Notes

Photochemistry of Anthrylethene Derivatives Containing Heteroaromatic Ring : Pyrrole and Indole Derivatives

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Received February 25, 2004

Key Words : Diarylethene, Pyrrole, Indole, Fluorescence, Intramolecular charge transfer

Diarylethenes are generally known to perform reversible photochemical *cis-trans* isomerization. However, 1-(9-anthryl)-2-phenylethene(9-APE) executes efficient *cis* → *trans* photoisomerization but do not undergo reverse *trans* → *cis* photoisomerization.[1-6] The excitation energy is extensively localized in the large anthracene moiety so that the transoid geometry corresponds to energy minima in the excited potential energy surface. The energy barrier to C=C bond twisting is too high for *t*-9-APE to undergo *trans* → *cis* photoisomerization.

Intramolecular charge transfer (ICT) could provide a way to lower the activation barrier to twisting of ethene bond in anthrylethene derivatives. Introduction of heteroaromatic ring into anthrylethene increases the dipole moment of the compound to initiate the excited state ICT processes.

Nitrogen-heteroaromatic derivatives of 9-APE containing pyridine,[8,9] pyrazine,[10] or quinoline ring[11,12] in place of phenyl ring perform *trans* → *cis* photoisomerization as well as *cis* → *trans* photoisomerization, depending on the medium. In comparison with parent 9-APE, the aza substitution changes the donor-acceptor properties of the molecules.[8-12] Pyridine is referred to as an electron-deficient heterocycle and has some analogy with a benzene ring that carries an electron-withdrawing substituent. As pyridine, pyrazine, or quinoline ring acts as an electron acceptor, intramolecular charge transfer processes should affect on the excited state properties of nitrogen-heteroaromatic derivatives of 9-APE. As reported in our previous papers, 1-(9-anthryl)-2-(*n*-pyridyl)ethenes(*n*-APyE, *n*=2 or 4)[8] and 1-(9-anthryl)-2-(*n*-quinolyl)ethenes(*n*-AQE, *n*=2 or 4),[12] mono-aza analogues of 9-APE, show efficient *trans* → *cis* photoisomerization in polar solvent, and 1-(9-anthryl)-2-pyrazinylethene(APzE),[10] a di-aza analogue of 9-APE, exhibits *transÆcis* photoisomerization even in nonpolar solvent.

On the other hand, pyrrole is referred to as an electron-rich heterocycle and has some analogy with a benzene ring that carries an electron-donating substituent. In this paper, we prepared 9-APE derivatives containing electron-rich pyrrole or indole ring and investigated their excited-state properties in comparison with electron-deficient pyridine derivative 4-APyE.

Absorption and fluorescence spectra of *t*-2-APyrE, *t*-2-AIE, and *t*-2-AMIE in cyclohexane and acetonitrile are shown in Figure 1. Table 1 summarizes absorption and fluorescence data of *t*-2-APyrE, *t*-2-AIE, and *t*-2-AMIE along with those of *t*-9-APE and *t*-4-APyE. Absorption spectral shape and its maxima are not nearly influenced by the solvent polarity for all the compounds studied.

In contrast to the absorption spectra, fluorescence maxima and quantum yields are strongly dependent on the solvent polarity as well as the kind of the heteroaromatic ring introduced into 9-APE. For a hydrocarbon *t*-9-APE, the fluorescence wavelength maxima and fluorescence quantum yields remain unchanged in the solvents of different polarity. However, a pyridine derivative *t*-4-APyE (see Table 1) shows large red-shift of the fluorescence maximum and remarkable decrease of fluorescence quantum yield in polar solvents. As for the fluorescence of indole derivative *t*-2-AIE, unusually large solvatochromic effect is observed. The fluorescence spectrum of *t*-2-AIE is much more red-shifted (62 nm) in polar solvents relative to that of *t*-4-APyE(26 nm), and their fluorescence quantum yields are greatly reduced in polar solvents (Figure 1 and Table 1). Fluorescence quantum yield of pyrrole derivative *t*-2-APyrE is much more reduced in polar solvent than that of indole derivative *t*-2-AIE. In fact, *t*-2-APyrE shows no fluorescence in acetonitrile. These solvatochromic effects on the fluorescence spectra are probably due to the stabilization of the excited intramolecular charge transfer (ICT) state in polar solvents. *t*-2-AMIE is less dependent on the solvent polarity than *t*-2-AIE for both fluorescence wavelength and quantum yield, and, even in cyclohexane, red-shifted fluorescence spectra are observed in much longer wavelength than that of *t*-9-APE.

All the compounds studied executed no photoisomerization in cyclohexane (see Table 1). In acetonitrile, photoisomerization reactions of pyrrole and indole heteroaromatic derivatives *t*-2-APyrE and *t*-2-AIE upon irradiation are relatively efficient like *t*-4-APyE. Photoisomerization quantum yield of *t*-2-AMIE in acetonitrile is smaller than those of *t*-2-APyrE and *t*-2-AIE. For *t*-2-APyrE, *t*-2-AIE, and *t*-2-AMIE, the decrease of the fluorescence quantum yields in polar solvents are compensated with the increase of the photo-

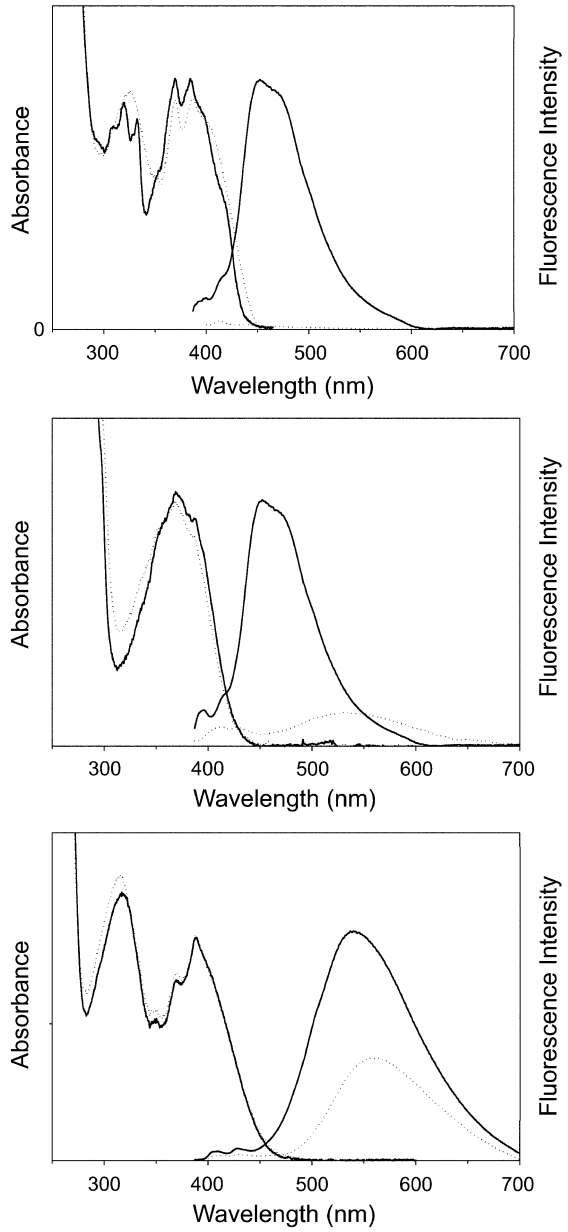


Figure 1. Absorption (left) and fluorescence (right) spectra of *t*-2-APyrE (upper), *t*-2-AIE (middle), and *t*-2-AMIE (lower) in cyclohexane (solid line) and acetonitrile (dotted line).

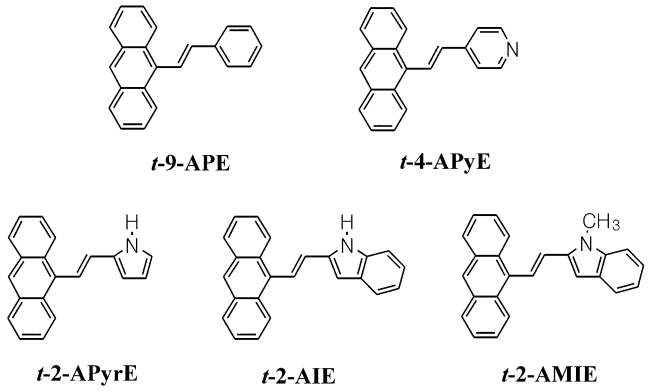
isomerization quantum yields compared with those in cyclohexane, as shown in Table 1.

The effect of introducing a heteroaryl ring such as pyrrole or indole into *t*-9-APE can be explained by a contribution of the excited intramolecular charge transfer state to the photoisomerization behavior and the photophysical properties. Fluorescence of electron-donating pyrrole and indole derivatives can be controlled by the solvent polarity, in similarity with electron-withdrawing pyridine derivative *t*-4-APyE. In particular, fluorescence of *t*-2-APyrE is completely switched off in polar solvent, while relatively strong in nonpolar solvent. Unusually large solvatochromic effect is observed for the fluorescence spectrum of *t*-2-AIE.

Table 1. Absorption maxima (λ_a^{max}), fluorescence maxima (λ_f^{max}), and quantum yields (Φ_f) of of *t*-9-APE, *t*-4-APyE, *t*-2-APyrE, *t*-2-AIE, and *t*-2-AMIE in cyclohexane and acetonitrile

compound	solvent	λ_a^{max}/nm	λ_f^{max}/nm	Φ_f	$\Phi_{t\rightarrow c}$
t-9-APE[a]	cyclohexane	385	468	0.44	< 0.01
	acetonitrile	385	476	0.45	0.003
t-4-APyE[b]	cyclohexane	386	473	0.44	< 0.01
	acetonitrile	388	499	0.04	0.37
t-2-APyrE	cyclohexane	385	471	0.42	< 0.01
	acetonitrile	387	not detected	~0	0.28
t-2-AIE	cyclohexane	371	471	0.32	< 0.01
	acetonitrile	370	533	0.02	0.20
t-2-AMIE	cyclohexane	389	540	0.34	< 0.01
	acetonitrile	387	558	0.13	0.07

[a]Data from *ref*. 13. [b]Data from *ref*. 9.



Scheme 1. Structures of *t*-9-APE, *t*-4-APyE, *t*-2-APyrE, *t*-2-AIE, and *t*-2-AMIE.

Experimental Section

Syntheses of 2-APyrE, 2-AIE, and 2-AMIE were accomplished by Wittig reactions between 9-anthrylmethyltriphenylphosphonium bromide and corresponding aldehydes, using similar method as reported previously.[13] Their structures were identified by ^{1}H-NMR and mass spectra.

t-2-APyrE: yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45-6.53 (2H, m, pyrrole H3, 4), 6.91-6.95 (1H, m, pyrrole H5), 7.34-7.52 (6H, m, anthracene H2, 3, 6, 7, central double bond CH), 7.80 (1H, s, NH), 7.98-8.06 (4H, m, anthracene H4, 5), 8.41-8.46 (3H, m, anthracene H1, 8, 10). MS m/e 269 (M^+).

t-2-AIE: yellow solid; ^{1}H-NMR ($CDCl_3$) δ 7.00-7.10 (2H, m, central double bond CH), 7.25-7.40 (3H, m, indole H3, 5, 6), 7.48-7.50 (4H, m, anthracene H2, 3, 6, 7), 7.62 (1H, d, J = 8 Hz, indole H7), 8.01-8.07 (2H, m, anthracene H4, 5), 8.10 (1H, d, J = 9 Hz, indole H4), 8.37-8.40 (2H, m, anthracene H1, 8), 8.45 (1H, s, anthracene H10). MS m/e 329 (M^+).

t-2-AMIE: yellow solid; ^{1}H-NMR($CDCl_3$) δ 3.82 (3H, s, N-CH_3), 6.99-7.09 (2H, m, central double bond CH), 7.29-7.45 (3H, m, indole H3, 5, 6), 7.48-7.51 (4H, m, anthracene

H2, 3, 6, 7), 7.68 (1H, d, J = 7.8 Hz, indole H7), 8.00-8.05 (2H, m, anthracene H4, 5), 8.20 (1H, d, J = 9 Hz, indole H4), 8.38-8.43 (2H, m, anthracene H1, 8), 8.47 (1H, s, anthracene H10). MS m/e 343 (M^+).

Acknowledgment. The author would like to thank KBSI for their help in the measurement of NMR and mass spectra. This work was supported by a grant No. R04-2002-000-00014-0 (2003) from Korea Science & Engineering Foundation.

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