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# Meso-Disubstituted Anthracenes with Fluorine-Containing Groups: Synthesis, Light-Emitting Characteristics, and Photostability

**Yoshio Matsubara,* Atsushi Kimura, Yoshihiro Yamaguchi, and Zen-ichi Yoshida***

*Faculty of Science and Engineering Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka, 577-8502, Japan*

*y-matsu@apch.kindai.ac.jp; yoshida@chem.kindai.ac.jp*

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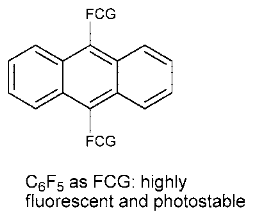
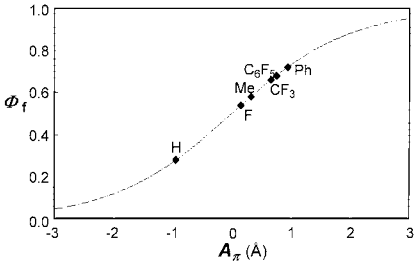
## ABSTRACT





**Synthesis, photophysical properties, and photostability of 9,10-disubstituted anthracenes with fluorine-containing groups (FCG) are described. The values of $\Phi_f$ and $\lambda_{em}$ greatly go up by the meso-substitution with FCG, and a nice corelationship between $\Phi_f$ and $A_\pi$ (magnitude of $\pi$ conjugation length in the excited single state) is observed. The $C_6F_5$ group at the meso positions exhibits an excellent ability in the photostability as well as in the emission efficiency.**

Acenes represented by anthracenes are a family of carbon-rich compounds of current interest[1] and are attracting considerable attention because of the light-emitting function leading to potential application as optoelectronic materials,[2] sensors,[3] and solar cells.[4] However, their biggest drawback is their lack of photostability due to ready oxygenation at the meso-positions. Thus, creation of highly fluorescent and photostable anthracenes should be an important and urgent subject.

We report here synthesis, light-emitting characteristics, and photostability (in the presence air) of 9,10- disubstituted anthracenes with fluorine-containing groups (abbreviated as FCG). To the best of our knowledge, light-emitting characteristics of FCG-substituted anthracenes have not been reported so far.

In regard to 9,10-diFCG-substituted anthracenes, we considered **2** (X = F), **4** (X = $CF_3$), and **6** (X = $C_6F_5$), and we employed **1** (X = H), **3** (X = Me), **5** (X = Ph) as the reference compounds to **2**, **4**, and **6**, respectively. Synthesis of **2** (X = F) and **4** (X = $CF_3$) was made by modification of the literature methods,[5,6] respectively.

For the synthesis of new compound **6**, we have devised a Cu-catalyzed coupling of pentafluorobenzene with 9,10-dibromoanthracene using $Ag_2O$ as a base as shown in

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(1) Haley, M. M.; Tykwinski, R. R.; Eds. *Carbon-Rich Compounds*; Wiley-VCH: Weinheim, 2006.

(2) For example, see: Magnera, T. F.; Casher, D. L.; Mulcahy, M. E.; Zheng, X.; Michl, J. ORGN-200. *Abstracts of Papers, 230th ACS National Meeting*; Aug 28−Sept 1, 2005, Washington, DC; American Chemical Society Washington, DC, 2005.

(3) For example, see: Fabbrizzi, L.; Licchelli, M.; Parodi, L.; Poggi, A.; Taglietti, A. *J. Fluoresc.* **1998**, *8*, 263–271.

(4) For example: Malliaras, G.; Friend, R. *Phys. Today* **2005**, *58*, 53–58.

(5) Duerr, B. F.; Chung, Y. S.; Czarnik, A. W. *J. Org. Chem.* **1988**, *53*, 2120–2122.

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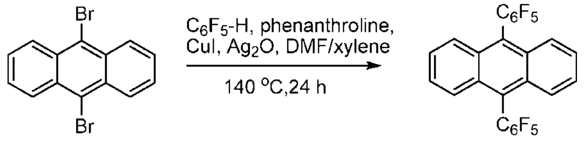
10.1021/ol802337v CCC: $40.75

**Table 1.** Photophysical Data of 9,10-Di-X-substituted Anthracenes in Cyclohexane[a]

| compd | $\Phi_f$[b] | $\lambda_{em}$ 0−0 (nm) | $\lambda_{abs}$[c] 0−0 (nm) | $\lambda_{em}$ 1−0 (nm) | $\lambda_{abs}$[c] 0−1 (nm) | $\tau$[d] (ns) | $k_r \times 10^7$ ($s^{-1}$) | $k_{nr} \times 10^7$ ($s^{-1}$) | $A_\pi$ (Å) |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.28 | 377 | 376 | 398 | 357 | 4.08 | 6.87 | 17.7 | −0.94 |
| **2** | 0.54 | 394 | 393 | 418 | 372 | 8.07 | 6.70 | 5.70 | 0.16 |
| **3** | 0.58 | 402 | 398 | 426 | 378 | 8.11 | 7.15 | 5.18 | 0.32 |
| **4** | 0.68 | 410 | 400 | 431 | 376 | 6.89 | 9.87 | 4.64 | 0.75 |
| **5** | 0.72 | 406 | 394 | 428 | 371 | 5.67 | 12.7 | 4.94 | 0.94 |
| **6** | 0.66 | 400 | 390 | 422 | 370 | 6.15 | 10.7 | 5.53 | 0.66 |

[a] All spectra were measured for $10^{-7}$ M solution at 295 K in contact with air. For details of the photophysical measurements, see the Supporting Information. [b] Quantum yield was calculated relative to quinine ($\Phi_f$ = 0.55 in 0.1 M $H_2SO_4$). [c] The log $\varepsilon$ values for $\lambda_{abs}$ (0−0 band) and $\lambda_{abs}$ (0−1 band) of **1**−**6** were approximately 3.6−4.0 and among 3.9−4.2, respectively. [d] $\tau$ values were obtained by time-resolved fluorescence spectroscopy using LaserStrobo fluorescence lifetime system (Photon Technology International). For details, see the Supporting Information.

**Scheme 1.** Synthesis of New Compound **6**



**6**

Scheme 1 (see the Supporting Information). Other bases (including $K_3PO_4$)[7] are not effective. Suzuki coupling and its modified method,[8,9] Goossen coupling,[10] and copper- and iron-catalyzed cross coupling using 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride[11−13] were not appropriate for the synthesis of **6**.

The photophysical data of 9,10-disubstituted anthracenes (**1**−**6**)[14] together with radiative rate constant ($k_r$), radiationless rate constant ($k_{nr}$), and emission lifetime ($\tau$) are summarized in Table 1. Since $k_r$ and $k_{nr}$ are related to the corresponding emission quantum yields and lifetimes by $\Phi_f = k_r \times \tau$ and $k_r + k_{nr} = \tau^{-1}$, it is possible to calculate the values of $k_r$ and $k_{nr}$ wherever quantum yield and lifetime data are available.[15]

As seen in Table 1, both $\lambda_{abs}$ (0−0 and 0−1 bands) and $\lambda_{em}$ (0−0 and 1−0 bands) values arising from the $S_0$−$S_1$ transition oriented along the short axis[16] in **1**−**6** increased by meso-substituents regardless of their electron-donating and -attracting nature, suggesting that the $\pi$ extension increases with the conjugative interaction between these substituents and the anthracene ring in the ground and excited states, even if the substituents ($C_6F_5$ and Ph) are not completely coplanar at both states.

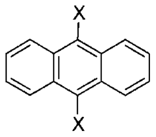


**Figure 1.** 9,10-Di-X-substituted anthracenes.

The fluorescence quantum yields ($\Phi_f$) also greatly increase by meso-substitution with FCG compared that of the parent anthracenes. Noteworthy is a considerably high emission efficiency ($\Phi_f$: 0.54−0.68) of 9,10-di-FCG-substituted anthracenes in contrast to those ($\Phi_f$: 0.1 for X = Br, $\Phi_f$: 0.48 for X = Cl) of 9,10-dihaloanthracenes.[17]

It is noted that the Me, $CF_3$, Ph, and $C_6F_5$ groups increase the $k_r$ values and decrease the $k_{nr}$ values compared with those of the parent anthracene. To get an insight into the emission efficiency, we have examined the relationship between $\Phi_f$ and magnitude ($A_\pi$) of $\pi$ conjugation length in the $S_1$ state of 9,10-disubstituted anthracenes in relation to the theoretically derived equation[18] $\Phi_f = 1/(\exp(-A_\pi) + 1)$, where $A_\pi = \ln(k_r / k_{nr})$.

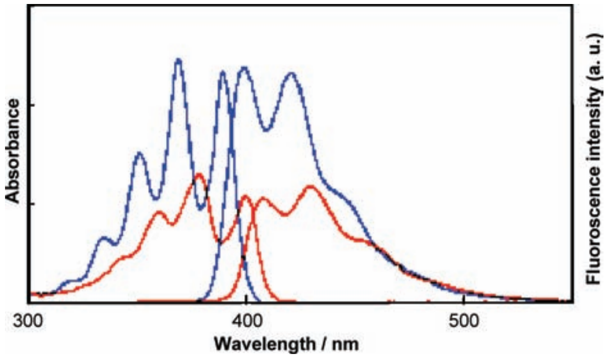


**Figure 2.** Absorption (left) and fluorescence (right) spectra of **4** (red) and **6** (blue) in cyclohexane. All spectra were measured for $10^{-7}$ M solution at 295 K in contact with air.

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(7) Do, H.-Q.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 1128–1129.

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(11) Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2417–2420.

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(14) The compounds (**1**−**6**) were purified by repeated column chromatography followed by recrystallization. Purity was checked by constancy of the fluorescence intensity at the maximum $\lambda_{em}$.

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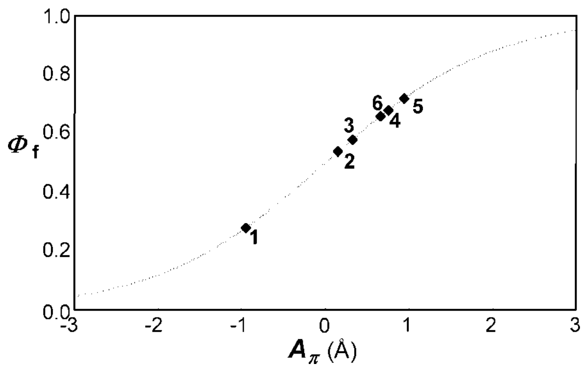

**Figure 3.** Correlation between fluorescence quantum yield ($\Phi_f$) and magnitude ($A_\pi$) of $\pi$ conjugation length in the $S_1$ state of 9,10-disubstituted anthracenes. Solid line: theoretical line based on $\Phi_f = 1/(\exp(-A_\pi) + 1)$.[18]

Consequently, we have found that all the plots of $\Phi_f$ against $A_\pi$ fall on the theoretical line (solid line) as shown in Figure 3. The $A_\pi$ values[19] obtained from $k_r$ and $k_{nr}$ values are shown in Table 1.

The result clearly indicates the increase in the $\pi$ conjugation between 9,10-substituents and anthracene ring in the $S_1$ state. This is also supported by the observed linear relationship with a positive slope between $\lambda_{em}$ and $A_\pi$ (Figure 4).

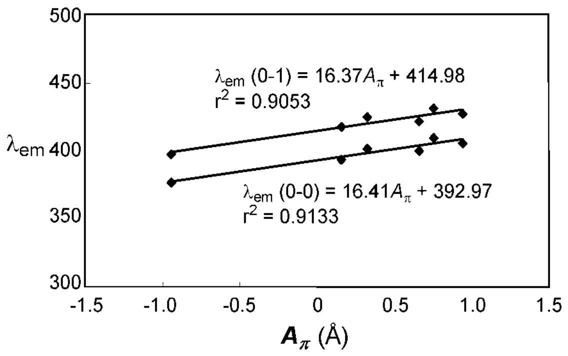

**Figure 4.** Correlation between fluorescence emission maximum ($\lambda_{em}$) and $A_\pi$.

In regard to the solvent effect on photophysical properties of 9,10-di-FCG-substituted anthracenes (**2**, **4**,and **6**), we have observed that the $\Phi_f$, $\lambda_{em}$, and $\lambda_{abs}$ values are slightly increased with solvent polarity (see the Supporting Information).

To pursue the photostability of anthracenes (**1**−**6**), we examined the relationship between fluorescence intensity and irradiation time using the reported apparatus.[20] The results are illustrated in Figure 5. The initial rate of decrease in fluorescence intensity is also shown in Table 2.

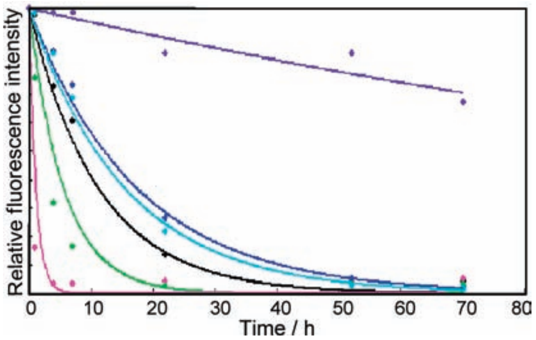

**Figure 5.** Relationship between fluorescence intensity and irradiation time: **1** (black), **2** (green), **3** (pink), **4** (light blue), **5** (dark blue), **6** (purple) Photoirradiation conditions: High-pressure Hg lamp (100 W) was placed 50 cm from the sample tube. The sample was dissolved in cyclohexane in the presence of air. Concentration of all anthracenes was $1 \times 10^{-6}$ M.

Both Figure 5 and Table 2 coincidentally indicate that the photostability is in the following order: **6** ≫ **5** > **4** > **1** > **2** > **3**. Thus, the $C_6F_5$ group exerts an excellent effect on photostability, although $CF_3$ and F groups are not so effective compared with the reference anthracenes.

**Table 2.** Initial Rate of Decrease in Fluorescence Intensity ($h^{-1}$) (Order of Photostability)

| compd (X) | **6** ($C_6F_5$) | **5** (Ph) | **4** ($CF_3$) | **1** (H) | **2** (F) | **3** (Me) |
|---|---|---|---|---|---|---|
| initial rate ($h^{-1}$) | 0.005 | 0.056 | 0.062 | 0.085 | 0.163 | 0.596 |

It is worth noting that 9,10-di(pentafluorophenyl)anthracene is much superior to the others with respect to both emission efficiency and photostability because high photostability is known to be incompatible with high emissivity.[20]

From HPLC, NMR, and peroxide tests of the sample solution under irradiation (see the Supporting Information), it is demonstrated that the decrease in fluorescence intensity is ascribed to the formation of the endoperoxide (abbreviated as EP). It is observed that EP is then converted to the corresponding 10-hydroxyanthrone, and eventually to anthraquinone for **1** (X = H) and even for **4** (X = $CF_3$). It is interesting that our photooxygenation products are very similar to those of the photosensitized oxygenation of anthracenes.[21]

The steric energy (kcal/mol) of EP of 9,10-di-FCG-substituted anthracenes (a measure for the difficulty in EP formation) is as follows: 51.9 for EP of **6** > 39.5 for EP of **4** > 32.3 for EP of **5** > 32.2 for EP of **2** > 21.5 for EP of **1**.

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(16) Valeur, B. *Molecular Fluorescence*; Wiley-VCH: Weinheim, 2002; p 27.

(17) Krasovitskii, B. M.; Bolotin, B. M. *Organic Luminescent Materials*; VCH: Weinheim, Germany, 1988; p 26.

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(19) $A_\pi$ values range from positive values to negative values because of the logarithmic values. However, the negative sign only means the value is smaller than the positive one. The absolute $A_\pi$ value could be given by $\ln(k_r/k_{nr}) - \{\ln(k_r/k_{nr})$ at $\Phi_f = 0.01\}$. The situation is similar to the case of temperature. The positive values (practical $A_\pi$, $A_\pi$*) can be obtained by $A_\pi^* = A_\pi + 4.6$, which is given by $A_\pi = \ln(k_r/k_{nr}) - \{\ln(k_r/k_d)$ at $\Phi_f = 0.01\}$.[18]

Interestingly a linear relationship seems to be observed between the initial rate of fluorescence intensity decrease and the MM2 steric energy of EP of 9,10-di-FCG-substituted anthracenes as shown in Figure 6, although the electronic effect of substituent should also be taken into consideration for EP formation.

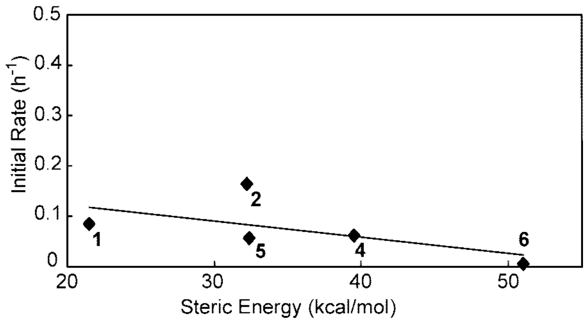

**Figure 6.** Relationship between initial rate of fluorescence intensity decrease and MM2 steric energy of EP of 9,10-di-FCG-substituted anthracenes.

In conclusion, (1) we prepared **6** by a Cu-catalyzed C−C cross-coupling between pentafluorobenzene and 9,10-dibromoanthracene. (2) The values of $\Phi_f$ and $\lambda_{em}$ are greatly increased by the meso-substitution with FCG. (3) We found a nice correlation between $\Phi_f$ and $A_\pi$. (4) The $C_6F_5$ groups at the meso positions exhibit an excellent ability in the photostability as well as in the emission efficiency. (5) The decrease in the fluorescence intensity is found to be due to the formation of 9,10-endoperoxide. The initial rate of decrease in fluorescence intensity correlates to the steric energy of the endoperoxides of 9,10-di-FCG-substituted anthracenes.

**Supporting Information Available:** Synthesis, NMR data, HRMS data, absorption and fluorescence spectra, solvent effect, photooxygenation products, and MM2 steric energy. This material is available free of charge via the Internet at http://pubs.acs.org.

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