

How the π Conjugation Length Affects the Fluorescence Emission Efficiency

Yoshihiro Yamaguchi,* Yoshio Matsubara, Takanori Ochi, Tateaki Wakamiya, and Zen-ichi Yoshida*

Department of Chemistry, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka, 577-8502, Japan

Received June 8, 2008; E-mail: yamaguch@chem.kindai.ac.jp; yoshida@chem.kindai.ac.jp

Recent developments in science and technology utilizing organic fluorescent materials have resulted in the increasing requirement for highly efficient fluorophores. For creation of such fluorophores it should be valuable to find some correlation between the fluorescent quantum yield and π structure of fluorophores,¹ since no general concept has been established yet. Thus the challenge of obtaining a novel concept for this issue has been undertaken by examining any relationship between fluorescent quantum yield and other photophysical characteristics of the typical π conjugated hydrocarbons² shown in Figure 1, the most fundamental fluorophores. Photoreactive hydrocarbons were excluded because of the reliability of photophysical data: 1. Rod- and star-shaped phenylacetylene architectures (1-7 in Figure 1); rod-shaped: three benzene ring system (1) to five benzene ring system (3); star-shaped: three benzene ring system (4) to seven benzene ring system (7). 2. Rodshaped oligophenylenes (P-0-P-3 in Figure 1) consisting of two, three, four, and five benzene rings. 3. Condensed aromatic hydrocarbons (C-1-C-4 in Figure 1) consisting of two, three, four, and five benzene rings.



Figure 1. Structures of π conjugated hydrocarbons used in this study.

The obtained photophysical properties are summarized in Table 1. We examined if any correlation exists between absolute fluorescent quantum yield (Φ_f) and λ_{em} , λ_{abs} , or ϵ for all hydrocarbons shown in Figure 1. However no simple correlation was found.

Hence we have examined correlation between the Φ_f and magnitude (A_{π}) of the π conjugation length in the excited singlet state (Figure 2). For this purpose it is necessary to derive A_{π} from, for instance, the radiative (rate constant: k_r) and radiationless process (rate constant: k_{nr}).³ Since k_r and k_{nr} are related to the corresponding emission quantum yields and lifetime by $\Phi_f = k_r \times \tau$ and $k_r + k_{nr} = \tau^{-1}$, we calculated the values of k_r and k_{nr} using quantum yield and lifetime data.⁴ The obtained k_r and k_{nr} values are shown in Table 1. As illustrated in Figure 2, the k_r is the rate constant for the return process of a π electron promoted to the excited singlet (S₁) state to the ground (S₀) state of a π conjugated molecule accompanying fluorescence emission, and the k_{nr} is the rate constant for radiationless process due to internal conversion and intersystem crossing. As demonstrated in Figure 2, A_{π} may be defined as the

Table 1. Photophysical Data of π Conjugated Hydrocarbons in ${\rm CHCl_3}^{a,b}$

compd	$\Phi_{\rm f}$	λ _{em} (nm)	$\log \epsilon$	λ _{abs} (nm)	τ (ns)	(s ⁻¹)	k _{nr} (s ⁻¹)	<i>Α</i> _π (Å)
1	0.83	348	4.59	328	5.51	1.51×10^{8}	3.09×10^{7}	1.59
2	0.87	389	4.77	343	6.01	1.45×10^{8}	2.16×10^{7}	1.90
3	0.93	389	5.13	354	6.27	1.48×10^{8}	1.12×10^{7}	2.59
4	0.14	330	4.70	302	5.46	2.56×10^{7}	1.58×10^{8}	-1.82
5	0.18	353	4.93	305	18.78	9.58×10^{6}	4.37×10^{7}	-1.52
6	0.57	391	5.13	315	6.11	9.33×10^{7}	4.04×10^{7}	0.28
7	0.27	449	5.07	349	21.64	1.25×10^{7}	3.37×10^{7}	-0.99
P-0	0.02	314	4.24	249	4.72	4.24×10^{6}	2.08×10^{8}	-3.89
P-1	0.49	342	4.49	280	4.38	1.12×10^{8}	1.16×10^{8}	-0.04
P-2	0.86	369	4.64	298	5.83	1.48×10^{8}	2.40×10^{7}	1.82
P-3	0.91	386	4.80	309	5.46	1.67×10^{8}	1.65×10^{7}	2.31
C-1	0.02	323	3.58	286	5.33	3.75×10^{6}	1.84×10^{8}	-3.89
C-2	0.13	383	3.85	379	5.75	2.26×10^{7}	1.51×10^{8}	-1.90
C-3	0.26	373	4.60	338	89.30	2.91×10^{6}	8.29×10^{6}	-1.05
C-4	0.90	448	4.53	438	6.49	1.39×10^8	1.54×10^{7}	2.20

^{*a*} All spectra were measured for 10^{-6} M solution at 295 K. In the case of C-3, cyclohexane was used as solvent. ^{*b*} Details of the photophysical measurements: see Supporting Information.



Figure 2. Schematic diagrams of light absorption (hv_a) , fluorescence emission (hv_f) , radiative (k_f) and radiationless (k_{nf}) processes, π conjugation length (A_{π}) at the S₁ state, and intramolecular electron transfer (ET) of a π conjugated molecule. The number (0 and 1) in parentheses corresponds to S₀ and S₁, respectively.

distance between dipoles arising from $S_0 \rightarrow S_1$ transition (light absorption). Thus k_{nr} is regarded as the rate constant of radiationless decay due to the electron transfer (ET) from the negative charge to the positive charge.

As shown in Table 1, the k_r values increase and the k_{nr} values decrease with π conjugation length of the rod-shaped molecules (**P-0–P-3**), suggesting that the k_r/k_{nr} value might be related to π extension in the S₁ state of the π conjugated molecule.

First, we derive A_{π} from $k_{\rm r}$ and $k_{\rm nr}$. From Einstein's equation⁵ (fundamental relationship of transition probability with absorption and emission), $k_{\rm r}$ is given by eq 1,

$$k_{\rm r} = A_{1,0}$$
 (1)

where $A_{1,0}$ is the Einstein transition rate constant for spontaneous emission from the S₁ to the S₀ state.



Figure 3. Correlation between fluorescence emission maximum (λ_{em}) and magnitude (A_{π}) of π conjugation length in the S₁ state of π conjugated hydrocarbons, **P0–P3**.

On the other hand, k_{nr} is known to follow the energy gap law: k_{nr} is proportional to $exp(-E_m)$, where E_m is the energy gap between the S₁ and S₀ state.^{6,7} This equation, however, does not contain A_{π} (or related term). As shown in Figure 2, k_{nr} can be regarded as the rate constant for the intramolecular electron-transfer process from S₁ to S₀. And so the Hush equation^{8,9} shown in eq 2 may serve our purpose, though it does not include the S₀ \rightarrow S₁ transition term.

$$k_{\rm ET} = k_0 \exp(-\beta R) \tag{2}$$

where k_0 is the rate constant at R = 0 and β is a constant. *R* is the distance between negative charge and positive charge.

Hence, k_{nr} is considered to be expressed by combining the Hush and Einstein equations for light absorption⁵ as shown in eq 3,

$$k_{\rm nr} = B_{0,1} \exp(-\beta A_{\pi}) \tag{3}$$

where $B_{0,1}$ is the Einstein transition probability, the rate of the molecule going from the S₀ to the S₁ state by absorption of radiation.⁵ Since $B_{0,1} = B_{1,0}$ (rate constant for induced emission from S₁ to S₀) and eq 4 (relationship between $B_{1,0}$ and $A_{1,0}$) is known,⁵ k_{nr} is expressed by eq 5,

$$B_{0,1} = B_{1,0} = (c^3 / 8\pi h \nu^3) A_{1,0} \tag{4}$$

where c is the speed of light, h is Planck's constant, and ν is the frequency of fluorescence emission maximum.

$$k_{\rm nr} = (c^3 / 8\pi h \nu^3) A_{1,0} \exp(-\beta A_{\pi})$$
(5)

From eqs 1 and 5, we get eq 6.

$$k_{\rm r}/k_{\rm nr} = (8\pi h v^3/c^3) \exp(\beta A_{\pi}) \tag{6}$$

Equation 6 is a k_r/k_{nr} relationship at arbitrary fluorescence quantum yield (Φ_f).

If we consider the case of $\Phi_f = 0.5$ as the reference standard (where, $k_r^s = k_{nr}^s$ and $A_{\pi}^s = 0$ as described later), we get eq 7.

$$(k_{\rm r}/k_{\rm nr})/(k_{\rm r}^{\rm s}/k_{\rm nr}^{\rm s}) = k_{\rm r}/k_{\rm nr} = (\nu^3/\nu^{\rm s3}) \exp(\beta A_{\pi})$$
 (7)

Assuming that $\nu \approx \nu^{s}$ based on the relationship between ν and A_{π} (Figure 3), eq 7 could be simplified as

$$k_{\rm r}/k_{\rm nr} = \exp(\beta A_{\pi}) \tag{8}$$

Though β should be experimentally determined, if we assume that β is 1 inferring from literature values,^{8,9} we get eqs 9 and 10.

$$k_{\rm r}/k_{\rm nr} = \exp(A_{\pi}) \tag{9}$$

$$A_{\pi} = \ln(k_{\rm r}/k_{\rm nr}) \tag{10}$$

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Figure 4. Correlation between absolute fluorescence quantum yield ($\Phi_{\rm f}$) and magnitude (A_{π}) of π conjugation length in the S₁ state of π conjugated hydrocarbons. Solid line: theoretical line based on eq 13.

Multiplication of both sides of eq 10 (unitless) by 1 Å gives the values in units of angstrom. The A_{π} values (Å) are summarized in Table 1. The practical π conjugation length (A_{π}^*) in the S₁ state could be given by $(A_{\pi} + 4.6)$ (Å) (Supporting Information).³ It is noted that a linear relationship with a positive slope between A_{π} and λ_{em} is observed for the rod-shaped π conjugated systems, **P0–P3** as shown in Figure 3.

Next, we derive the relationship between $\Phi_{\rm f}$ and A_{π} . From $\Phi_{\rm f} = k_{\rm r} \times \tau$ and $k_{\rm r} + k_{\rm nr} = \tau^{-1}$ as described before, we get eq 11.

$$\Phi_{\rm f} = k_{\rm r} / (k_{\rm nr} + k_{\rm r}) \tag{11}$$

Upon dividing the denominator and the numerator in eq 11 by k_{r_s} we obtain eq 12.

$$\Phi_{\rm f} = 1/((k_{\rm m}/k_{\rm r}) + 1) \tag{12}$$

By using simple mathematics based on eqs 9 and 12, we have eq 13.

$$\Phi_{\rm f} = 1/(\exp(-A_{\pi}) + 1) \tag{13}$$

This is the theoretically derived relationship between $\Phi_{\rm f}$ and A_{π} .

Equation 13 gives a sigmoid relationship between $\Phi_{\rm f}$ and A_{π} as shown by the solid line in Figure 4. The plot (blue color) of $\Phi_{\rm f}$ against A_{π} for all compounds listed in Table 1 falls on the theoretical line. Thus we have been able to elucidate how the π conjugation length affects fluorescence emission efficiency, providing a new concept for molecular design for highly fluorescent organic compounds. The approximately linear portion observed between $\Phi_{\rm f} = 0.1$ and $\Phi_{\rm f} = 0.9$ is particularly useful for this purpose. In Figure 4 A_{π} becomes 0 when $\Phi_{\rm f}$ is 0.5 (where $k_{\rm r} = k_{\rm nr}$ from $\Phi_{\rm f} =$ $k_r/(k_{\rm r} + k_{\rm nr})$). As a tool to predict $\Phi_{\rm f}$ from a structural model, ($\tilde{v}_{\rm a}$ $- \tilde{v}_{\rm f})^{1/2} \times a^{3/2}$ ($\tilde{v}_{\rm a}$: wavenumber of absorption maximum, $\tilde{v}_{\rm f}$: wavenumber of emission maximum, a: molecular radius) could be used instead of A_{π} (Supporting Information).

We have preliminarily examined the correlation between $\Phi_{\rm f}$ and A_{π} for the following substituted π systems: (1) donor(OMe)/ acceptor(CN)-substituted diphenylacetylene^{1f} (8), (2) donor(OMe)/ acceptor(CN)-substituted pentakis(*p*-phenylene ethynylene (9), and (3) donor(OMe)-substituted 5^{1d} (10). The new compound 9 was synthesized by the reactions shown in Scheme 1 (synthetic procedures, Supporting Information). Their photophysical data are shown in Table 2.

As shown in Figure 4 (red), it is of particular interest that the plot of $\Phi_{\rm f}$ against A_{π} for **8**, **9**, and **10** also falls on the solid line. The significant increase in $\Phi_{\rm f}$ and $\lambda_{\rm em}$ occurs by the introduction of donor/acceptor groups (**8** and **9**) or donor groups (**10**).

Scheme 1



Table 2.	Photophy	vsical Data	of Subs	tituted π	Systems	in CHCl ₃ ^a
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compd ^b	$\Phi_{\rm f}$	λ _{em} (nm)	$\log \epsilon$	λ_{abs} (nm)	τ (ns)	(s ⁻¹)	$k_{nr} (s^{-1})$	Α _π (Å)
8 9	0.44 0.88	374 527	4.40 4.72	326 456	5.86 6.29	7.51×10^{7} 1.40×10^{8}	9.56×10^{7} 1.91×10^{7}	-0.24 1.99
10	0.40	384	4.65	334	6.47	6.18×10^{7}	9.28×10^{7}	-0.41

 a All spectra were measured for 10^{-6} M solution at 295 K. b Structures of **8**, **9**, and **10** are as follows.





Figure 5. Fluorescence spectrum and color of 9 in CHCl₃.

In the donor/acceptor-substituted linear π conjugated systems, an increase in π conjugation length in the excited singlet state is considered to bring about the increase in both Φ_f and λ_{em} .

It should be of great interest that the remarkably intense green fluorophore **9** ($\Phi_f 0.88$, $\lambda_{em} 527$ nm, log $\epsilon 4.72$) (Figure 5), having

a similar emission characteristic to that of a green fluorescent protein (Topaz, T203Y type, $\Phi_f 0.60$, λ_{em} 527 nm, log ϵ 4.98) of current topic,¹⁰ has been created based on our concept.

Although it is necessary to establish the generality of this concept by the experimental examination for various other π systems, this concept should be valuable for (1) examination of an excited singlet state structure (for instance, coplanarity of excited-state molecules) and (2) molecular design of novel materials, in which the excited singlet state plays an important role, such as highly efficient fluorophores, electroluminescent materials, photoconducting materials, and nonlinear optical materials.

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Supporting Information Available: Materials and methods, synthetic procedures, correlation of the $(\tilde{v}_a - \tilde{v}_f)^{1/2} \times a^{3/2}$ with Φ_f and practical A_{π} values. This material is available free of charge via the Internet at http://pubs.acs.org.

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