Chromophoric System of Unsymmetrical Indamine Dyes Derived from (Diethylamino)thiazole Dimer

Jae Joon Kim, Kazumasa Funabiki, Katsuyoshi Shibata, Hiroshige Muramatsu, Hisayoshi Shiozaki,[†] and Masaki Matsui*
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193
[†]*Technology Research Institute of Osaka Prefecture, 2-7-1 Ayumino, Izumi, Osaka 594-1157*

Unsymmetrical indamine dyes have been synthesized by the reaction of (diethylamino)thiazole dimer with 4-nitrosoanilines followed by heating with metal salts. The chromophoric system for these indamine dyes was described as the mixture of the $\pi-\pi^*$ transition coming from the alternant chromophore inside the bithiazolyl moiety and the charge-transfer from anilino to bithiazolyl moieties.

Indamine dyes are interesting compounds due to their bathochromicity.[1,2] Although symmetrical indamine dyes such as Bindschedler's Green have been reported to have an alternant chromophoric system,[2] no paper concerning the property of unsymmetrical indamine dyes has been reported so far. We report here the UV–vis absorption spectra and the chromophoric system of unsymmetrical indamine dyes derived from (diethylamino)thiazole dimer.

Scheme 1 shows the synthesis of indamine dyes **3**.[3] These dyes were prepared by the reaction of (diethylamino)thiazole dimer **1**[4] with 4-nitrosoanilines **2** followed by heating with metal salts. Nickel(II) tetrafluoroborate was the best metal salt to synthesize the indamine dyes **3**.
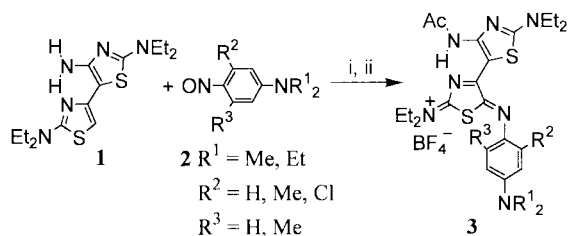
Scheme 1. Reaction conditions: i, acetic anhydride, r.t., 0.5 h; ii, Ni(BF$_4$)$_2$, 100 °C, 0.5 h.

The UV–vis absorption spectrum of dye **3a** is depicted in Figure 1. The first and second absorption bands were observed at $\lambda = 648$ ($\varepsilon = 38000$ dm^3 mol^{-1} cm^{-1}) and 506 ($\varepsilon = 26000$) nm in dichloromethane, respectively. The observed UV–vis absorption spectra for indamine dyes **3** are summarized in Table 1. The diethylamino derivative **3b** was more bathochromic than the dimethylamino one **3a**. Griffiths and Cox have reported that the symmetrical indamine dye has an alternant chromophoric system and that the electron-donating and -withdrawing groups attached to unstarred positions induced hypsochromic and bathochromic shifts in the first absorption band, respectively.[2] Among dyes **3b–d**, the bathochromicity was in the order of dyes: **3c** ($\Delta\lambda = 21$ nm) > **3b** ($\Delta\lambda = 0$ nm) > **3d** ($\Delta\lambda = -9$ nm). This result is not suited to the alternant chromophoric system of usual indamine dyes. To elucidate this substituent effects, the semi-empirical MO calculation was carried out.[5]
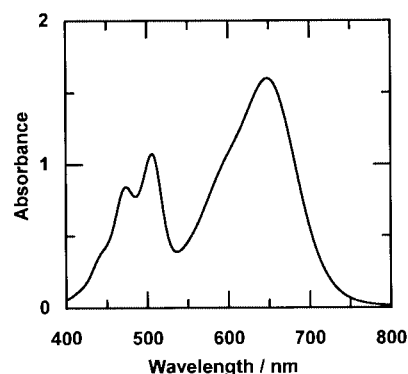

Figure 1. UV–vis absorption spectrum of dye **3a** in dichloromethane.

Table 1. The observed and calculated UV–vis absorption spectra for indamine dyes **3**

Dye	R^1	R^2	R^3	$\dfrac{\lambda_{max}}{nm}(\varepsilon_{max})^a$	$\dfrac{\Delta\lambda^b}{nm}$	Dihedral angle $(\theta)^c$ degree	$\dfrac{\lambda_{max}^{\ d}}{nm}$	f^e
3a	Me	H	H	506 (26000)	−15	0.1	356	0.66
				648 (38000)			452	0.88
3b	Et	H	H	509 (29000)	0	0.1	368	0.66
				663 (51000)			460	0.88
3c	Et	Me	H	517 (23000)	21	9.5	380	0.24
				684 (39000)			471	0.86
3d	Et	Cl	H	514 (25000)	−9	0.6	374	0.30
				654 (38000)			455	0.88
3e	Et	Me	Me	519 (24000)	62	65.2	389	0.83
				725 (3900)			505	0.16

^{a}Measured in dichloromethane. $^b\Delta\lambda = \lambda_{max}$ (**3a–e**)$-\lambda_{max}$ (**3b**). ^{c}The PM3-optimized dihedral angle between bithiazolyl and anilino segments. ^{d}Calculated by the INDO/S method. ^{e}Oscillator strength.

Geometry optimizations were carried out using the PM3 method, and the absorption spectra were studied with the INDO/S method. In the INDO/S calculation, the parameter of sulfur atom (Es = 21.02, Ep = 10.97, Bsp = 13.5, G = 10.01)[6] was added for the calculations, and 100 configurations were considered for the configuration interaction. The calculated absorption bands are also shown in Table 1. The calculated first and second absorption bands showed good linear correlations with those of the observed ones. The first absorption band was assigned as the HOMO–LUMO transition. The schematic representation of HOMO, LUMO and the difference in electron density between the ground and first excited states in dye **3b** are shown in Figure 2. The first excitation was described as the mixture of the $\pi-\pi^*$ transition coming from the alternant chromophore inside the bithiazolyl moiety and the charge-transfer
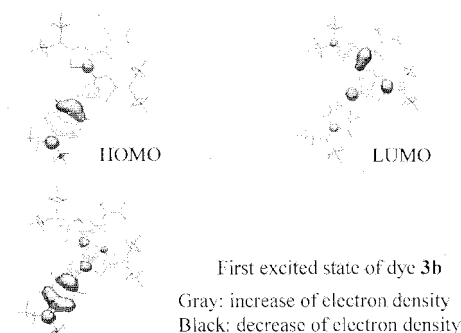
Figure 2. Schematic representation of HOMO, LUMO and the difference in electron density between the HOMO and LUMO of indamine dye **3b** calculated by the INDO/S method for the PM3-optimized geometry.

from the anilino to bithiazolyl moieties. Namely, the anilino moiety is not included in the alternant chromophoric system but acts as an electron-donating group in the first excitation. The substituent effect on the ortho position of the anilino moiety can be explained by the HOMO and LUMO's coefficients of 0.163 and 0.138, respectively. For example, a chlorine atom on the ortho position stabilizes the HOMO more than the LUMO, increasing the energy gap between them.

The largest bathochromicity was observed in dye **3e**. Bulky group introduced into naphthoquinone methide dye has been reported to cause a bathochromic shift.[7] The dihedral angles (θ) between the bithiazolyl and anilino moieties in the optimized structures of dyes **3b–d** were calculated to be 0.1–9.5°. These results indicate that they are almost coplanar. Meanwhile, the dihedral angle in dye **3e** was calculated to be 65.2°. The character of the first excitation of **3e** was also assigned as HOMO–LUMO, π–π^* transition including intramolecular charge-transfer from anilino to bithiazolyl moieties. The relationship between HOMO–LUMO energy levels and dihedral angles in dye **3b** is shown in Figure 3. The larger was the twisting between the bithiazolyl and anilino moieties, the higher was the energy level of HOMO, resulting in
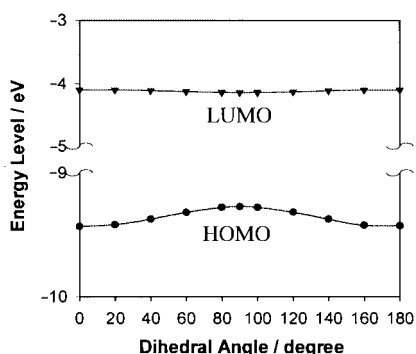

Figure 3. Relationship between HOMO–LUMO energy level and dihedral angle (θ) for dye **3b**.

bathochromic shift. Therefore, the bathochromicity of dye **3e** comes from the twisting between them due to the steric hindrance of methyl groups on the ortho positions in the anilino moiety. The decrease of oscillator strength in dye **3e** can be also explained by a poor overlap of wave functions between the donor and acceptor moieties.

In conclusion, we have synthesized indamine dyes derived from (diethylamino)thiazole dimer. Their first absorption bands were observed around $\lambda = 648$–725 nm in dichloromethane. The substituent effect and INDO/S calculation showed that these unsymmetrical indamine dyes have both the alternant and intramolecular charge-transfer chromophoric systems.

Reference and Notes

1   A. Kanitz and H. Hartmann, *J. Prakt. Chem.*, **338**, 414 (1996).
2   J. Griffiths and R. Cox, *Dyes Pigm.*, **42**, 29 (1999).
3   Typical procedure for the synthesis of dyes **3**: A mixture of 4-amino-2-diethylamino-5-(2-diethylamino-4-thiazolyl)thiazole **1** (0.5 mmol) and 4-nitrosoanilines **2** (0.5 mmol) in acetic anhydride (20 mL) was stirred at room temperature for 0.5 h. To the mixture was added an acetic anhydride solution (1 mL) of nickel(II) tetrafluoroborate (0.25 mmol) and heated at 100 °C for 0.5 h. After cooling, to the reaction mixture was added ethyl acetate (100 mL). The resulting precipitate was filtered and recrystallized from a chloroform–hexane mixed solution. All products showed satisfactory spectral and elemental analysis data. Selected data for dye **3b**: yield 52%; mp 278–279 °C ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.26 (t, $J = 7.1$ Hz, 6H), 1.39 (t, $J = 7.2$ Hz, 3H), 1.45 (t, $J = 7.2$ Hz, 3H), 1.47 (t, $J = 7.2$ Hz, 3H), 1.48 (t, $J = 7.2$ Hz, 3H), 2.65 (s, 3H), 3.49 (q, $J = 7.1$ Hz, 4H), 3.74 (q, $J = 7.2$ Hz, 2H), 3.76 (q, $J = 7.2$ Hz, 2H), 3.93 (q, $J = 7.2$ Hz, 2H), 3.95 (q, $J = 7.2$ Hz, 2H), 6.83 (d, $J = 9.0$ Hz, 2H), 7.47 (d, $J = 9.0$ Hz, 2H), 11.92 (s, 1H); MS (m/z) 528 (M$^+$ − BF$_4$, 75%), 499 (46), 486 (100); Anal. Calcd for C$_{26}$H$_{38}$BF$_4$N$_7$OS$_2$: C, 50.73; H, 6.22; N, 15.93%. Found: C, 50.35; H, 6.09; N, 15.67%.
4   R. Flaig and H. Hartmann, *J. Heterocycl. Chem.*, **34**, 1291 (1997).
5   WinMOPAC ver. 2.0 package (Fujitsu, Chiba, Japan).
6   a) S. Uchiyama, T. Santa, and K. Imai, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 2525. b) D. J. Sandman, G. P. Ceaser, A. P. Fisher, III, E. Schramm, D. D. Titus, and A. D. Baker, *Chem. Mater.*, **1**, 421 (1989). c) H. Bauman, CNDUV99 Quantum Chemistry Program Exchange #333, (http://qcpe.chem.indiana.edu/catalog.html).
7   Y. Kubo, K. Yoshida, M. Adachi, S. Nakamura, and S. Maeda, *J. Am. Chem. Soc.*, **113**, 2868 (1991).