Excited State Behavior of 1-(9-Anthryl)-2-(2-thienyl)ethene

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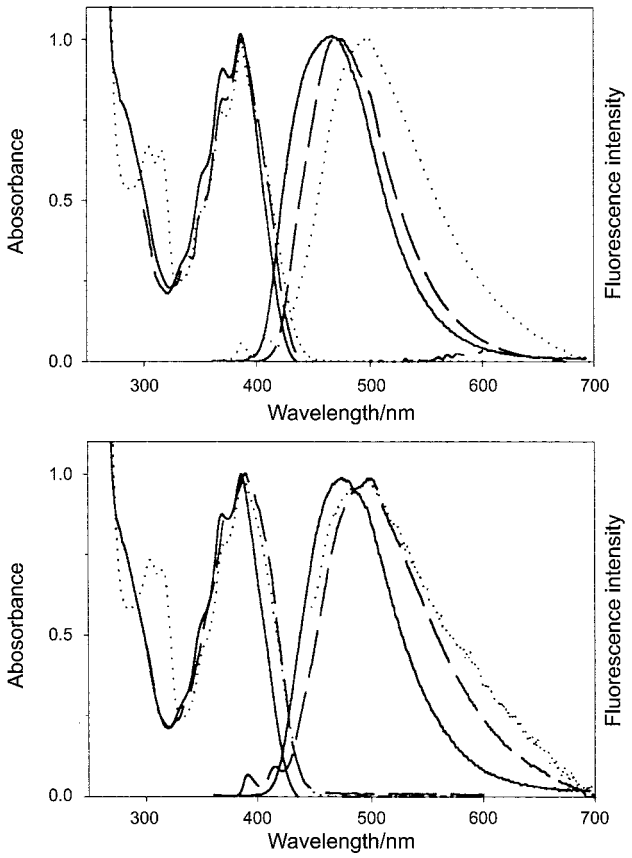
Photochemistry and photophysics of diarylethenes[1-4] have been extensively studied because of the potential applicability in optical memory and optoelectronic devices. The excited state properties of their nitrogen heteroaryl derivatives[5-11] have also been investigated. However, the excited state behavior of diarylethenes bearing sulfur heterocyclic rings[12-14] is much less known, although special attention has been paid to 1,2-diarylethenes having thiophene ring as photochromic molecules[4] in the last ten years because of their thermal and optical stability and fatigue resistance. We report here the preparation of *trans*-1-(9-anthryl)-2-(2-thienyl)ethene (*t*-AThE), a thiophene derivative of *trans*-1-(9-anthryl)-2-phenylethene (*t*-APE), and its absorption and fluorescence spectral data and photoisomerization behavior.

While stilbene shows very weak fluorescence due to very efficient two-way photoisomerization,[1-4] 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.[15-17] The reason why *trans*-anthrylarylethenes are photochemically unreactive 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 including stilbene derivatives.[18-21] 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.[11] Photoisomerization reactions and very weak fluorescence have been observed in polar solvent for N-heteroaromatic derivatives of *t*-APE, [22-26] probably due to the contribution of the ICT state, in contrast that no photoisomerization and relatively strong fluorescence was observed for *t*-APE itself. It is likely that other heteroaromatic derivatives such as thiophene increases the donor-acceptor ability to favor the formation of the excited ICT state and leads to influence fluorescence and photoisomerization characteristics.

Absorption and fluorescence spectra of *t*-AThE in cyclohexane and acetonitrile are shown and compared with those of *t*-APE and *t*-APyE in Figure 1. Table 1 summarizes the lowest excited singlet state parameters of *t*-AThE as well as *t*-APE and *t*-APyE. Absorption spectral shape and its maxima are similar for *t*-APE, *t*-APyE, and *t*-AThE and not nearly influenced by the solvent polarity as shown in Table 1. However, the longest absorption bands of *t*-AThE and *t*-APyE are similar to each other and are broader than that of a hydrocarbon molecule, *t*-APE.

The situation is different for fluorescence spectra. In contrast to the absorption spectra, fluorescence spectra are greatly influenced by the heteroaromatics introduced in anthrylarylethenes and the solvent polarity for their intensity or position. For a hydrocarbon *t*-APE, the fluorescence wavelength maxima and fluorescence quantum yield are not so different in the solvents of different polarity. However, the solvatochromic effect on the fluorescence spectra is observable for *t*-APyE. In acetonitrile, *t*-APyE shows large red-shift of *ca*. 17 nm and remarkable decrease of fluorescence



Fgure 1. Absorption and fluorescence spectra of *t*-APE (solid line), *t*-APyE (dashed line), and *t*-AThE (dotted line) in cyclohexane (upper) and acetonitrile (lower).

Table 1. Absorption and fluorescence data of *t*-APE, *t*-APyE, and *t*-AThE in cyclohexane and acetonitrile

Compound	Solvent	λ_a^{max}/nm	λ_f^{max}/nm	Φ_f	$\Phi_{t\rightarrow c}$
t-APE[a]	cyclohexane	385	468	0.44	<0.01
	acetonitrile	385	476	0.45	0.003
t-APyE[a]	cyclohexane	386	476	0.44	<0.01
	acetonitrile	386	493	0.04	0.37
t-AThE	cyclohexane	387	502	0.28	<0.01
	acetonitrile	387	502	0.02	0.20

[a]Data from ref. 24.

Table 2. Absorption and fluorescence data of *t*-AThE in various solvents

Solvent	$E_T(30)^a$	λ_a^{max}/nm	λ_f^{max}/nm	Φ_f
cyclohexane	31.2	387	502	0.28
toluene	33.9	390	502	0.24
tetrahydrofuran	37.4	389	502	0.072
dichloromethane	38.1	390	502	0.066
ethyl acetate	41.1	388	498	0.086
acetonitrile	46.0	388	502	0.015
ethanol	51.9	387	502	0.044
methanol	55.5	387	502	0.018

[a]Dimroth's empirical solvent polarity parameter.

quantum yield relative to in cyclohexane (see Table 1). In nonpolar solvents, efficient fluorescence was observed. On the other hand, polar solvents result in the drastic reduction of fluorescence quantum yield. These results for *t*-APyE are probably due to the stabilization of intramolecular charge transfer (ICT) excited state in polar solvent. For *t*-AThE, even in cyclohexane, red-shifted fluorescence spectrum is observed relative to that of *t*-APE. But, the solvatochromic shift of the fluorescence spectrum is not observed in contrast to *t*-APyE, *viz.* fluorescence maximum of *t*-AThE in acetonitrile is the same as in cyclohexane, while the fluorescence quantum yield is greatly reduced in polar solvents. Absorption and fluorescence maxima and quantum yields of *t*-AThE are shown in Table 2 in various solvents. The above three compounds respond differently to the solvent polarity for fluorescence behavior, which are well compared in Figure 2.

For both *t*-AThE and *t*-APyE 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.

In cyclohexane, *t*-AThE underwent no photoisomerization, similar to *t*-APE and *t*-APyE (see Table 1). In acetonitrile, photoisomerization of *t*-AThE upon irradiation is relatively efficient like *t*-APyE. On irradiation at 366 nm, absorption spectral change of *t*-AThE is shown in Figure 3. When irradiated in acetonitrile, absorption spectrum of *t*-AThE becomes more structured and shows the decrease of its intensity, due to *trans* → *cis* photoisomerization. For *t*-AThE and *t*-APyE in acetonitrile, the decrease of the fluorescence quantum yields are compensated with the increase of the photoisomerization quantum yields contrast to those in

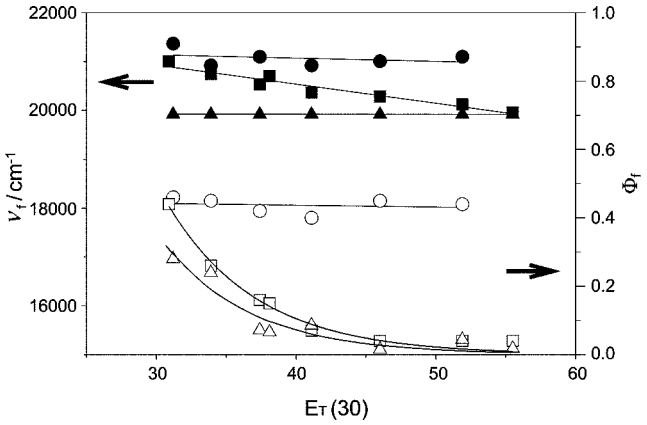


Figure 2. Dependence of fluorescence maximum ν_f (closed symbol) and fluorescence quantum yield Φ_f (open symbol) for *t*-APE (circle), *t*-APyE (rectangle), and *t*-AThE (triangle) on the solvent polarity. E_T(30) represents Dimroth's empirical solvent polarity parameter.

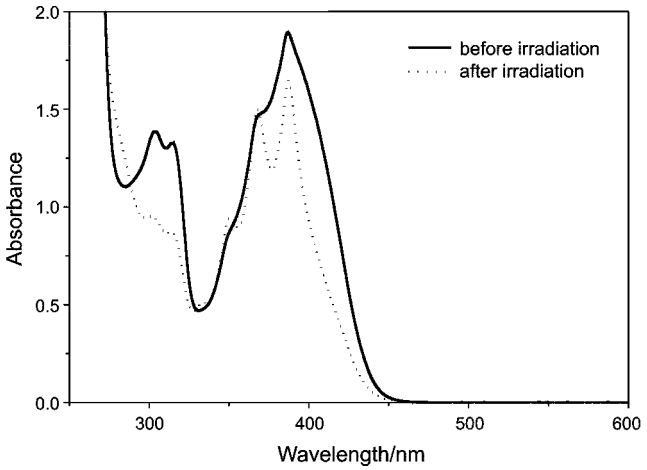
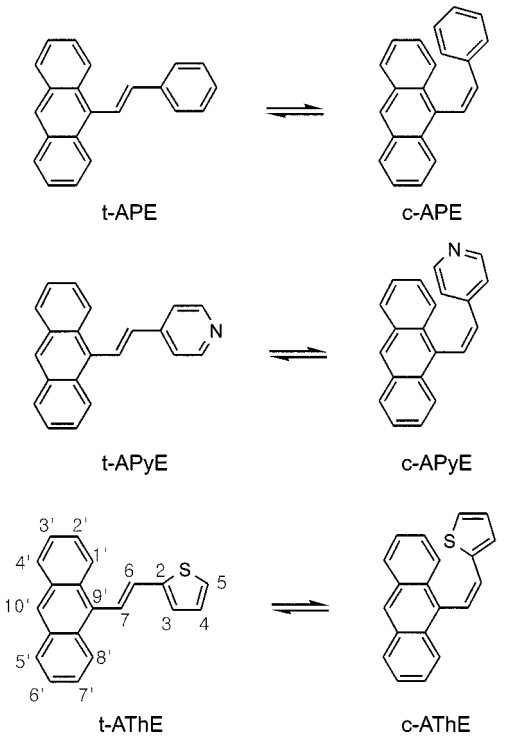


Figure 3. Absorption spectral change of *t*-AThE in acetonitrile on irradiation at 366 nm.

cyclohexane remaining constant, as shown in Table 1. 1-(9-Anthryl)-2-phenylethene, a hydrocarbon derivative without any heteroatom is well known to undergo no *trans* → *cis* photoisomerization. The effect of introducing a heteroaryl ring such as thiophene and pyridine in *t*-APE can be explained by a contribution of the excited intramolecular charge transfer state to the photoisomerization behavior as well as the photophysical properties. $\Phi_{t\rightarrow c}$ of *t*-AThE(0.20) is lower than that of *t*-APyE(0.37) in acetonitrile. This reflects that a lower degree of intramolecular charge transfer character induced by less electronegative sulphur than nitrogen makes *trans* → *cis* photoisomerization less feasible.

In conclusion, the absorption and fluorescence and photoisomerization quantum yields of *t*-AThE were measured in cyclohexane and acetonitrile at room temperature. The observations in *t*-AThE are different with either *t*-APE or *t*-APyE. Both absorption and fluorescence maxima of *t*-AThE remain unchanged in various solvents. The fluorescence in polar solvents is extremely weak in contrast to moderate fluorescence quantum yield in nonpolar solvents. In cyclo-



Scheme 1. Structures of APE, APyE, and AThE.

hexane, a nonpolar solvent, efficient fluorescence was observed, while no photoisomerization was observed as *t*-APyE. Acetonitrile, a polar solvent, result in the drastic reduction of fluorescence quantum yield and increase of photoisomerization quantum yield similar to *t*-APyE, but no shift of fluorescence maximum in contrast to *t*-APyE.

Experimental Section

Materials. *trans*-1-(9-Anthryl)-2-(2-thienyl)ethene (*t*-AThE) was prepared from Wittig coupling of 9-bromomethylanthracene[23] and 2-thiophenealdehyde. The structure was identified by IR, ^{1}H NMR, and mass spectra. *t*-AThE: yellow solid; IR 3049, 1619, 1440, 1261, 1093, 1018, 959, 808, 738, 695 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06-7.11 (2H, m, H4, 7), 7.23 (1H, d, J = 3.3 Hz, H3), 7.31 (1H, d, J = 5.1 Hz, H5), 7.46-7.50 (4H, dd, J = 6.4 Hz, 3.3 Hz, H2', 3', 6', 7'), 7.77 (1H, d, J = 16.5 Hz, H6), 8.00-8.03 (2H, dd, J = 6.4 Hz, 3.3 Hz, H4', 5'), 8.34-38 (2H, dd, J = 6.4 Hz, 3.3 Hz, H1', 8'), 8.40 (1H, s, H10'). MS m/e 286 (M^+). *c*-AThE: pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.42 (1H, d, J = 5.9 Hz, H7), 6.88-6.98 (2H, m, H3, 4), 7.15 (1H, d, J = 4.6 Hz, H5), 7.40-7.50 (5H, m, H2', 3', 6', 7', 10'), 7.64 (1H, d, J = 5.9 Hz, H6), 8.00-8.03 (2H, dd, J = 6.4 Hz, 3.3 Hz, H4', 5'), 8.18-22 (2H, dd, J = 6.4 Hz, 3.3 Hz, H1', 8'). MS m/e 286 (M^+).

Spectroscopic and Photochemical Measurements. IR spectra were obtained in KBr pellets on Midac Prospect-IR spectrometer. ^{1}H NMR spectra were measured on a 300 MHz Bruker DRX300 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 an 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 (Φ_f = 0.55 in 0.1 M H_2SO_4).[27] For the determination of photoisomerization quantum yield, irradiation wavelength of 366 nm isolated with Corning glass filters (CS 0-52 and 7-60) was employed in argon-saturated solution using a home-built merry-go-round system equipped with a Hanovia 450W medium-pressure Hg arc lamp. Potassium ferrioxalate was used for chemical actinometry.[27] Concentration for the measurements of quantum yield of photoisomerization was adjusted to be *ca.* 8×10^{-4} M in which all incident light was absorbed. Quantitative analyses of the *trans* $\rightarrow$ *cis* photoisomerization reaction were carried out by HPLC at a flow rate of 1 mL min^{-1} using methanol as an eluent. HPLC was accomplished using Merck LiChrosorb RP-18 analytical column on a Spectra-Physics SP precision isocratic pump, a Spectra 100 variable wavelength detector, and a SP4290 integrator.

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