

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

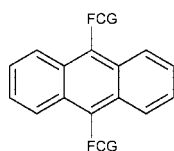
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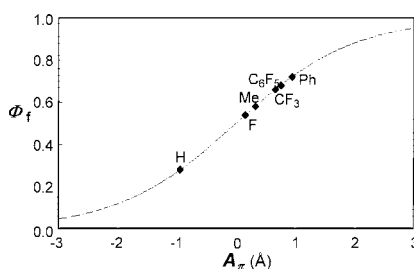
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ABSTRACT



C₆F₅ as FCG: highly fluorescent and photostable



Synthesis, photophysical properties, and photostability of 9,10-disubstituted anthracenes with fluorine-containing groups (FCG) are described. The values of Φ_f and λ_{em} greatly go up by the meso-substitution with FCG, and a nice corelationship between Φ_f and A_π (magnitude of π conjugation length in the excited single state) is observed. The C₆F₅ 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 interest¹ 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 = CF₃), and **6** (X = C₆F₅), 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 = CF₃) 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 Ag₂O as a base as shown in

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(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: Fabbri, 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.

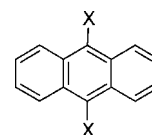
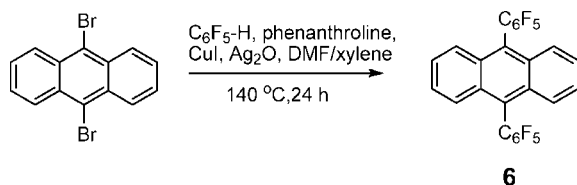
(5) Duerr, B. F.; Chung, Y. S.; Czarnik, A. W. *J. Org. Chem.* **1988**, 53, 2120–2122.

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

compd	Φ_f^b	λ_{em} 0–0 (nm)	λ_{abs}^c 0–0 (nm)	λ_{em} 1–0 (nm)	λ_{abs}^c 0–1 (nm)	τ^d (ns)	$k_r \times 10^7$ (s ⁻¹)	$k_{nr} \times 10^7$ (s ⁻¹)	$A_\pi(\text{\AA})$
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 H₂SO₄). ^c The log ϵ values for λ_{abs} (0–0 band) and λ_{abs} (0–1 band) of **1–6** were approximately 3.6–4.0 and among 3.9–4.2, respectively. ^d τ values were obtained by time-resolved fluorescence spectroscopy using LaserStrobe fluorescence lifetime system (Photon Technology International). For details, see the Supporting Information.

Scheme 1. Synthesis of New Compound **6****Figure 1.** 9,10-Di-X-substituted anthracenes.

Scheme 1 (see the Supporting Information). Other bases (including K₃PO₄)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**.

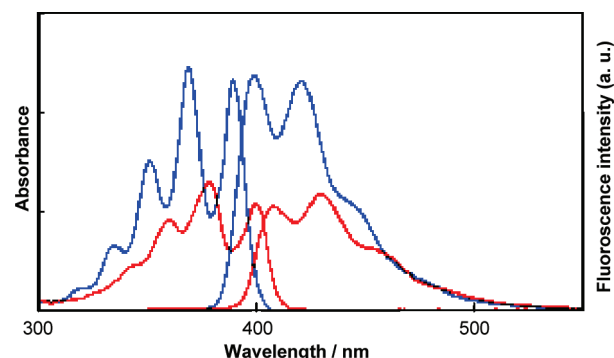
The photophysical data of 9,10-disubstituted anthracenes (**1–6**)¹⁴ together with radiative rate constant (k_r), radiationless rate constant (k_{nr}), and emission lifetime (τ) are summarized in Table 1. Since k_r and k_{nr} are related to the corresponding emission quantum yields and lifetimes by $\Phi_f = k_r \times \tau$ 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 λ_{abs} (0–0 and 0–1 bands) and λ_{em} (0–0 and 1–0 bands) values arising from the S₀–S₁ transition oriented along the short axis¹⁶ in **1–6** increased by meso-substituents regardless of their electron-donating and -attracting nature, suggesting that the π extension

increases with the conjugative interaction between these substituents and the anthracene ring in the ground and excited states, even if the substituents (C₆F₅ and Ph) are not completely coplanar at both states.

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

It is noted that the Me, CF₃, Ph, and C₆F₅ 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 Φ_f and magnitude (A_π) of π conjugation length in the S₁ state of 9,10-disubstituted anthracenes in relation to the theoretically derived equation¹⁸ $\Phi_f = 1/(\exp(-A_\pi) + 1)$, 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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(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 λ_{em} .

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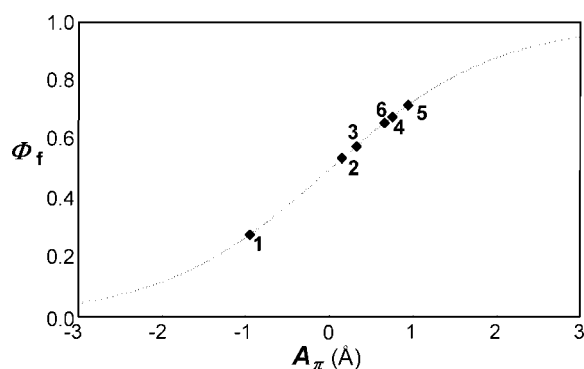


Figure 3. Correlation between fluorescence quantum yield (Φ_f) and magnitude (A_π) of π conjugation length in the S_1 state of 9,10-disubstituted anthracenes. Solid line: theoretical line based on $\Phi_f = 1/(\exp(-A_\pi) + 1)$.¹⁸

Consequently, we have found that all the plots of Φ_f against A_π fall on the theoretical line (solid line) as shown in Figure 3. The A_π values¹⁹ obtained from k_r and k_{nr} values are shown in Table 1.

The result clearly indicates the increase in the π 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 λ_{em} and A_π (Figure 4).

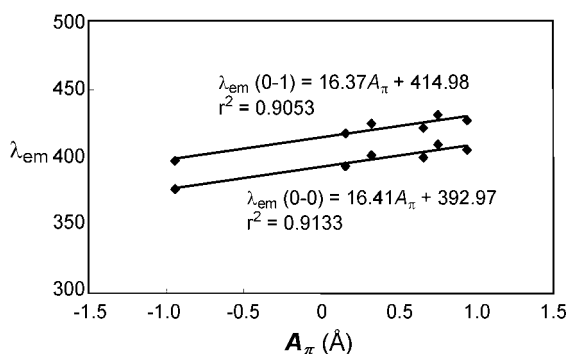


Figure 4. Correlation between fluorescence emission maximum (λ_{em}) and A_π .

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 Φ_f , λ_{em} , and λ_{abs} values are slightly increased with solvent polarity (see the Supporting Information).

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(19) A_π 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_π value could be given by $\ln(k_r/k_{nr}) - \{\ln(k_r/k_{nr}) \text{ at } \Phi_f = 0.01\}$. The situation is similar to the case of temperature. The positive values (practical A_π , A_π^*) can be obtained by $A_\pi^* = A_\pi + 4.6$, which is given by $A_\pi = \ln(k_r/k_{nr}) - \{\ln(k_r/k_d) \text{ at } \Phi_f = 0.01\}$.¹⁸

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.

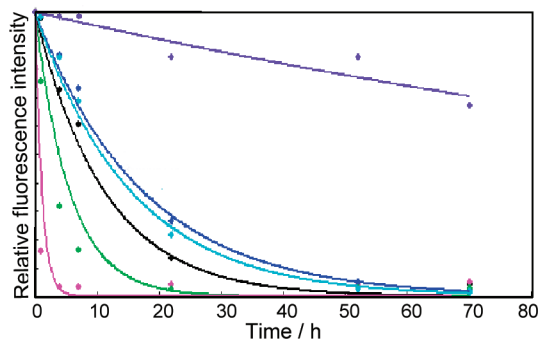


Figure 5. Relationship between fluorescence intensity and irradiation time: **1** (black), **2** (green), **3** (pink), **4** (light blue), **5** (dark blue), **6** (purple) Photoirradiation conditions: High-pressure Hg lamp (100 W) was placed 50 cm from the sample tube. The sample was dissolved in cyclohexane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

Both Figure 5 and Table 2 coincidentally indicate that the photostability is in the following order: **6** \gg **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**.

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.

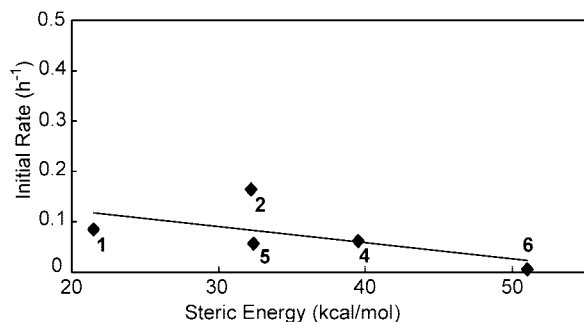


Figure 6. Relationship between initial rate of fluorescence intensity decrease and MM2 steric energy of EP of 9,10-di-FCG-substituted anthracenes.

In conclusion, (1) we prepared **6** by a Cu-catalyzed C–C cross-coupling between pentafluorobenzene and 9,10-dibromoanthracene. (2) The values of Φ_f and λ_{em} are greatly increased by the meso-substitution with FCG. (3) We found a nice correlation between Φ_f and A_{π} . (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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