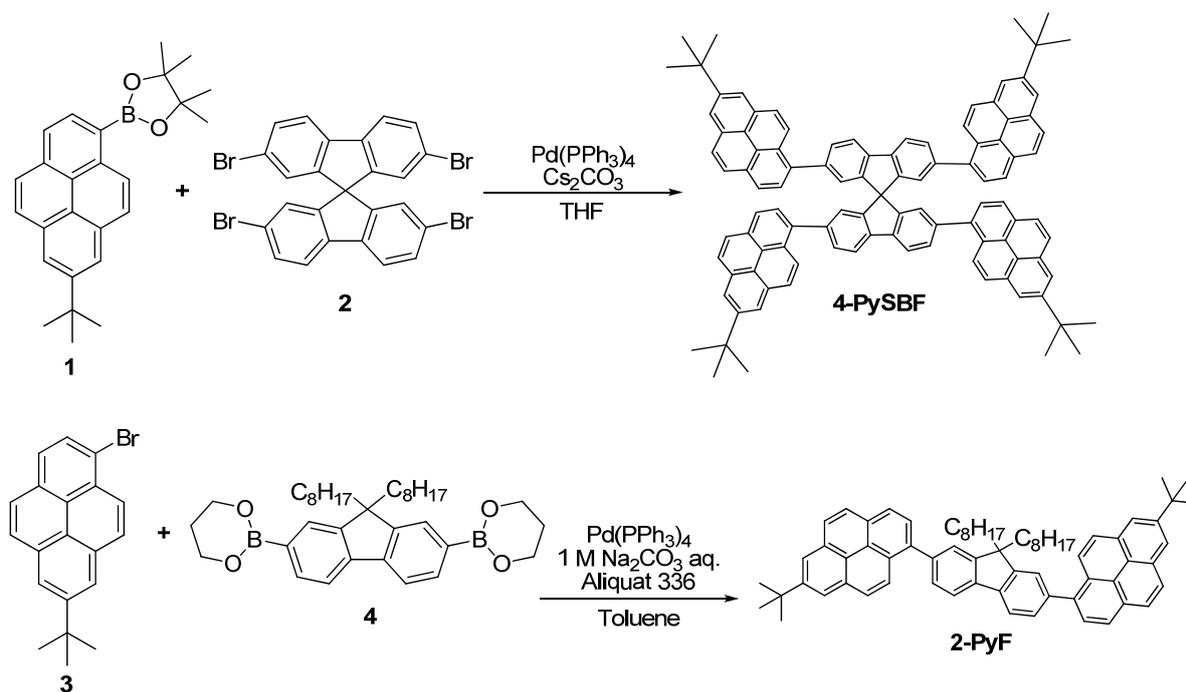
because their perpendicular conformations that are based on the spiro-linkage efficiently suppress intermolecular interactions between π -systems. Recently, several studies were conducted on introducing dyes into a molecule for π -conjugation in three dimensions. Examples of such studies include those on the introduction of dyes into the spirobifluorene skeleton [12-19]. Because of the high thermal stability and unique characteristics of the spirobifluorene skeleton, it has been adopted in various materials [20-22].

In this paper, we report the synthesis and characterization of a new pyrene dye that is based on the spirobifluorene skeleton. Pyrene derivatives are highly absorptive [23-26]; further, the introduction of pyrene substituents into spirobifluorene derivatives is expected to improve the fluorescence quantum yield and thermal stability of the derivatives because the substituents are highly emissive, bulky, and rigid.

Results and Discussion

A spirobifluorene dye, 2,2',7,7'-tetrakis(7-*tert*-butyl-1-pyrenyl)-9,9'-spirobi[9H-fluorene] (**4-PySBF**), and a model compound, 9,9'-dioctyl-2,7-bis(7-*tert*-butyl-1-pyrenyl)-9H-fluorene (**2-PyF**), were synthesized in 37% and 24% yields, respectively, by palladium-catalyzed Suzuki-Miyaura coupling reactions (Scheme 1). The precursors, 7-*tert*-butylpyrene-1-boronic acid pinacol ester (**1**) and 1-bromo-7-*tert*-butylpyrene (**3**), were prepared from pyrene according to a previously reported method [27]. The chemical structures of **4-PySBF** and **2-PyF** were confirmed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FT-IR spectroscopy. Each compound was found to be soluble in various organic solvents such as chloroform, tetrahydrofuran (THF), dichloromethane, and toluene. It should be noted that the *tert*-butyl group is necessary for the successful synthesis of **4-PySBF**; we found that without *tert*-butyl groups, the solubility is quite poor, making purification and structural analysis by techniques such as $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ rather difficult.

Scheme 1. Synthesis of spirobifluorene dye and model compound.



We measured the UV-Vis spectra, fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes, and lifetimes of **4-PySBF** and **2-PyF** in CH_2Cl_2 solution. The UV-Vis spectra (Figure 2, left side) show that the absorption maxima (λ_{max}) of **4-PySBF** and **2-PyF** are at 360 nm and 359 nm, with molar absorption (λ_{max}) coefficients ϵ of 131,000 and 71,000 $\text{M}^{-1} \text{cm}^{-1}$, respectively. The finding that the ϵ value of **4-PySBF** is about twice that of **2-PyF** is in accordance with the fact that **4-PySBF** has two chromophores per molecule whereas **2-PyF** has but one.

The observed fluorescence spectra (Figure 2, right side) show that **4-PySBF** and **2-PyF** exhibit intense blue emissions (λ_{em}) at 441 nm ($\Phi = 0.92$) and 421 nm ($\Phi = 0.90$), respectively, in CH_2Cl_2 solution ($\lambda_{\text{ex}} = 360 \text{ nm}$; $c = 1.0 \times 10^{-6} \text{ M}$). The fluorescence spectra also reveal that the fluorescence intensity of **4-PySBF** is about twice that of **2-PyF**, again because **4-PySBF** has two chromophores per molecule. A 20-nm red-shift between **4-PySBF** and **2-PyF** was observed. It is noted that we observed a spiroconjugation (a large red shift in the fluorescence spectrum and no red shift in the absorption spectrum in this **4-PySBF** and **2-PyF** pair). We hypothesize that this observed red-shift could be due to conjugation of **4-PySBF** *via* the spiro carbon [28-32] in the excited state [33]. Another possibility is a through-space interaction between upper and lower pyrene chromophores.

Figure 1. Absorption and emission spectra of **2-PyF** and **4-PySBF** in CH_2Cl_2 ; $c = 10 \mu\text{M}$, $\lambda_{\text{ex}} = 360 \text{ nm}$.

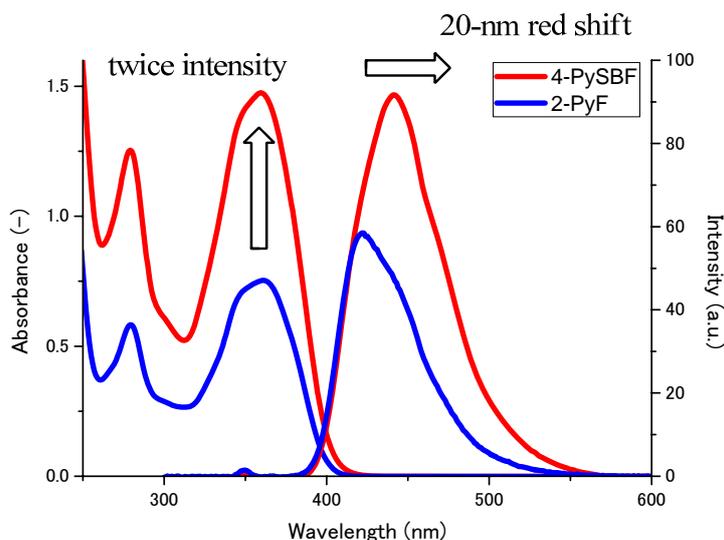


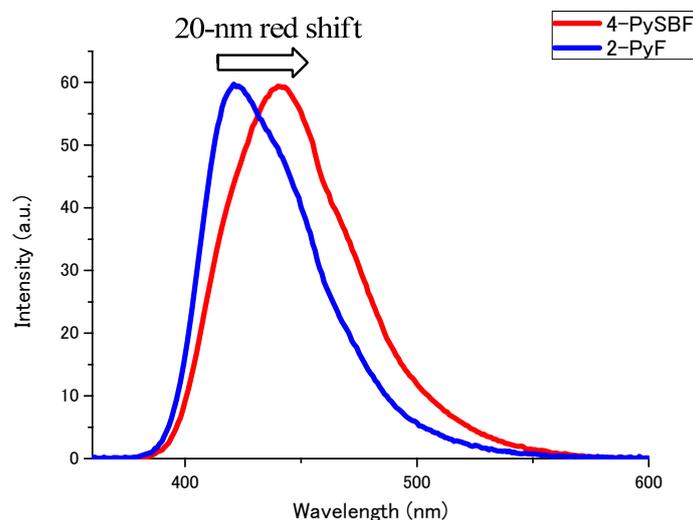
Table 1. Photochemical data for compounds **4-PySBF** and **6**.

dye	λ_{ab} [nm]	$\epsilon (\times 10^5)$ [l/mol·cm]	$\log \epsilon$	λ_{em} [nm]	Φ	τ [ns]	$k_f (\times 10^8)$ [S^{-1}]	$k_{\text{isc}} + k_{\text{nr}}$ ($\times 10^7$) [S^{-1}]
4-PySBF	360	1.31	5.12	441	0.92	1.52	6.1	5.3
2-PyF	359	0.71	4.85	421	0.90	1.88	4.8	5.3

Measurement of the photophysical properties of both compounds at the same concentration confirm that **4-PySBF** had twice the number of chromophores in solution as compared to **2-PyF**. Next, we measured the fluorescence spectra of both compounds under the same absorption conditions. We then found that the solutions of **4-PySBF** and **2-PyF** had the same number of chromophores. The fluorescence spectra (Figure 3) revealed that both **4-PySBF** and **2-PyF** had approximately the same

fluorescence intensity. This result shows that the spirobifluorene derivatization doubled the performance of the chromophores by preventing intramolecular energy transfer and/or electron transfer, although the pyrene chromophores are placed close together. The compound **4-PySBF** was found to have ideal luminescence properties ($\log \epsilon > 5.0$, $\Phi > 0.9$).

Figure 2. Emission spectra of **2-PyF** and **4-PySBF** in CH_2Cl_2 ; Abs = 0.1, $\lambda_{\text{ex}} = 360$ nm.



Fluorescence quantum yield can be expressed as $\Phi_f = k_f \tau_s$, or $\Phi_f = k_f / (k_f + k_{\text{isc}} + k_{\text{nr}} + k_{\text{q}}[\text{O}_2])$, where k_f , k_{isc} , k_{nr} , and $k_{\text{q}}[\text{O}_2]$ denote the rate constants for fluorescence radiation, intersystem crossing, nonradiative decay, and fluorescence quenching by oxygen, respectively, and τ_s denotes the lifetime ($s = \text{singlet}$) [14]. Table 1 summarizes the values of k_f and $k_{\text{isc}} + k_{\text{nr}}$ for **4-PySBF** and **2-PyF**, calculated from the experimental values of Φ_f and τ_s under degassed conditions, that is, under the assumption that $k_{\text{q}}[\text{O}_2] = 0$. As k_{nr} for aromatic hydrocarbons is known to be negligible [34], k_{isc} should be the dominant component in $k_{\text{isc}} + k_{\text{nr}}$ [35–38]. Under aerated conditions, $k_{\text{q}}[\text{O}_2]$ is estimated to be nearly diffusion controlled (up to $3.89 \times 10^{10} \text{ m}^{-1} \text{ s}^{-1}$ in hexane) [34,39], and $[\text{O}_2]$ is less than $2.0 \times 10^{-3} \text{ M}$ in usual solvents. These data imply that the maximum possible value of $k_{\text{q}}[\text{O}_2]$ is $8.0 \times 10^7 \text{ s}^{-1}$. As can be seen from Table 1, the k_f values for **4-PySBF** and **2-PyF** are much larger than the $k_{\text{q}}[\text{O}_2]$ values. This situation is most probably responsible for the observed large values of Φ_f for both compounds, even in the presence of oxygen.

Conclusions

In summary, we have synthesized a highly luminescent spirobifluorene dye ($\log \epsilon > 5.0$, $\Phi > 0.9$) with tetrapylene chromophores (**4-PySBF**) and measured its photophysical properties. In comparison to a model compound, **2-PyF**, the emission spectrum of **4-PySBF** exhibited a red shift of 20 nm, but its UV-Vis spectrum remained unchanged. It is not easy to find a satisfactory explanation for this observed red-shift at the present stage. However, in our next study, we intend to calculate the electron states of these compounds in the ground and excited states by the molecular orbital (MO) method and examine this conjugation system in greater detail. Further, we intend to apply **4-PySBF** in a previously developed cholesteric liquid crystal laser (distributed feedback laser) as the laser dye in the future.

Experimental

Instruments

All the ^1H - and ^{13}C -NMR spectra were recorded on a 400 MHz JEOL LMN-EX400 instrument with tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded on a JASCO FT-IR 469 plus spectrometer. Melting points were obtained by a Stuart Scientific Melting Point Apparatus SMP3. MS spectra (FAB) were obtained by JEOL JMS700 mass spectrometer. UV-Vis spectra were recorded with a Beckman Coulter DU800 UV-Vis Spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 Spectrofluorometer. Quantum Yields were measured by a Hamamatsu Photonics C9920-02 Absolute PL Quantum Yield Measurement system. Fluorescence lifetimes were measured using a Hamamatsu Photonics OB 920 Fluorescence Lifetime Spectrometer.

Materials

Unless otherwise noted, all reagents, chemicals and solvents were obtained from commercial sources and used without further purification. Pyrene, 2-chloro-2-methylpropane, $\text{Pd}(\text{PPh}_3)_4$, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane were obtained from TCI. 9,9-Dioctyl-fluorene-2,7-bis(trimethyleneborate) (**4**) and $\text{PdCl}_2(\text{PPh}_3)_2$, were obtained from Aldrich. 2,2',7,7'-Tetrabromospirobifluorene (**2**) was a gift of JFE Chemical Coporation (Japan).

2,2',7,7'-tetrakis(7-tert-Butyl-1-pyrenyl)-9,9'-spirobi [9H-fluorene] (**3**, **4-PySBF**)

Under an argon atmosphere, 2,2',7,7'-tetrabromospirobifluorene (0.25 g, 0.4 mmol), 7-tert-butylpyrene-1-boronic acid pinacol ester (0.77 g, 2.0 mmol) and cesium carbonate (5.21 g, 16 mmol) were mixed together with $\text{Pd}(\text{PPh}_3)_4$ (100 mg, 0.1 mmol) and degassed THF (30 mL). The mixture was refluxed for 24 h. After cooling to room temperature, the resulting mixture was extracted with chloroform. The organic extract was washed sequentially with water and brine and then dried over MgSO_4 . After removal of the solvent, the residue was purified by column chromatography (chloroform:hexane = 1:5) and preparative HPLC (CHCl_3). After removal of the solvent, the product was recrystallized from cyclohexane to afford **4-PySBF** as a yellow powder in 37% yield. ^1H -NMR (400 MHz, THF-d_8): δ 8.23–7.36 (m, Ar-H, 44H), 1.53 (s, *tert*-butyl-H, 36H) ppm.; ^{13}C -NMR (100 MHz, CDCl_3): δ 149.3, 149.1, 140.9, 140.7, 137.4, 131.3, 130.7, 130.5, 130.3, 128.4, 128.2, 128.1, 127.7, 127.5, 127.3, 127.2, 126.5, 125.0, 124.9, 124.4, 123.1, 122.4, 122.0, 120.2 (aromatic C), 66.3 (spiro-C), 35.2 (Ar-C (CH_3)₃), 31.9 (Ar-C (CH_3)₃) ppm; FT-IR (KBr): 3042, 2961, 2901, 2867, 1594, 1457, 1227 cm^{-1} ; mp 286–288 °C; HR-MS (FAB⁺) Calcd. for $\text{C}_{105}\text{H}_{80}$ [M] 1341.6294, found [M⁺] 1341.6290.

9,9'-Dioctyl-2,7-bis (7-tert-butyl-1-pyrenyl)-9H-fluorene (**6**, **2-PyF**)

Under an argon atmosphere, 2-bromo-7-tert-butylpyrene (0.8 g, 2.4 mmol) and 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) (0.28 g 0.5 mmol) were mixed together with $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.05 mmol), degassed toluene (20 mL), one drop of Aliquat 336, and 1M aqueous sodium carbonate solution (2 mL). The resulting mixture was refluxed for 24 h. After cooling to room

temperature, the mixture was extracted with chloroform. The organic extract was washed sequentially with water and brine and then dried over MgSO_4 . After removal of the solvent, the residue was purified by column chromatography using chloroform/hexane (5:1, v/v) following HPLC (CHCl_3). After subsequent recrystallization in ethanol, **2-PyF** was obtained as a yellow powder in 24% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.27–7.97 (m, Ar-H, 18H), 7.69–7.67 (m, Ar-H, 4H), 2.12–2.08 (s, Ar-CH-Ar, 2H), 1.60 (s, *tert*-butyl-H, 18H), 1.25–1.19 (m, alkyl-H, 20H), 0.96 (m, alkyl-H, 4H), 0.82 (t, $J = 6.84$, alkyl-H, 6H) ppm; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 151.2, 149.1, 140.1, 140.0, 138.1, 131.4, 130.9, 130.4, 129.4, 128.4, 127.6, 127.5, 127.3, 125.4, 125.3, 125.0, 124.5, 123.2, 122.4, 122.0, 119.8 (aromatic C), 55.3 (spiro-C), 40.4 (alkyl-C), 35.2 (Ar-C (CH_3)₃), 31.9 (Ar-C (CH_3)₃), 30.1, 29.7, 29.4, 29.3, 24.2, 22.7, 14.2 (alkyl-C) ppm; FT-IR (KBr): 3050, 2953, 2925, 2853, 1608, 1481, 1457, 1310 cm^{-1} ; mp 206–208 °C; HR-MS (FAB⁺) calcd. for $\text{C}_{69}\text{H}_{74}$ [M] 902.5791, found [M⁺] 902.5786.

Acknowledgements

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Appendix

$^1\text{H-NMR}$ and $^{13}\text{C NMR}$ spectra of **3** and **6**

Figure S1. $^1\text{H-NMR}$ spectrum of 2,2',7,7'-tetrakis(7-*tert*-butyl-1-pyrenyl)-9,9'-spirobi [9H-fluorene] (**4-PySBF**, 400 MHz, THF-d_8).

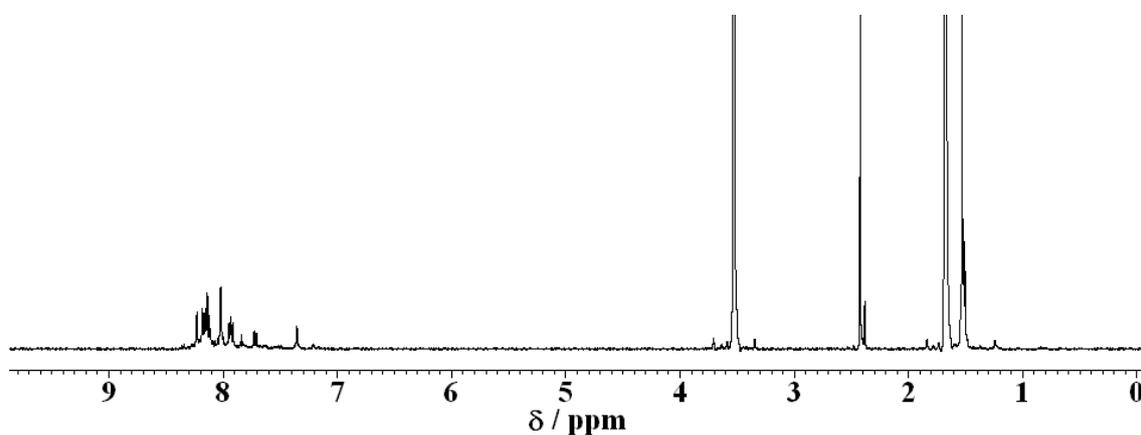


Figure S2. ^{13}C -NMR spectrum of 2,2',7,7'-tetrakis(7-*tert*-butyl-1-pyrenyl)-9,9'-spirobi[9H-fluorene] (**4-PySBF**, 100 MHz, CDCl_3).

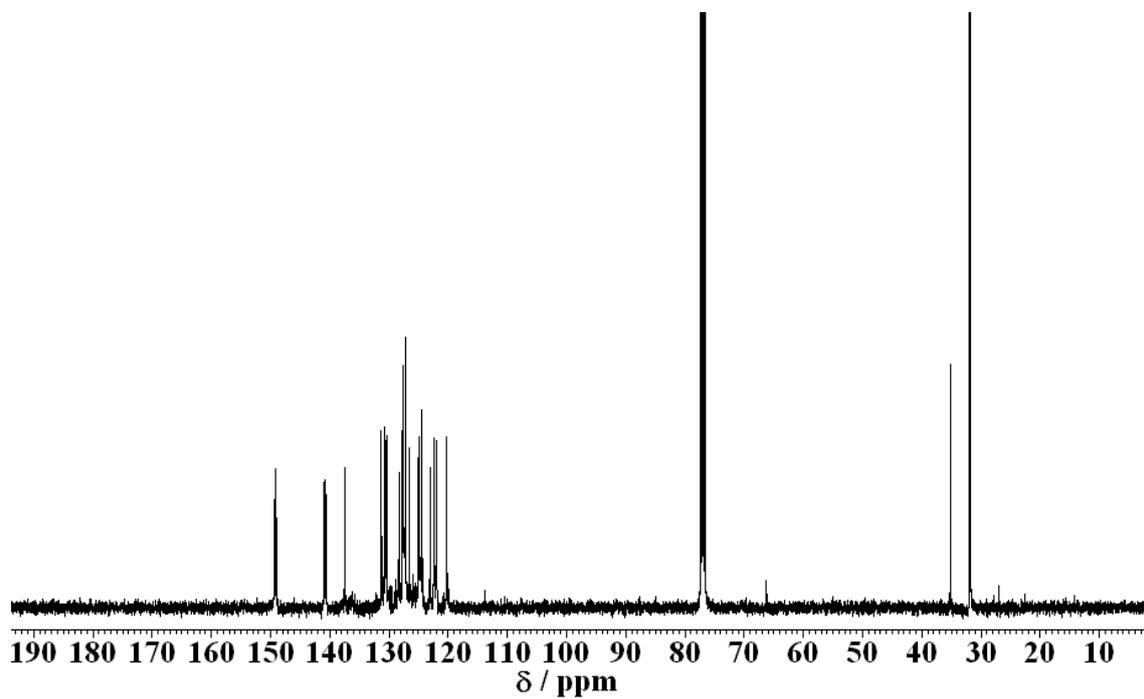


Figure S3. ^1H -NMR spectrum of 9,9'-dioctyl-2,7-bis(7-*tert*-butyl-1-pyrenyl)-9H-fluorene (**2-PyF**, 400 MHz, CDCl_3).

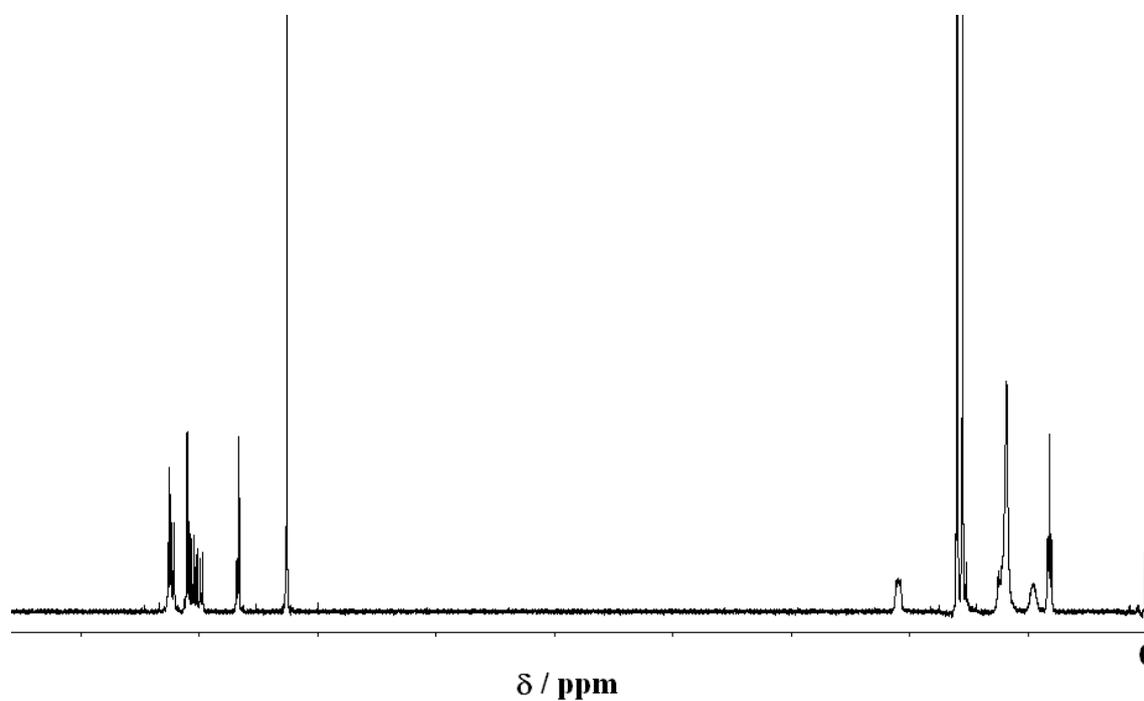
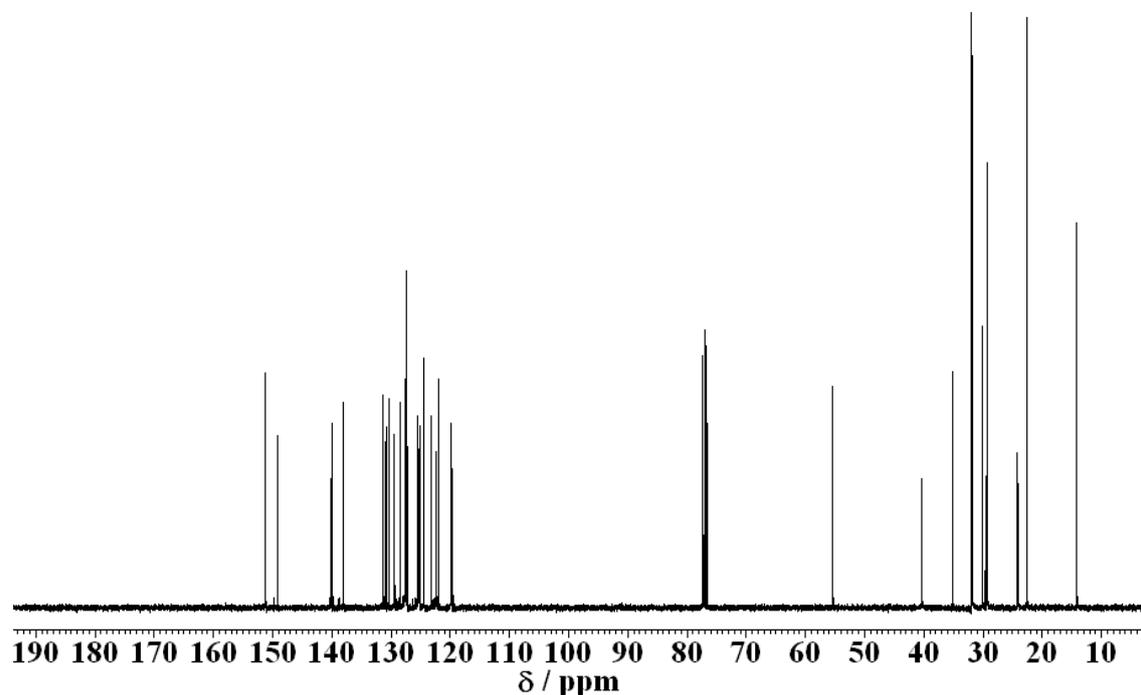


Figure S4. ^{13}C -NMR spectrum of 9,9'-dioctyl-2,7-bis (7-*tert*-butyl-1-pyrenyl)-9H-fluorene (**2-PyF**, 100 MHz, CDCl_3).



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33. This phenomenon is thought to be caused by intramolecular overlapping of the electron clouds of the 2,7-dipyrenylfluorene units. Few researchers have successfully observed distinct and strong spiroconjugation in the excited state [29,30]. However, in general, observed spiroconjugations were weak [31]. For example, in ref. [31], the authors reported that a compound in which two pyrenes were introduced into the spirobifluorene skeleton (2,7-dipyrene-9,9'-spirobifluorene, **SDPF**) showed a red-shift of 4 nm (in the ground state) and 1 nm (in the excited state) in comparison with a model compound, 2,7-dipyrene-9,9'-dimethyl fluorene (**DPF**). Furthermore in ref. [32], the authors compared UV-Vis spectra between a spiro-compound and an appropriate model compound by using MO calculations. However, to the best of our knowledge, no comparison between a 2,7-diarylfluorene and an appropriate spiro-compound (2,2',7,7'-tetraarylspirobifluorene) has been carried out yet to investigate the spiroconjugation by experimental methods. This pyrene-fluorene-conjugated compound (**4-PySBF**) exhibited extremely large red-shift of fluorescence (20 nm). This phenomenon is very interesting. We

intend to calculate the electron states of these compounds in the ground and excited states by the MO method and discuss this conjugation system in greater detail.

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Sample Availability: Available from GK.

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