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Photochemistry of anthrylethene derivatives containing heteroaromatic ring: Thiophene, furan, and their fused ring derivatives

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Abstract

Four 1-(9-anthryl)-2-heteroarylethene derivatives containing sulfur or oxygen atom such as 1-(9-anthryl)-2-(2-thiophenyl)ethene (ATE), 1-(9-anthryl)-2-(2-benzo[*b*]thiophenyl)ethene (ABTE), 1-(9-anthryl)-2-(2-furanyl)ethene (AFE), and 1-(9-anthryl)-2-(2-benzofuranyl)ethene (ABFE) have been prepared and their excited state properties have been investigated in cyclohexane, acetonitrile, and methanol. These sulfur- or oxygen-heteroaromatic ring derivatives show solvent-dependent fluorescence and photoisomerization behavior, due to the intramolecular charge-transfer character of the lowest S_1 state. Substituent effect on fluorescence and photoisomerization of ATE further supports the contribution of the intramolecular charge-transfer character to the lowest S_1 state, which is more increased by the introduction of electron-withdrawing substituent into anthracene ring.

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1. Introduction

Reversible *trans–cis* photoisomerization of stilbene and their heteroaryl derivatives have been extensively investigated because of the potential applicability in optical memory and optoelectronic devices [1]. However, on irradiation, *trans*-1-(9-anthryl)-2-phenylethene shows no photoreactivity including *trans* → *cis* photoisomerization, but high fluorescence quantum yield [2–7]. The excitation energy is extensively localized in the large anthracene moiety for the energy of the excited transoid geometry to be considerably low in the excited potential energy surface. In order to make *trans* → *cis* photoisomerization possible, energy barrier going from the low-lying excited *trans* geometry to twisted geometry should be lowered. Intramolecular charge transfer (ICT) processes [8–11], which could be initiated by the introduction of heteroaromatic ring into diarylethene [12], could provide a way to lower the activation barrier to C=C bond twisting in diarylethene containing large aromatic ring such as anthracene.

APE derivatives [13–18] containing electron-deficient nitrogen-heteroaromatics such as pyridine [13,14], pyrazine [15], or quinoline ring [16,17] have so high dipole moment to carry out *trans* → *cis* photoisomerization as well as *cis* → *trans* photoisomerization by the aid of ICT processes, depending on the medium.

From the viewpoint of correlating the photophysical properties and photoisomerization behavior of 1-(9-anthryl)-2-arylethenes with the size and heteroatom substitution of aryl groups, our study has been extended to thiophene and benzothiophene derivatives containing sulfur atom, and furan and benzofuran derivatives containing oxygen atom. In addition to that, it is expected that introduction of heteroatom induces the change of the energy surface in the excited state and in turn makes photoisomerization possible. To find out the way to lower energy barrier to photoisomerization, various heteroaromatic rings bearing oxygen or sulfur are introduced into *trans*-1-(9-anthryl)-2-phenylethene. We prepare two furan derivatives of 1-(9-anthryl)-2-phenylethene - 1-(9-anthryl)-2-(2-furanyl)ethene (AFE) and 1-(9-anthryl)-2-(2-benzofuranyl)ethene (ABFE)—and two thiophene derivatives—1-(9-anthryl)-2-(2-thiophenyl)ethene (ATE)

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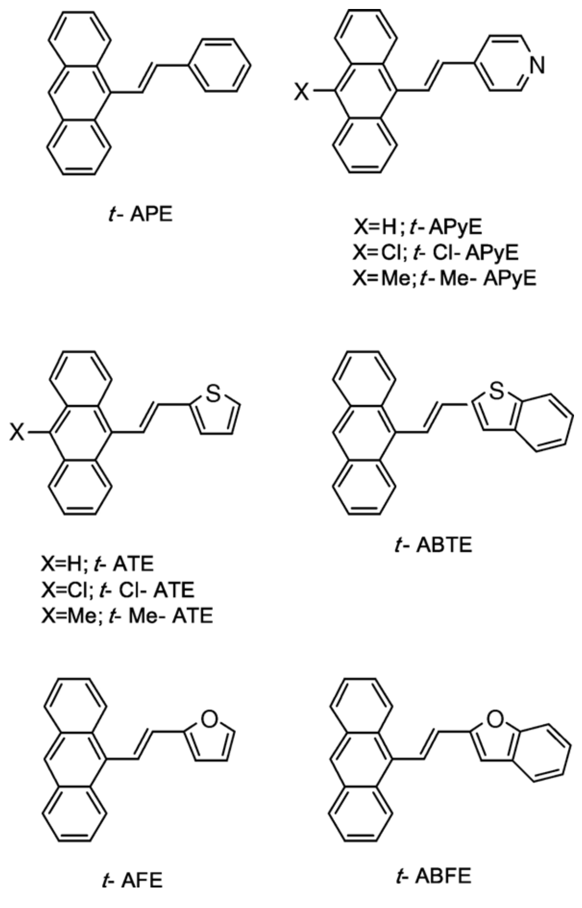
and 1-(9-anthryl)-2-(2-benzo[*b*]thiophenyl)ethenes (ABTE). The present work deals with the properties of the excited state of ATE, ABTE, AFE, and ABFE including absorption, steady state fluorescence, fluorescence decay, and photoisomerization behavior. Substituent effect on the excited state properties of ATE has been also investigated by introducing the substituents into 10-position of anthracene ring.

2. Experimental

2.1. Synthesis

The syntheses of ABTE, AFE, and ABFE were accomplished by Wittig reaction between 9-anthrylmethyltriphenylphosphonium bromide and corresponding aldehyde, using similar method as preparing ATE [19]. 1-(10-Chloro-9-anthryl)-2-(2-thiophenyl)ethene (Cl-ATE) and 1-(10-methyl-9-anthryl)-2-(2-thiophenyl)ethene (Me-ATE) were also prepared by Wittig reaction between 10-X-9-anthraldehyde (X = Cl or CH_3) and 2-bromomethylthiophene. Their structures were identified by ^1H NMR and mass spectra (Scheme 1).



Scheme 1. Structures of *t*-APE, *t*-APyE, and S- and O-heteroaromatic derivatives of *t*-APE.

t-ABTE: greenish yellow solid; IR 3031, 1649, 1540, 1513, 1456, 1422, 1082, 882, 732 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.52 (8H, m), 7.80 (1H, s), 7.98–8.06 (4H, m), 8.41–8.46 (3H, m). MS *m*/*e* 336 (M^+).

t-AFE: yellow solid; IR 3049, 1623, 1440, 1271, 1093, 1018, 963, 808, 738, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.51–6.55 (1H, m, furan H3), 6.83–6.88 (1H, m, furan H4), 6.98 (1H, d, $J = 16$ Hz, ethene H1), 7.48–7.51 (5H, m, furan H5, anthracene H2, 3, 6, 7), 8.01–8.07 (2H, m, anthracene H4, 5), 8.10 (1H, d, $J = 16$ Hz, ethene H2), 8.37–8.40 (2H, m, anthracene H1, 8), 8.50 (1H, s, anthracene H10). MS *m*/*e* 270 (M^+).

t-ABFE: yellow solid; IR 3053, 1539, 1514, 1457, 1379, 1279, 1124, 802, 735 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.75 (1H, s, benzofuran H3), 6.91 (1H, d, $J = 16$ Hz, ethene H1), 7.24–7.28 (2H, m, benzofuran H5, 6), 7.33–7.36 (1H, m, benzofuran H4), 7.48–7.51 (4H, m, anthracene H2, 3, 6, 7), 7.57–7.60 (1H, m, benzofuran H7), 8.01–8.07 (2H, m, anthracene H4, 5), 8.19 (1H, d, $J = 16$ Hz, ethene H2), 8.39–8.42 (2H, m, anthracene H1, 8), 8.50 (1H, s, anthracene H10). MS *m*/*e* 320 (M^+).

t-Cl-ATE: yellow solid; ^1H NMR ($CDCl_3$): δ 7.06 (1H, d, $J = 16.3$ Hz, ethene H1), 7.12 (1H, dd, $J = 3.6$ and 5.1 Hz, thiophene H4), 7.18 (1H, d, $J = 3.6$ Hz, thiophene H3), 7.35 (1H, d, $J = 5.1$ Hz, thiophene H5), 7.55 (2H, ddd, $J = 1.2$, 8.0, and 8.8 Hz, anthracene H2, 7), 7.64 (2H, ddd, $J = 1.2$, 8.0, and 8.8 Hz, anthracene H3, 6), 7.73 (1H, d, $J = 16.3$ Hz, ethene H2), 8.40 (2H, td, $J = 0.8$ and 8.8 Hz, anthracene H1, 8), 8.59 (2H, dd, $J = 0.8$ and 8.0 Hz, anthracene H4, 5). MS *m*/*e* 320 (M^+).

t-Me-ATE: yellow solid; ^1H NMR ($CDCl_3$): δ 3.06(3H, s, CH_3), 6.95 (1H, d, $J = 16.3$ Hz, ethene H1), 7.01 (1H, dd, $J = 3.5$ and 5.1 Hz, thiophene H4), 7.07 (1H, dd, $J = 0.5$ and 3.5 Hz, thiophene H3), 7.23 (1H, m, thiophene H5), 7.41–7.46 (4H, m, anthracene H2, 3, 6, 7), 7.69 (1H, d, $J = 16.3$ Hz, ethene H2), 8.26 (2H, dd, $J = 0.7$ and 9.1 Hz, anthracene H4, 5), 8.32 (2H, dd, $J = 0.7$ and 7.9 Hz, anthracene H1, 8). MS *m*/*e* 300 (M^+).

2.2. Spectroscopic measurements

IR spectra were obtained in KBr pellets on Midac Prospect-IR spectrometer. ^1H NMR spectra were measured on a 300 MHz Bruker DRX300 or 400 MHz Bruker Avance 400 NMR spectrometer in chloroform-d_1. Mass spectra were obtained on Micromass Platform II GC-MS spectrometer. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Steady-state fluorescence spectra were recorded on a SLM-Aminco AB2 luminescence spectrophotometer. 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 ($\Phi_f = 0.55$ in 0.1 M H_2SO_4) [20]. Time-resolved fluorescence decay was measured on a Edinburgh FL900 picosecond time-resolved luminescence spectrometer equipped with Mira Model 900-P Laser.

2.3. Photoisomerization quantum yield determination

Quantum yields of photoisomerization were determined in a home-made merry-go-round system equipped with a Hanovia 450 W medium pressure Hg arc lamp. Corning glass filters CS 0–52 and 7–60 were employed to isolate the wavelength of 366 nm. Potassium ferrioxalate was used for chemical actinometry. The concentration of 1×10^{-3} M was employed where the absorbance of the solution was above 2 and all the incident light was absorbed. Photolysis was carried out to below 5% conversion to avoid competition of the back and the paralled reactions.

Quantitative analyses for the photochemical *trans–cis* isomerization reaction were carried out by HPLC at flow rate of 1 ml/min using methanol as eluent. HPLC was accomplished with Merck LiChrosorb RP-18 analytical column on a Spectra-Physics SP 8810-010 liquid chromatograph equipped with SP8810 precision isocratic pump, Spectra 100 variable wavelength detector, and SP4290 integrator.

3. Results and discussion

3.1. Excited state properties of t-ATE, t-ABTE, t-AFE, and t-ABFE

Absorption spectra for thiophene or furan derivatives of 1-(9-anthryl)-2-phenylethene (*t*-APE) were obtained in cyclohexane, acetonitrile, and methanol. Absorption spectra of four compounds, *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE, are similar to one another, regardless of the kind of heteroaromatic ring, and also similar in the solvents of varying polarity (Table 1). Their longest absorption band maxima lie around 386–388 nm.

Fluorescence spectra of electron-rich sulfur- or oxygen-containing heteroaromatic derivatives, *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE, were observed in much longer wavelength, even in nonpolar solvent of cyclohexane, than that of hydrocarbon reference compound *t*-APE (Table 1). *t*-ABFE shows longest fluorescence wavelength maximum of 524 nm among the compounds listed in Table 1. Table 1 summarizes absorption maxima, fluorescence maxima, fluorescence lifetimes, fluorescence quantum yields, and photoisomerization quantum yields for *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE with those of a hydrocarbon reference compound *t*-APE and an electron-poor pyridine derivative *trans*-1-(9-anthryl)-2-(4-pyridyl)ethene (*t*-APyE). Fluorescence maxima of *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE are nearly unchanged in the solvents of different polarity. This is in contrast to electron-poor pyridine heteroaromatic compound *t*-APyE, showing large red-shift (29 nm, 473 nm → 502 nm) of fluorescence maximum on going from cyclohexane to methanol.

In contrast to the solvent-independent absorption and fluorescence maxima, other fluorescence properties such as quantum yield and lifetime of *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE are greatly influenced by the solvent polarity. For a hydrocarbon model compound *t*-APE, fluorescence quantum yield and fluorescence lifetime as well as fluorescence wavelength maximum remain unchanged in the solvents of different polarity (Table 1). However, for an electron-poor pyridine derivative *t*-APyE, large red-shift of fluorescence wavelength maximum and remarkable decrease of fluorescence quantum yield and lifetime in polar solvents have been observed

Table 1
Absorption maxima (λ_a^{max}), fluorescence maxima (λ_f^{max}), and quantum yields (Φ_f) of of *t*-APE, *t*-APyE, and their S- and O-heteroaromatic derivatives in cyclohexane, acetonitrile, and methanol

Compound	Solvent	λ_a^{max}(nm)	λ_f^{max}(nm)	τ_f (ns)	Φ_f	$\Phi_{t\to c}$
t-APE[a]	Cyclohexane	385	468	3.6	0.44	<0.01
	Acetonitrile	385	476	4.3	0.45	0.003
t-APyE[b]	Cyclohexane	386	473	3.6	0.44	<0.01
	Acetonitrile	388	499	0.3	0.04	0.37
	Methanol	386	502	–	0.04	0.35
t-ATE[a]	Cyclohexane	387	502	3.4	0.28	<0.01
	Acetonitrile	388	502	0.3 (86 %) 1.7 (14 %)	0.02	0.20
	Methanol	387	502	–	0.02	0.18
t-ABTE	Cyclohexane	387	502	2.5	0.19	<0.01
	Acetonitrile	387	502	1.2	0.03	0.15
	Methanol	387	502	–	0.05	0.14
t-AFE	Cyclohexane	386	500	4.3	0.47	<0.01
	Acetonitrile	386	500	1.1	0.07	0.38
	Methanol	386	500	–	0.12	0.35
t-ABFE	Cyclohexane	388	521	4.2	0.43	<0.01
	Acetonitrile	388	524	4.6	0.38	0.04
	Methanol	388	524	–	0.39	0.04

[a] Taken from Ref. [16].
[b] Taken from Refs. [13,14].

(Table 1), probably due to the stabilization of intramolecular charge transfer (ICT) excited state in polar solvents.

For electron-rich sulfur- or oxygen-containing heteroaromatic derivatives, *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE, most salient feature different from electron-poor pyridine heteroaromatic derivative *t*-APyE is that their fluorescence wavelength maxima are not shifted in polar solvents, although their fluorescence quantum yields and lifetimes are greatly reduced in polar solvents. Intramolecular charge transfer between electron-rich sulfur- or oxygen-containing heteroaromatic ring and π electron-rich anthracene ring in *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE is expected to be less efficient than intramolecular charge-transfer between an electron-poor pyridine ring and π electron-rich anthracene ring in *t*-APyE. Therefore, less contribution of ICT to the S_1 state leads to solvent-independent fluorescence maxima in the solvents of varying polarity for electron-rich sulfur- or oxygen-containing heteroaromatic derivatives, *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE. Sulfur- or oxygen-containing monocyclic heteroaromatic derivatives *t*-ATE and *t*-AFE are more sensitive to the solvent polarity for fluorescence behavior than sulfur- or oxygen-containing fused-ring heteroaromatic derivatives *t*-ABTE and *t*-ABFE.

Fluorescence quantum yield and lifetime of *t*-ATE are 0.28 and 3.4 ns in cyclohexane and 0.02, 0.3, and 1.7 ns in acetonitrile (Table 1), and those of *t*-AFE are 0.47 and 4.3 ns in cyclohexane and 0.07 and 1.1 ns in acetonitrile. On the other hands, fluorescence quantum yield and lifetime of *t*-ABTE are 0.19 and 2.5 ns in cyclohexane and 0.03 and 1.2 ns in acetonitrile, and those of *t*-ABFE are 0.43 and 4.2 ns in cyclohexane and 0.38 and 3.6 ns in acetonitrile. Fluorescence quantum yields and lifetimes of monocyclic heteroaromatic derivatives *t*-ATE and *t*-AFE are more greatly reduced in polar solvents than those of their fused ring derivatives *t*-ABTE and *t*-ABFE. Especially, *t*-ABFE are nearly unchanged for fluorescence wavelength maximum, quantum yield, and lifetime regardless of the solvent polarity. Sulfur-containing heteroaromatic derivatives *t*-ATE and *t*-ABTE show weaker fluorescence than oxygen-containing heteroaromatic derivatives *t*-AFE and *t*-ABFE. It is probably due to more efficient intersystem crossing in the presence of heavy sulfur atom. Fluorescence of *t*-ATE shows most strongly dependent on the solvent polarity among the compounds studied. Fluorescence of *t*-ATE is extremely weak in acetonitrile.

Furan, thiophene, and benzothiophene derivatives display solvent dependent fluorescence properties, while fluorescence of benzofuran derivative is much less sensitive to the solvent polarity. All the heteroaromatic derivatives studied in this study accomplish *trans* → *cis* photoisomerization in polar solvents.

In cyclohexane, all the compounds studied, *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE, accomplish no photoisomerization (see Table 1). On the other hand, upon irradiation in acetonitrile, *trans* → *cis* photoisomerization reactions of these four compounds except *t*-ABFE are relatively efficient like *t*-APyE. For electron-rich thiophene or furan derivatives *t*-ATE, *t*-ABTE, and *t*-AFE as well as electron-poor pyridine derivative *t*-APyE, the decrease of the fluorescence quantum yields in polar solvent is compensated with the increase of the photoisomerization quantum yields, as shown in Table 1.

It couldn't be completely excluded the contribution of the triplet state on the excited state properties including the photoisomerization. Although 1-(9-anthryl)-2-phenylethene does not carry out the *trans* → cis photoisomerization and

Table 2
Absorption maxima (λ_a^{max}), fluorescence maxima (λ_f^{max}), and quantum yields (Φ_f) of *t*-ATE, *t*-Cl-ATE, and *t*-Me-ATE along with *t*-APyE, *t*-Cl-APyE, and *t*-Me-APyE in cyclohexane, acetonitrile, and methanol

Compound	Solvent	λ_a^{max}(nm)	λ_f^{max}(nm)	τ_f (ns)	Φ_f	$\Phi_{t\to c}$
t-APyE[a]	Cyclohexane	386	473	3.6	0.44	<0.01
	Acetonitrile	388	499	0.3	0.04	0.37
	Methanol	386	502	–	0.04	0.35
t-Cl-APyE[a]	Cyclohexane	398	482	3.6	0.43	<0.01
	Acetonitrile	400	499	0.5	0.07	0.40
	Methanol	398	504	–	0.04	0.35
t-Me-APyE[a]	Cyclohexane	398	502	4.3	0.53	<0.01
	Acetonitrile	400	551	0.2	0.015	0.45
	Methanol	398	561	–	0.008	0.35
t-ATE	Cyclohexane	387	502	3.4	0.28	<0.01
	Acetonitrile	387	502	0.3 (86 %) 1.7 (14 %)	0.02	0.20
	Methanol	387	502	–	0.02	0.18
t-Cl-ATE	Cyclohexane	399	502	2.7	0.21	<0.01
	Acetonitrile	402	503	0.16 (88 %) 1.7 (12 %)	0.004	0.31
	Methanol	399	503	–	0.008	0.28
t-Me-ATE	Cyclohexane	398	501	3.6	0.30	<0.01
	Acetonitrile	399	512	1.8 (43 %) 3.5 (57 %)	0.17	0.15
	Methanol	398	510	–	0.18	0.15

[a] Taken from Ref. [14].

its derivatives containing various substituents on the phenyl ring are known to conduct the *trans* → *cis* photoisomerization on the excited singlet energy surface [3–6]. Formation of the triplet state could be a competing decay process with fluorescence emission and photoisomerization.

For sulfur- or oxygen-containing heteroaromatic derivatives in polar solvents, it is inferred that intramolecular charge transfer plays a role in causing Φ_f and τ_f to decrease by lowering the barrier to C=C bond twisting, and opens other radiationless or reactive pathways, such as intersystem crossing or photoisomerization.

3.2. *Substituent effect on the excited state properties of t-ATE*

As mentioned above, the excited state properties of *t*-ATE are most dependent on the solvent polarity, among electron-rich thiophene or furan derivatives *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE. To examine the contribution of the intramolecular charge transfer to the excited state properties, some *t*-ATE derivatives substituted at 10-position of anthracene moiety have been prepared and their excited state properties have been investigated.

Absorption maxima, fluorescence maxima, fluorescence lifetimes, fluoresence quantum yields, and photoisomerization quantum yields for electron-rich thiophene derivatives *t*-ATE, *t*-Cl-ATE, and *t*-Me-ATE are presented in Table 2 with those of electron-poor pyridine derivatives *t*-APyE, *t*-Cl-APyE, and *t*-Me-APyE.

Among electron-poor pyridine derivatives, *t*-Me-APyE containing electron-donating methyl substituent displays strongest dependence on the solvent polarity for the excited state properties. Absorption wavelength maximum remain unchanged at 386 nm in the solvents of varing polarity for *t*-APyE. Cl- or Me-substituted compounds show more red-shifted absorption maxima around 400 nm than the unsubstituted one. Fluorescence spectral shift and reduction of fluorescence quantum yield in polar solvent are largest for electron-donating methyl substituted derivative *t*-Me-APyE, while smallest for electron-withdrawing Cl substituted derivative *t*-Cl-APyE. For *t*-Me-APyE, shift of fluorescence maximum is as large as 49 nm and fluorescence quantum yield is greatly reduced on going from cyclohexane (0.53) to acetonitrile (0.015). On the contrary, for electron-rich thiophene derivatives, reduction of fluorescence quantum yield and lifetime in polar solvent are largest for electron-withdrawing Cl substituted derivative *t*-Cl-ATE, while smallest for electron-donating methyl substituted derivative *t*-Me-ATE.

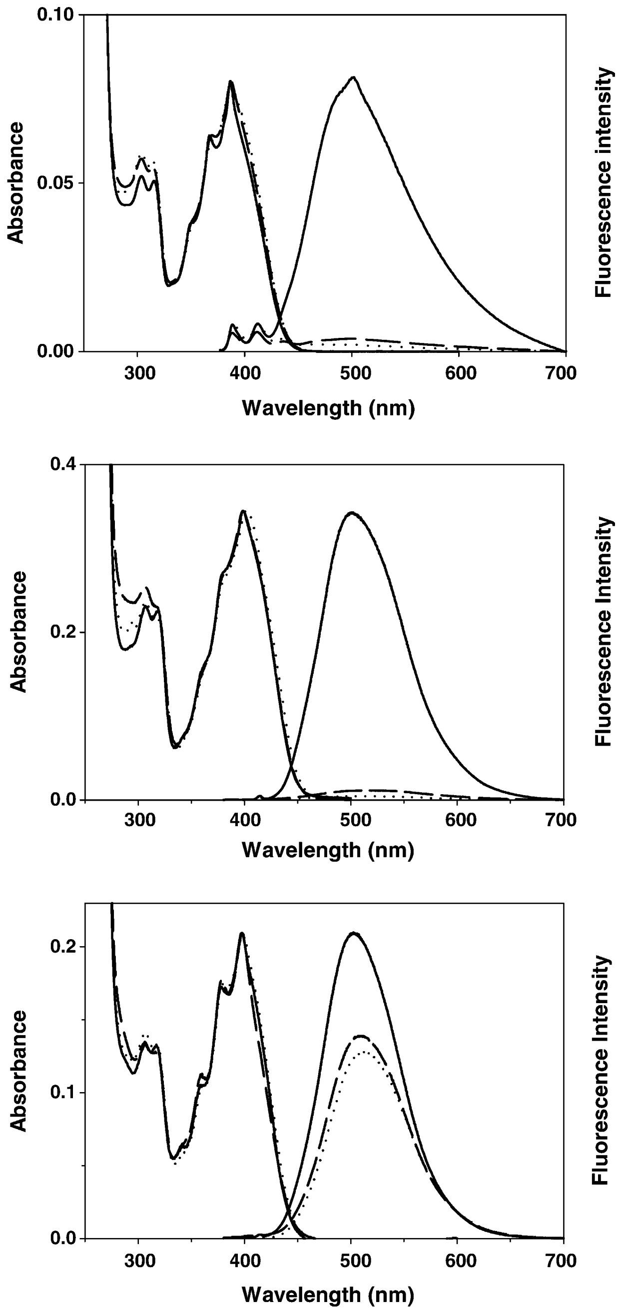


Fig. 1. Absorption and fluorescence spectra of *t*-ATE (top), *t*-ClATE (middle), and *t*-MeATE (down) in cyclohexane (solid line), acetonitrile (dotted line), and methanol (dashed line).

Absorption spectra for *t*-X-ATE (X = H, Cl, or Me) were obtained in cyclohexane, acetonitrile, and methanol (Fig. 1). Absorption spectra of three compounds *t*-ATE, *t*-Cl-ATE, and *t*-Me-ATE are similar to one another and also similar in the solvents of varying polarity. Absorption wavelength maximum remains unchanged at 387 nm in the solvents of varing polarity for *t*-ATE. Cl- or Me-substituted compounds *t*-Cl-ATE and *t*-Me-ATE show more red-shifted absorption maxima around 400 nm than the unsubstituted one *t*-ATE.

As shown in Fig. 1, for *t*-X-ATE, their fluorescence wavelength maxima are not shifted in polar solvents, although their fluorescence quantum yields and lifetimes are greatly reduced in polar solvents. Fluorescence quantum yield of *t*-ATE are 0.28 in cyclohexane and 0.02 in acetonitrile. For *t*-Cl-ATE, fluorescence maximum remains unchanged in contrast to *t*-Me-APyE showing red-shift in polar solvent as large as 49 nm. However, fluorescence quantum yield is greatly

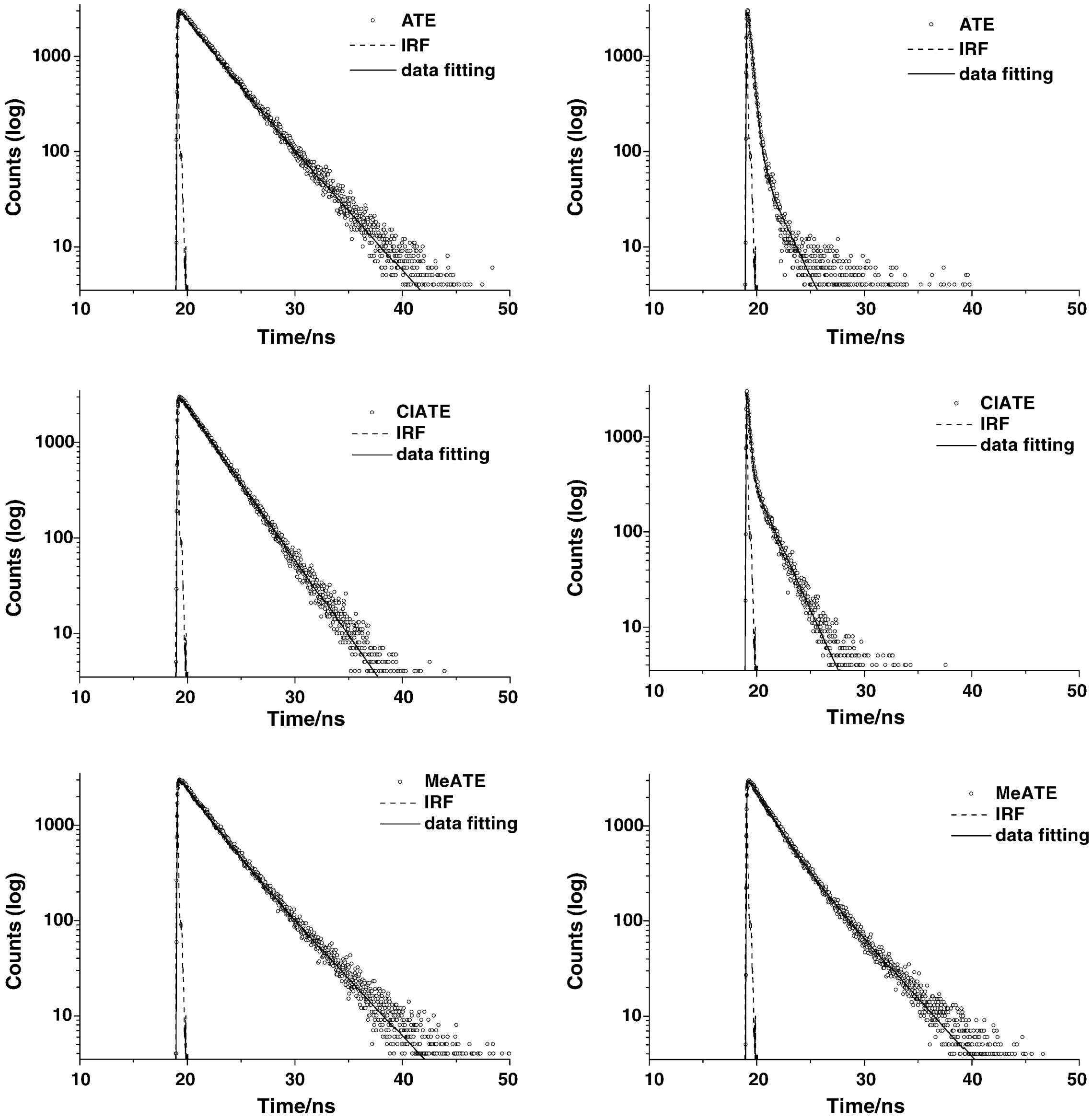


Fig. 2. Fluorescence decay curve of of *t*-ATE (upper), *t*-Cl-ATE (middle), and *t*-Me-ATE (lower) in cyclohexane (left) and acetonitrile (right).

reduced on going from cyclohexane (0.21) to acetonitrile (0.004). Fluorescence maximum of *t*-Me-ATE also remains unchanged, but fluorescence quantum yield is only moderately reduced on going from cyclohexane (0.30) to acetonitrile (0.17).

Fig. 2 shows fluorescence decay curves of *t*-ATE, *t*-Cl-ATE, and *t*-Me-ATE in cyclohexane and acetonitrile. In cyclohexane, only one component for all three *t*-X-ATE derivatives is observed in fluorescence decay. However, fluorescence emission decay profiles in acetonitrile follow bi-exponential decay kinetics for all three *t*-X-ATE. These observations indicate that two decay components from *trans* isomer and *cis* isomer are observed in acetonitrile because *trans* → *cis* photoisomerization occurs in acetonitrile, while only one decay component from *trans* isomer is observed in cyclohexane because no *trans* → *cis* photoisomerization occurs in cyclohexane. As shown in Table 2, fluorescence decay of *t*-ATE changes from mono-exponential to bi-exponential and becomes faster on going from cyclohexane (3.4 ns) to acetonitrile (0.3 and 1.7 ns). Fluorescence lifetime of *t*-Cl-ATE is also greatly shortened on going from cyclohexane (2.7 ns) to acetonitrile (0.16 and 1.7 ns). For *t*-Me-ATE, although fluorescence decay still changes from mono-exponential to bi-exponential on going from cyclohexane (3.5 ns) to acetonitrile (1.8 and 3.6 ns), lifetime of longer component does not change in acetonitrile (3.5 ns) in comparison with that in cyclohexane (3.6 ns), reflecting inefficient *trans* → *cis* photoisomerization of *t*-Me-ATE. We assume that for each *t*-X-ATE derivative, longer component is due to *trans* isomer and shorter component to *cis* isomer. Dependence of fluorescence properties on the solvent polarity decreases in the the order of *t*-Cl-ATE > *t*-ATE > *t*-Me-ATE.

For all electron-rich thiophene derivatives *t*-X-ATE (X = H, Cl, or Me), in the polar solvent, the photoisomerization quantum yields increase while the fluorescence quantum yields decrease, as shown in Table 2. All three *t*-X-ATE executed no photoisomerization in nonpolar solvent, but relatively efficient photoisomerization in polar solvent. *t*-Cl-ATE shows most increased photoisomerization quantum yield in polar solvent among all three *t*-X-ATE.

Prominent difference between electron-rich thiophene derivatives *t*-X-ATE (X = H, Cl, or Me) and electron-poor pyridine derivatives *t*-X-APyE (X = H, Cl, or Me) is that *t*-Cl-ATE containing electron-withdrawing Cl substituent among electron-rich thiophene derivatives *t*-X-ATE displays strongest dependence on the solvent polarity for the excited state properties, while *t*-Me-APyE containing electron-donating methyl substituent displays strongest dependence among electron-poor pyridine derivatives *t*-X-APyE.

4. Conclusion

The effect of introducing a heteroaryl ring such as thiophene, furan, or pyridine into *t*-APE could be explained by a contribution of the excited intramolecular charge transfer state to the photoisomerization behavior as well as the photophysical properties. Fluorescence properties of electron-rich thiophene or furan ring derivatives *t*-ATE, *t*-ABTE, *t*-AFE, and *t*-ABFE are dependent on the solvent polarity for its intensity and decay rate, but solvent-independent for its wavelength maximum, on the contrary that fluorescence properties of an electron-poor pyridine derivative *t*-APyE are solvent-dependent for all its wavelength maximum, intensity, and lifetime. This indicates a lower degree of intramolecular charge transfer character induced by electron-rich thiophene or furan ring than electron-poor pyridine ring, because anthracene ring in the other end of the molecules is electron-rich to some extent. Substituent effect on the excited state properties of *t*-ATE further supports the facts that the intramolcular charge transfer contributes to the remarkable reduction of fluorescence in polar solvent. Among the electron-rich thiophene derivatives *t*-X-ATE (X = H, Cl, Me), reduction of fluorescence quantum yield and lifetime in polar solvent is largest for electron-withdrawing Cl substituted derivative. Fluorescence of *t*-Cl-ATE is practically off in polar solvent and efficiently switchable so that *t*-Cl-ATE serves as an on-off switch on fluorescence by controlling the medium polarity.

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References

[1] J. Saltel, Y.-P. Sun, Photochromism; Molecules and Systems, Elsevier, Amsterdam, 1990.
[2] T. Arai, K. Tokumaru, Photochemical one-way adiabatic isomerization of aromatic olefins, Chem. Rev. 93 (1993) 23–39.
[3] T. Arai, K. Tokumaru, Present status of the photoisomerization about ethylenic bonds, Adv. Photochem. 20 (1995) 1–57.
[4] G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, G. Orlandi, G. Poggi, A photophysical and theoretical study of styrylanthracenes, J. Chem. Soc. Faraday Trans. 2 84 (1988) 385–399.
[5] G. Bartocci, U. Mazzucato, A. Spalletti, G. Orlandi, G. Poggi, Effect of the nature of the aromatic groups on the lowest excited states of *trans*-1,2-diarylethenes, J. Chem. Soc. Faraday Trans. 88 (1992) 3139–3144.
[6] K. Bhattacharyya, S.K. Chattopadhyay, S. Baral-Tosh, P.K. Das, Excited-state properties of *trans*-(9-anthryl)ethylenes. Effects of geometric distortion about single bond, J. Phys. Chem. 90 (1986) 2646–2651.
[7] G. Bartocci, A. Spalletti, U. Mazzucato, Solvent and temperature effects on the fluorescence and competitive photoreactions of *cis*-9-styrylanthracene, Res. Chem. Intermed. 21 (1995) 735–747.
[8] Z.R. Grabowski, Electron transfer in flexible molecules and molecular ions, Pure Appl. Chem. 65 (1993) 1751–1756.
[9] M. Hashimoto, H. Hamaguchi, Structure of the twisted-intramolecular-charge-transfer excited singlet and triplet states of 4-(dimethylamino)benzonitrile as studied by nanosecond time-resolved infrared spectroscopy, J. Phys. Chem. 99 (1995) 7875–7877.
[10] T. Scherer, I.H.M. van Stokkum, A.M. Brouwer, J.W. Verhoeven, Excited-state conformational dynamics of flexibly and semi-rigidly bridged electron donor-acceptor systems in solution Influence of temperature and solvent viscosity, J. Phys. Chem. 98 (1994) 10539–10549.
[11] W. Rettig, Photophysical and photochemical switches based on twisted intramolecular charge transfer (TICT) states, Appl. Phys. B 45 (1988) 145–149.
[12] S.-L. Wang, T.-I. Ho, Substituent effects on intramolecular charge-transfer behavior of styrylheterocycles, J. Photochem. Photobiol. A 135 (2000) 119–126.
[13] E.J. Shin, E.Y. Bae, S.H. Kim, H.K. Kang, S.C. Shim, Photophysical properties and photoisomerization behavior of 1-(9-anthryl)-2-(*n*-pyridyl)ethenes($n = 2$, 3 or 4), aza analogues of 1-(9-anthryl)-2-phenylethene, J. Photochem. Photobiol. A 107 (1997) 137–146.
[14] E.J. Shin, S.H. Lee, Substituent effect on fluorescence and photoisomerization of 1-(9-anthryl)-2-(4-pyridyl)ethenes, Bull. Korean Chem. Soc. 23 (2002) 1309–1314.
[15] E.J. Shin, S.W. Choi, Photoisomerization behavior of 1-(9-anthryl)-2-(9-pyrazinyl)ethene, a diaza analogue of 1-(9-anthryl)-2-phenylethene, J. Photochem. Photobiol. A 114 (1998) 23–30.
[16] E.J. Shin, Fluorescence properties and photoisomerization behavior of 1-(9-anthryl)-2-(2-quinolinyl)ethene, Bull. Korean Chem. Soc. 20 (1999) 1263–1268.
[17] E.J. Shin, R. Stackow, C.S. Foote, Excited state properties of some 1-(9-anthryl)-2-naphthylethene and 1-(9-anthryl)-2-quinolylethene derivatives, Phys. Chem. Chem. Phys. 4 (2002) 5088–5095.
[18] U.W. Grummt, E. Birckner, H. Lindauer, B. Beck, R. Rotomskis, deactivation of excited 4′-dialkylamino-9-styrylacridines, J. Photochem. Photobiol. A: Chem. 104 (1997) 69–76.
[19] E.J. Shin, Excited state behavior of 1-(9-anthryl)-2-(2-thienyl)ethene, Bull. Korean Chem. Soc. 23 (2002) 1685–1688.
[20] J.G. Calvert, J.N. Pitts Jr., Photochemistry, Wiley, New York, 1966.