Substituent Effect on Fluorescence and Photoisomerization of 1-(9-Anthryl)-2-(4-pyridyl)ethenes†

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The fluorescence and photoisomerization quantum yields of *trans*-1-(9-anthryl)-2-(4-pyridyl)ethene (*t*-4-APyE), 1-(10-methyl-9-anthryl)-2-(4-pyridyl)ethene (*t*-4-MeAPyE), and 1-(10-chloro-9-anthryl)-2-(4-pyridyl)ethene (*t*-4-ClAPyE) were measured in cyclohexane, acetonitrile, and methanol at room temperature. Polar solvents result in the drastic reduction of fluorescence quantum yield and increase of photoisomerization quantum yield for all three compounds. These results are probably due to the stabilization of intramolecular charge transfer (ICT) excited state in polar solvent. The higher contribution of ICT in the presence of more electron-donating methyl substituent, manifested by largest positive fluorescence solvatochromism, indicates that the pyridine ring acts as an electron acceptor. Protonation or methylation makes pyridine ring stronger electron acceptor and causes long-wavelength ground state charge transfer absorption band and complete quenching of fluorescence. The fluorescence from *t*-4-APyE derivatives can be switched off responding external stimuli *viz.* medium polarity, protonation, or methylation.

Key Words : Diarylethene, Substituent effect, Fluorescence, Photoisomerization

Introduction

Recently, molecular systems from which emission or geometrical change can be switched on or off by external stimuli or environmental changes such as light, pH, or medium have been widely studied for potential applications as optical switches or gates. [1-6] In this aspect, the light-driven *cis-trans* isomerization of stilbenes and other diarylethenes have undergone active investigation both through fundamental studies[7,8] and practical applications.[9,10] While stilbene itself shows very weak fluorescence due to very efficient two-way photoisomerization, relatively strong fluorescences are observed in *trans*-diarylethenes containing large polyaromatic group such as anthracene, which carry out only one-way *cis* to *trans* photoisomerization.[11-13] One-way photoisomerization is due to high activation barrier to twisting of C=C bond by the localization of the excitation energy on large polyaromatic moiety.

Intramolecular charge transfer (ICT) processes have been extensively studied for a number of donor- and acceptor-containing compounds.[14-17] A large number of dye systems are currently being used as fluorescence probes of microenvironment in organized media.[18-20] A majority of these polarity sensitive fluorescence probes are bichromophoric systems comprised of electron donor and acceptor groups. The sensitivity of the fluorescence maxima and quantum yields on the polarity of the media in these systems results from ICT character of the lowest singlet state. Investigation of ICT molecules focused on systems in which donor and acceptor groups are directly connected through a single bond or π bond. The charge separation is most favorable in a twisted conformation, where the two moieties involved in charge transfer, the donor and the acceptor, are orbitally decoupled, *i.e.*, nearly perpendicular. This twisted intramolecular charge transfer (TICT) states were first introduced by Grabowski *et al.*[21] TICT states are accessible in multichromophoric systems possessing an electron donor and an electron acceptor only if they are weakly coupled. Experimentally, the large charge separation of TICT states manifests itself by a strong red-shift of fluorescence in polar solvents, which is due to the formation of the TICT which is usually characterized by enhanced or reversed charge transfer associated with rotation around a chemical bond.

ICT is expected not only to make the fluorescence sensitive to the solvent polarity, but also to provide a way to lower the activation barrier to twisting of ethene bond in diarylethene containing large aromatic ring. Introduction of heteroaromatic ring into diarylethene increases the dipole moment of the compound to initiate the excited state ICT processes.[22] Actually, in polar solvents, two-way $t \rightarrow c$ and $c \rightarrow t$ photoisomerization reactions and greatly reduced fluorescence have been observed in N-heteroaromatic derivatives of 1-(9-anthryl)-2-phenylethenes, probably due to the contribution of the ICT state.[23-25] It is likely that suitable substituent increases the donor-acceptor ability to favor the formation of the excited ICT state and leads to influence fluorescence and photoisomerization characteristics.

trans-1-(9-Anthryl)-2-(4-pyridyl)ethene (*t*-4-APyE),[23] an aza derivative of anthrylphenylethene, displays solvent-dependent photoisomerization behavior. While, in nonpolar solvent, *trans* isomer undergoes no *trans* to *cis* photoisomerization and shows strong fluorescence, fluorescence is very weak and photoisomerization is observed in polar

†Dedicated to the late Professor Sang Chul Shim, a great teacher and scholar, for his distinguished achievement in organic photochemistry.

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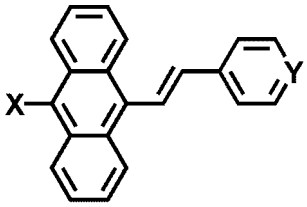


***t*-4-APyE**	**X=H,**	**Y=N**
***t*-4-MeAPyE**	**X=Me,**	**Y=N**
***t*-4-ClAPyE**	**X=Cl,**	**Y=N**
***t*-4-APyE-N-MeI**	**X=H,**	**Y=N$^+$-MeI$^-$**
***t*-4-MeAPyE-N-MeI**	**X=Me,**	**Y=N$^+$-MeI$^-$**
***t*-4-ClAPyE-N-MeI**	**X=Cl,**	**Y=N$^+$-MeI$^-$**

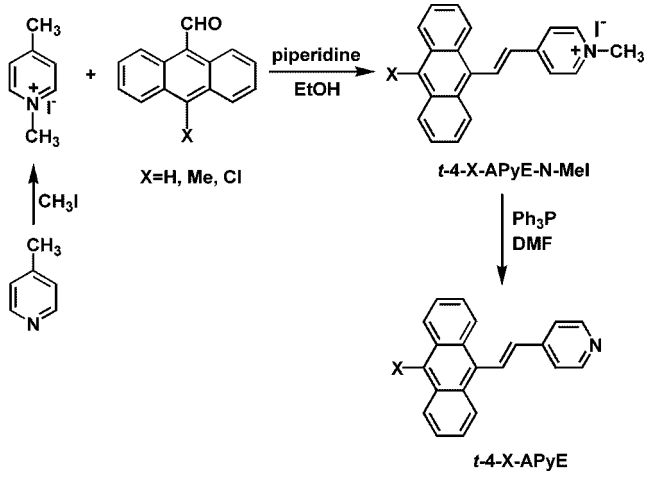
Scheme 1. Structure of the compounds in this study.

solvent. It indicates that solvent may offer on/off tools for luminescence and/or structural change. The introduction of suitable substituent may lead to complete quenching of fluorescence and/or more efficient photoisomerization in polar solvent by more efficient ICT.

The present paper presents a photophysical investigation on some substituted *trans*-1-(10-X-9-anthryl)-2-(4-pyridyl)-ethene derivatives (*t*-4-XAPyE and *t*-4-XAPyE-N-MeI, X= H, Me, Cl, see Scheme 1) by steady-state and time-resolved fluorimetry. The characteristics of the lowest excited singlet state have been studied, together with the influence of substituent, solvent, and pH on fluorescence and photoisomerization.

Experimental Section

Materials. *Trans*-1-(10-methyl-9-anthryl)-2-(4-pyridyl)-ethene (*t*-4-MeAPyE), 1-(10-chloro-9-anthryl)-2-(4-pyridyl)-ethene (*t*-4-ClAPyE), 1-(10-methyl-9-anthryl)-2-(4-(N-methyl)-pyridinium)ethene iodide (*t*-4-MeAPyE-N-MeI), and 1-(10-chloro-9-anthryl)-2-(4-(N-methyl)pyridinium)ethene iodide (*t*-4-ClAPyE-N-MeI) were prepared as shown in Scheme 2 from corresponding 10-substituted-9-anthraldehyde and 4-picoline by similar procedure as used in the preparation of



Scheme 2. Synthesis of *t*-4-X-APyE and *t*-4-X-APyE-N-MeI.

trans-1-(9-anthryl)-2-(4-pyridyl)ethene (*t*-4-APyE).[23] Their structures were identified by IR and ^{1}H NMR spectra. 10-Methyl-9-anthraldehyde, 10-chloro-9-anthraldehyde, 4-picoline, triphenylphosphine, piperidine, and methyl iodide (Aldrich) were used as received. Cyclohexane and acetonitrile (Fisher) were purified using standard procedure prior to use.

t-4-*MeAPyE* (yellow solid); IR 3068, 1645, 1541, 1513, 749 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.17(3H, s, CH_3), 7.02 (1H, d, J = 16.3 Hz, H8), 7.50-7.60 (4H, m, H2', 3', 6', 7'), 7.86 (2H, d, J = 6.6 Hz, H2, 6), 8.26 (2H, m, H4', 5'), 8.39 (2H, m, H1', 8'), 8.46 (1H, d, J = 16.3 Hz, H7), 8.74 (2H, d, J = 6.6 Hz, H3, 5).

t-4-*ClAPyE* (bright yellow solid); IR 3069, 1646, 1541, 1519, 748 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (1H, d, J = 16.6 Hz, H8), 7.51-7.66 (6H, m, H2', 3', 6', 7', 2, 6), 8.11 (1H, d, J = 16.6 Hz, H7), 8.30 (2H, d, J = 8.7 Hz, H1', 8'), 8.59 (2H, d, J = 8.7 Hz, 4', 5'), 8.70 (2H, d, J = 4.5 Hz, H3, 5).

t-4-*MeAPyE-N-MeI* (red solid); IR 3068, 1699, 1645, 1541, 1513, 749 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.13 (3H, s, CH_3), 4.32 (3H, s, N-CH_3), 7.24 (1H, d, J = 16.5 Hz, H8), 7.57-7.64 (4H, m, H2', 3', 6', 7'), 8.06 (2H, d, J = 7.5 Hz, H2, 6), 8.35-8.49 (4H, m, H1', 8', 4', 5'), 8.93 (1H, d, J = 16.5 Hz, H7), 8.96 (2H, d, J = 7.5 Hz, H3, 5).

t-4-*ClAPyE-N-MeI* (bright orange solid); IR 3069, 1699, 1646, 1541, 1519, 748 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.33 (3H, s, N-CH_3), 7.32 (2H, d, J = 7.6 Hz, H2, 6), 7.58 (1H, d, J = 12.3 Hz, H8), 7.60-7.78 (4H, m, H2', 3', 6', 7'), 8.01 (1H, d, J = 12.3 Hz, H7), 8.13 (2H, d, J = 7.6 Hz, H3, 5), 8.47-8.54 (4H, m, H1', 8', 4', 5').

Spectroscopic and Photochemical Measurements. ^{1}H NMR spectra were measured on a 300 MHz Bruker DRX300 in chloroform-d_1. Absorption spectra were recorded on a Hitachi U-3210 spectrophotometer. Steady-state fluorescence spectra were recorded on an Aminco-Bowman Series 2 luminescence spectrometer. The concentrations were controlled to be *ca.* 1×10^{-5} M, where the absorbances of the solutions at the excitation wavelength of 360 nm were usually at the value of 0.07-0.08, to avoid inner filter effects. Fluorescence quantum yields (Φ_f) were determined using quinine bisulfate as a standard (Φ_f = 0.55 in 0.1 M H_2SO_4).[26] For the determination of photoisomerization quantum yield, irradiation wavelength of 366 nm was employed in argon-saturated solution. Concentration for the measurements of quantum yield of photoisomerization was adjusted to be *ca.* 6×10^{-4} M in which all incident light was absorbed.

Results and Discussion

Absorption and Fluorescence Spectra. Absorption spectra of *t*-4-APyE, *t*-4-MeAPyE, and *t*-4-ClAPyE in cyclohexane, acetonitrile, and methanol are shown in Figure 1. Absorption maxima are not influenced by the solvent polarity, but depend on the substituent. Methyl derivative (*t*-4-MeAPyE) shows longer absorption maximum than Cl derivative (*t*-4-ClAPyE), which in turn shows longer absorption maximum

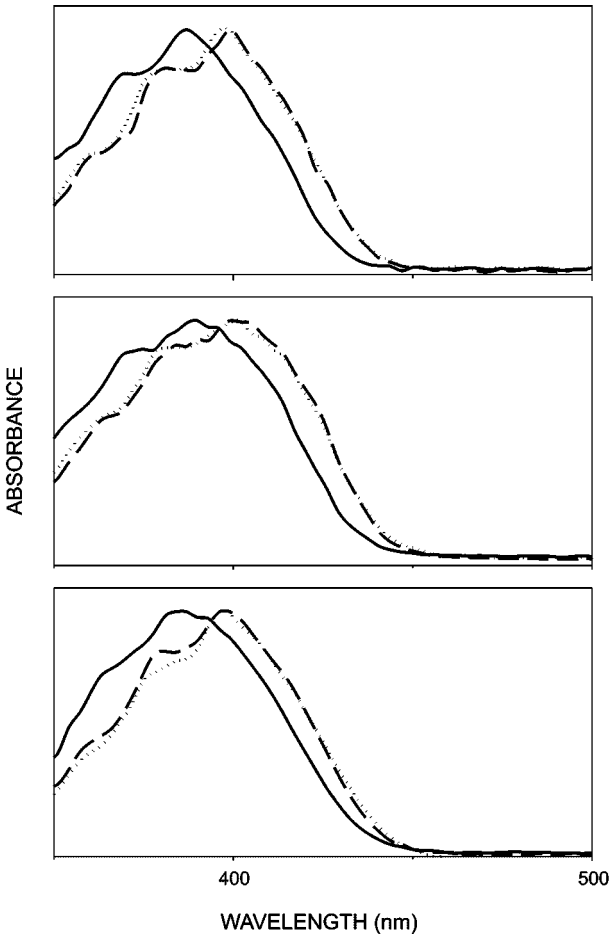


Figure 1. Absorption spectra of *t*-4-APyE (solid line), *t*-4-MeAPyE (dotted line), and *t*-4-ClAPyE (dashed line) in cyclohexane (upper), acetonitrile (middle), and methanol (lower).

than unsubstituted one (*t*-4-APyE) (see Table 1).

Fluorescence spectra of *t*-4-APyE, *t*-4-MeAPyE, and *t*-4-ClAPyE are shown in Figure 2. The observed fluorescence spectra for all the compounds are broad and structureless. In contrast to the absorption spectra, fluorescence spectra are greatly influenced by the solvent polarity for both their intensity and position. The solvatochromic effect on the fluorescence spectra is observable for all three compounds. Especially, *t*-4-MeAPyE shows largest red-shift of *ca*. 60 nm in acetonitrile relative to in cyclohexane (see Table 1).

Introduction of a substituent at the 10 position of anthracene ring causes red-shift of the fluorescence maximum. Fluorescence wavelength maximum is in the order of *t*-4-MeAPyE > *t*-4-ClAPyE > *t*-4-APyE, regardless of the solvent polarity. It indicates that more electron donating substituent at the 10 position of anthracene ring leads to more efficient ICT and thus pyridine moiety should act as an electron acceptor. For pyridine, the lone pair electrons of the nitrogen atom are in an orbital which is perpendicular to the π-ring system, and it is difficult for this nitrogen to become a donor through the resonance effect. Also, nitrogen is more electronegative than carbon atom and this makes pyridine act only as an acceptor in the ICT interaction.

Table 1. Absorption maxima, fluorescence maxima and quantum yields, and photoisomerization quantum yields of *t*-4-X-APyE and *t*-4-X-APyE-N-MeI (X=H, Me, Cl) in cyclohexane, acetonitrile, and methanol

Compound	Solvent	λ_a^{max}	λ_f^{max}	Φ_f	$\Phi_{t\rightarrow c}$
t-4-APyE	cyclohexane	386	473	0.44	<0.01
	acetonitrile	388	499	0.04	0.37
	methanol	386	502	0.04	0.35
t-4-MeAPyE	cyclohexane	398	502	0.53	<0.01
	acetonitrile	400	551	0.015	0.45
	methanol	398	561	0.008	0.35
t-4-ClAPyE	cyclohexane	398	482	0.43	<0.01
	acetonitrile	400	499	0.07	0.40
	methanol	398	504	0.04	0.35
t-4-APyE-N-MeI	acetonitrile	435	630	<0.004	~0
	methanol	442	630	<0.004	~0
t-4-MeAPyE-N-MeI	acetonitrile	448	678	<0.004	~0
	methanol	456	656	<0.004	~0
t-4-ClAPyE-N-MeI	acetonitrile	430	630	<0.003	~0
	methanol	434	628	<0.005	~0

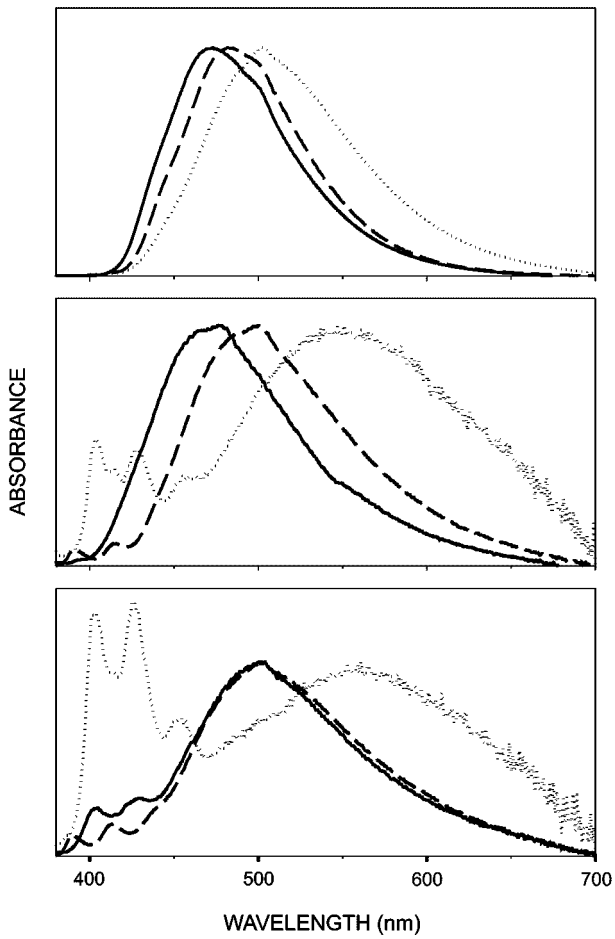


Figure 2. Fluorescence spectra of *t*-4-APyE (solid line), *t*-4-MeAPyE (dotted line), and *t*-4-ClAPyE (dashed line) in cyclohexane (upper), acetonitrile (middle), and methanol (lower).

Table 1 summarizes the lowest excited singlet state parameters of *t*-4-XAPyE (X=H, Me, Cl). For all three compounds,

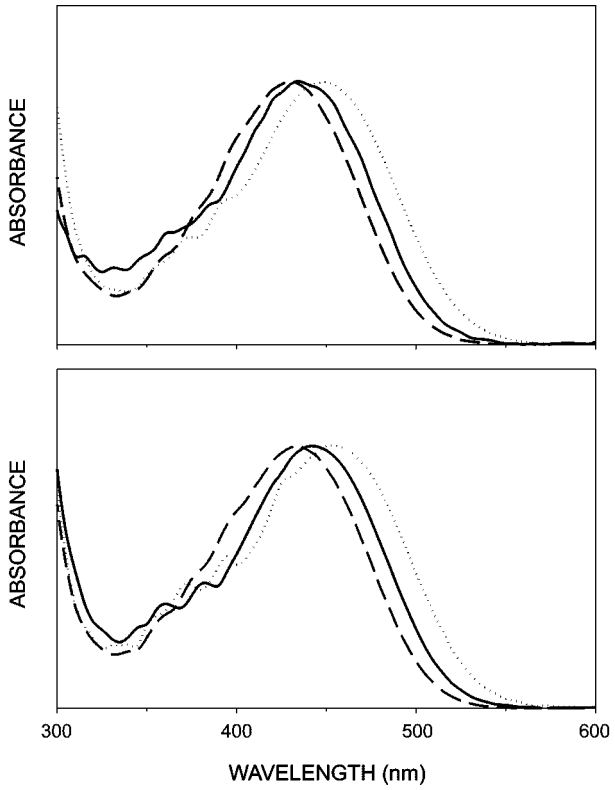


Figure 3. Absorption spectra of *t*-4-APyE-N-MeI (solid line), *t*-4-MeAPyE-N-MeI (dotted line), and *t*-4-ClAPyE-N-MeI (dashed line) in acetonitrile (upper), and methanol (lower).

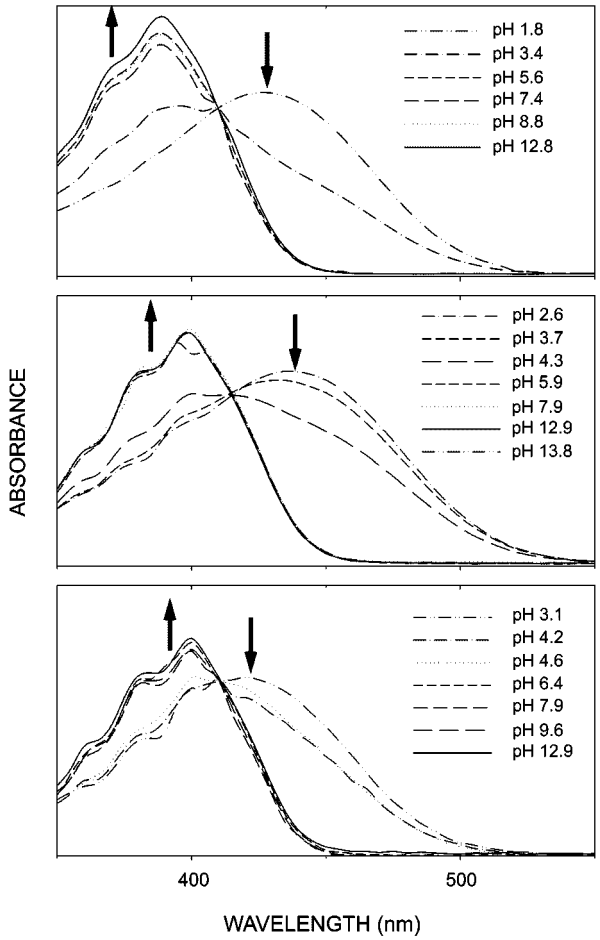


Figure 4. Absorption spectra of *t*-4-APyE (upper), *t*-4-MeAPyE (middle), and *t*-4-ClAPyE (lower) at various pH in acetonitrile/water (7/3, v/v).

fluorescence quantum yield is considerably high in cyclohexane, while extremely low in polar solvents, due to the formation of the ICT. Especially. *t*-4-MeAPyE containing electron-donating substituent is practically nonfluorescent in acetonitrile and methanol. In polar solvents, it is inferred that ICT plays a role in causing Φ_f to decrease, and opens other radiationless or reactive pathways, such as photoisomerization.

Effect of N-Methylation. In the case of their N-methylpyridinium derivatives such as 4-APyE-N-MeI, 4-MeAPyE-MeI, and 4-ClAPyE-N-MeI, absorption maxima are considerably red-shifted relative to their parent compounds (Figure 3), because the electron-accepting ability of pyridine increases on methylation. Among these three compounds, 4-MeAPyE-MeI shows longest absorption maximum, indicating that the more electron-donating substituent leads to more efficient intramolecular charge transfer in the ground state (see Table 1), and the compounds are more stabilized in polar solvents. N-methylation leads to make all three *t*-4-X-APyE derivatives nearly nonfluorescent. The wavelength of the observed weak emission is not very sensitive to solvent polarity.

Many TICT states are nonluminescent and are responsible for the rapid nonradiative decay of numerous important dyes leading to intramolecular fluorescence quenching.[27] A hemicyanine dye, 4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium iodide (HR),[28] one of the most widely used species in Langmuir-Blodgett(LB) film preparation, has the electron donor -$N(CH_3)_2$ on the end and the electron acceptor methylpyridinium on the other end. Because of its large second hyperpolarizability β and other interesting features, HR has gained much attention in nonlinear optical research and molecular electronics. Similar to HR, since there is an electron donor and an electron acceptor in the same molecule, intramolecular charge transfer is expected when *t*-4-APyE-N-MeI derivatives are excited. The wavelengths of the observed fluorescence, even though extremely weak, are not very sensitive to solvent polarity. While the maximum of the absorption spectrum shifts slightly to the red and the maximum of the fluorescence spectrum shifts slightly to the blue in more polar solvents. This is in contrast to most ICT state compounds, where both absorption and fluorescence maxima shift to the red in polar solvents. This suggests that fluorescence originates from a non-ICT state and that ICT state formation lowers fluorescence quantum yield. Rotations of the pyridyl ring and the anthryl ring enhance the charge transfer in the first excited state. The high-energy barrier to rotation around the central double bond is the cause of the low photoisomerization yield.

pH Effect. Nitrogen atom on the pyridine ring is protonated in highly acidic media. As pH decreases, the

Table 2. Absorption maxima at low and high pH, and ground and excited state pK_a values of *t*-4-X-APyE (X=H, Me, Cl) in acetonitrile/water (7/3, v/v)

Compound	λ_a^{max}, nm		pK_a	pK_a^*
	low pH	high pH		
t-4-APyE	425	390	4.1	8.5
t-4-MeAPyE	435	400	4.8	9.0
t-4-ClAPyE	420	400	4.7	7.2

absorption maximum is red-shifted. Absorption maxima of N-protonated compounds are very similar to those of corresponding N-methylated derivatives. Figure 4 represents the absorption spectra of *t*-4-APyE, *t*-4-MeAPyE, and *t*-4-ClAPyE, respectively, at various pH in acetonitrile/water (7/3, v/v). The absorption maxima of *t*-4-APyE, *t*-4-MeAPyE, and *t*-4-ClAPyE at high and low pH are listed in Table 2. The difference of absorption maxima between protonated and non-protonated species is largest in *t*-4-MeAPyE. Absorption maxima for protonated compounds are more red-shifted as the electron-donating ability of the substituent at the 10 position of the anthracene ring increases. If ICT molecule protonates at the acceptor site, the basicity of the acceptor will increase in the excited state and the protonated species are stabilized in polar solvents. The absorption maximum of *t*-4-XAPyE shows a red-shift on protonation. Thus, the pyridine ring acts only as electron acceptor.

The pK_a values (Table 2) of the ground and excited states in *t*-4-APyE, *t*-4-MeAPyE, and *t*-4-ClAPyE are listed in Table 2. In the excited states, the pK_a values can be obtained by the Förster cycle equation.

$$pK_a = pK_a^* + 2.1 \times 10^{-3}\,\Delta\nu \text{ (at 298 K)}$$

where, pK_a^* is excited state pK_a, and $\Delta\nu$ is defined as the excitation energy difference (cm^{-1}) between protonated and non-protonated species.

The pK_a values of the ground and excited states are greatest for *t*-4-MeAPyE, where the electron donating substituent probably makes the basicity of pyridine increase.

As pH decreases, fluorescence is efficiently quenched. No fluorescence is observed in highly acidic media. Figure 5 represents the fluorescence spectra of *t*-4-APyE, *t*-4-MeAPyE, and *t*-4-ClAPyE at various pH in acetonitrile/water (7/3, v/v). Neither shift in fluorescence nor new fluorescence band is observed. In protonated compounds, because ICT state is probably nonfluorescent, ICT state formation lowers fluorescence quantum yield similar to N-methylated compounds. Protonation leads to make *t*-4-X-APyE nonfluorescent.

Photoisomerization. In cyclohexane, none of the compounds studied underwent photoisomerization. In acetonitrile, photoisomerization was observed for all *t*-4-X-APyE (X=H, Me, Cl) upon irradiation. 1-(9-Anthryl)-2-phenylethene, a hydrocarbon derivative without nitrogen atom is well known to undergo no *trans* → *cis* photoisomerization in any solvent. The effect of introducing a pyridine ring in 1-(9-anthryl)-2-phenylethene can be explained by a contribution

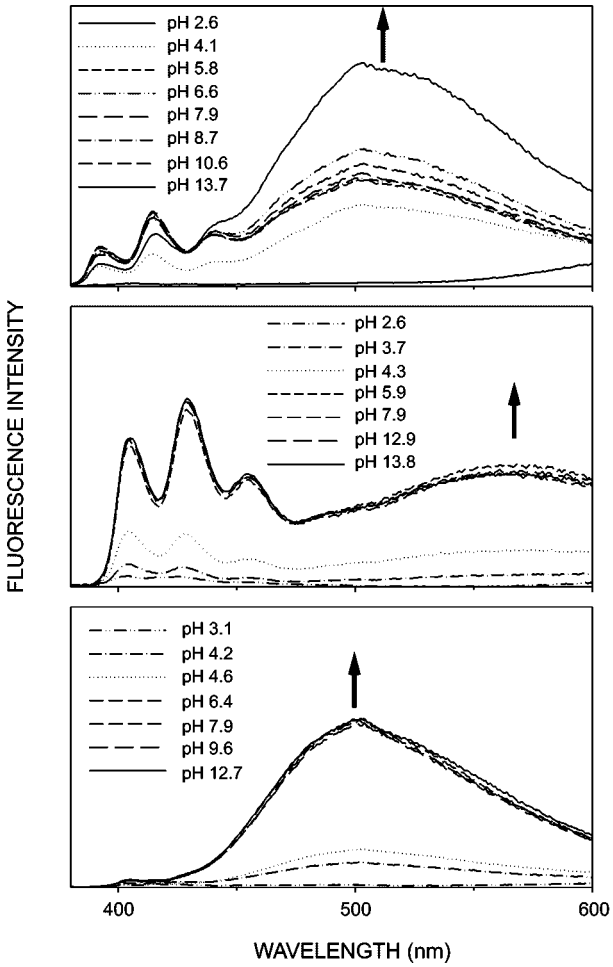


Figure 5. Fluorescence spectra of *t*-4-APyE (upper), *t*-4-MeAPyE (middle), and *t*-4-ClAPyE (lower) at various pH in acetonitrile/water (7/3, v/v).

of the excited intramolecular charge transfer state to the photoisomerization behavior as well as the photophysical properties. $\Phi_{t\to c}$ of *t*-4-MeAPyE is higher than that of *t*-4-ClAPyE, which is in turn higher than that of *t*-4-APyE in acetonitrile. This reflects that a higher degree of intramolecular charge transfer character induced by more electron-donating substituent makes *trans* → *cis* photoisomerization more feasible.

In acetonitrile, the fluorescence quantum yields are decreased and the photoisomerization quantum yields are increased compared to those in cyclohexane. Therefore, the photoisomerization probably proceeds *via* the excited singlet state.

Conclusion

The excited singlet state properties of *t*-4-XAPyE (X=H, Me, Cl) have been investigated. Their excited state properties are strongly solvent-dependent. While their absorption spectra remain unchanged in various solvents, fluorescence maxima are greatly red-shifted in polar solvents compared with in nonpolar solvents. The fluorescences in polar solvents

are extremely weak in contrast to moderate fluorescence quantum yields in nonpolar solvents. The *trans* → *cis* photoisomerization reactions are observed in acetonitrile and methanol, while they carry out no *trans* → *cis* photoisomerization in cyclohexane. From the fact that photoisomerization is observed in polar solvents in which fluorescence quantum yields are greatly reduced, it is believed that *trans* → *cis* photoisomerization should proceed *via* a singlet manifold. In polar solvent, *trans* → *cis* photoisomerization becomes feasible through the excited state ICT.

Moreover, substituent at the 10 position of anthracene markedly affects on the excited singlet state properties. Electron-donating substituent (*t*-4-MeAPyE) causes more red-shift of the fluorescence maximum, indicating more efficient excited state ICT, where pyridine ring acts as an electron acceptor. Methylation or protonation on nitrogen atom develops positive charge on the nitrogen atom. Therefore, electron-accepting ability on going from pyridine to pyridinium ring increases and ground state ICT has been observed.

Amongst tested compounds, *t*-4-MeAPyE manifests most sensitive response to external stimuli such as light, solvent, or pH. While strong fluorescence is observed in nonpolar solvents, *t*-4-MeAPyE exhibits extremely weak fluorescence in polar solvents. On irradiation, *t*-4-MeAPyE undergoes efficient photoisomerization in polar solvents, while it doesn't photoisomerize in nonpolar solvents. At low pH, protonated *t*-4-MeAPyE shows considerably red-shifted absorption and completely quenched fluorescence. In short, the fluorescence from *t*-4-APyE derivatives is switched off responding external stimuli *viz.* medium polarity, protonation, or methylation.

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