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PREPARATION AND PROPERTIES OF DEHYDROTRICHOTOMINE-TYPE DYES: A NEW NEAR-INFRARED ABSORBING INDIGOID

Hiroyuki Hashimoto, Kimiaki Shiratori, Keitaro Kawakita, Tomoaki Tanaka, Rika Sekine, and Hajime Irikawa*

Department of Chemistry, Faculty of Science, Shizuoka University, 836 Ohya, Shizuoka 422-8529, Japan E-mail: schirik@ipc.shizuoka.ac.jp

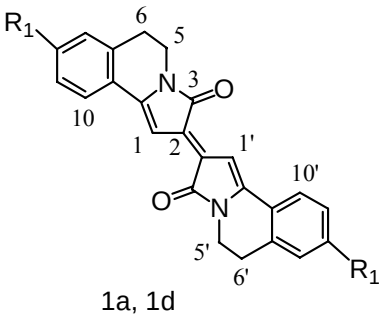
Abstract – Dehydrotrichotomine-type dyes have been prepared from Pechmann dyes and shown to exhibit the λ_{max} at near-infrared region. The large bathochromic shift (109 nm) caused by introduction of a double bond into the trichotomine-type chromophore suggests that the dehydrotrichotomine-type dyes have a different intrinsic chromophore, and are regarded as a new indigoid.

INTRODUCTION

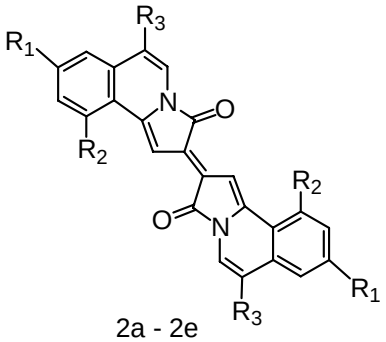
A variety of dyes have been found, and their structural modification has been studied for obtaining functional dyes.[1] Recently, near-infrared (NIR) absorbing dyes (λ_{max} > 700 nm) have attracted a considerable attention in optical recording and biological probes, etc.[2] Indigo is a well-known dye and modified to NIR absorbing dyes.[3] In a previous paper, we reported the preparation of a dye (**1a**), which exhibited the λ_{max} at 632 nm.[4] The dye (**2a**) is a dehydro-type of **1a**, and expected to show the λ_{max} at NIR region due to the π conjugation extended through the C5 = C6 and C5' = C6' double bonds. In this paper we wish to report our approach to prepare dehydro-type dyes (**2a** — **2e**).

RESULTS AND DISCUSSION

Preparation of the dye (**1a**) was carried out by an intramolecular Friedel-Crafts reaction of **3a**.[4] In order to prepare the dyes (**2a** — **2d**), cyclization of acetals (**4a** — **4d**) was examined. Aminolysis of a Pechmann dye (**5a**)[4,5] with 2-aminoacetaldehyde dimethyl acetal, followed by cyclization with 10% HCl gave the acetal (**4a**). On treatment with $AlCl_3$, **4a** yielded a solid (**2a**), which was very slightly soluble in hot $CHCl_3$ and difficult to purify. But, in the absorption spectrum of **2a**, the first absorbing band was observed at 850 nm. Solubility of **2a** will be due to π-stacks.[6] Aromatic rings bearing alkyl groups at

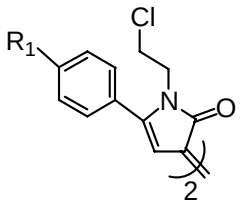


1a, 1d

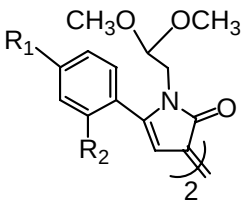


2a - 2e

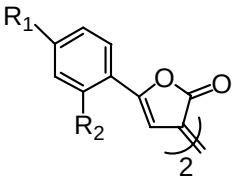
a $R_1 = R_2 = R_3 = H$
b $R_1 = R_3 = H$ $R_2 = CH_3$
c $R_1 = (CH_3)_3C$ $R_2 = R_3 = H$
d $R_1 = n\text{-}C_8H_{17}$ $R_2 = R_3 = H$
e $R_1 = (CH_3)_3C$ $R_2 = H$ $R_3 = CH_3$



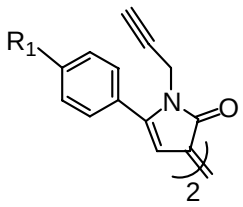
3a , 3d



4a - 4d



5a - 5d



6e

ortho positions are reported to increase solubility.[7] Subsequently, we examined to prepare a dye (**2b**) which had methyl groups on the C10 and C10'. An acetal (**4b**) was similarly derived from a Pechmann dye (**5b)**[4]. On treatment with $AlCl_3$, **4b** gave the solid (**2b**), which was slightly soluble in hot $CHCl_3$, but also difficult to purify. The obtained **2b** exhibited the λ_{max} at 866 nm. From the viewpoint of solubility, a pechmann dye (**5c**) bearing 1,1-dimethylethyl groups and **5d** having octyl groups were prepared from 4-[4-(1,1-dimethylethyl)phenyl]-4-oxo-2-butenoic acid,[8] and from 4-(4-octylphenyl)-4-oxo-2-butenoic acid,[8] respectively. The dyes (**5c** and **5d**) were similarly converted into the acetals (**4c** and **4d**), respectively. Cyclization of **4c** and **4d** was carried out using trifluoromethanesulfonic acid (TfOH). On treatment with TfOH, the acetals (**4c** and **4d**) gave dyes (**2c** and **2d**), respectively. The obtained dyes (**2c** and 2**d**) indicated higher solubility in $CHCl_3$ than **2b**. The solubility of **2a** — **2d** in $CHCl_3$ is in the order of **2a** < **2b** < **2d** < **2c**. The ^{1}H NMR spectrum of **2c** showed two doublet signals at δ = 6.11 (J = 7.0 Hz, C6, 6'-H) and 7.27 (J = 7.0 Hz, C5, 5'-H), being in agreement with the described structure. In the absorption spectra of **2c** and **2d**, the λ_{max} were observed at 857 and 858 nm, respectively. Structural characterization of **2c** and **2d** will support the formation of **2a** and 2**b**. On the other hand, aminolysis of **5c** with propargylamine, followed by cyclization with *p*-toluenesulfonic acid (TsOH) gave a compound (**6e**). On treatment with $AlCl_3$, **6e** yielded the dye (**2e**), whose ^{1}H NMR spectrum showed a methyl signal at δ = 2.18. The λ_{max} of **2e** is observed at 881 nm, which is longer than that of **2c** by 24 nm. Formation of **2e** will proceed via 6-Exo-Dig cyclization (Baldwin rule), followed by shifts of the exo-methylene double bonds into the C5 — C6 and C5' — C6' positions.

In order to know the conjugation effect of the C5 = C6 and C5' = C6' double bonds in **2d**, a reference

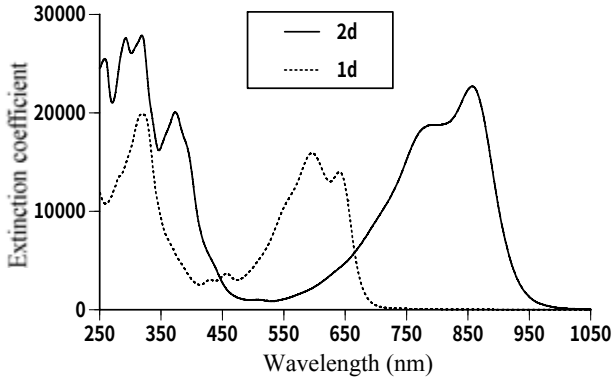


Figure 1. Absorption spectra of **1d** and **2d**.

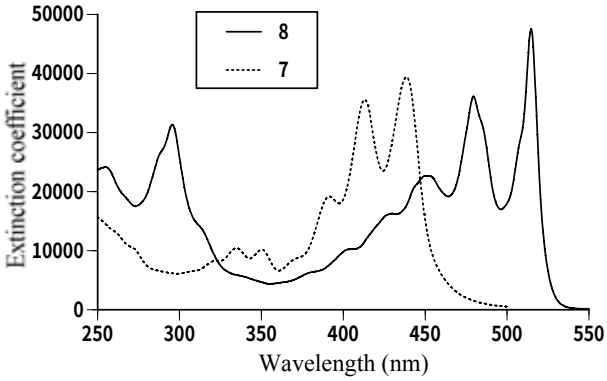
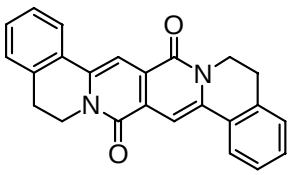
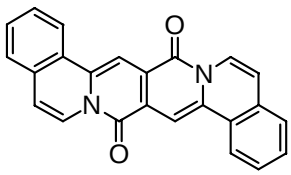


Figure 2. Absorption spectra of **7** and **8**.

compound (**1d**) was prepared. On aminolysis with 2-aminoethanol, followed by cyclization with 10% HCl, and then by chlorination with CCl_4 and Ph_3P, **5d** gave a chloride (**3d)**. Treatment of **3d** with $AlCl_3$ yielded the compound (**1d**), whose ^1H NMR spectrum showed two triplets at δ = 3.02 (J = 6.3 Hz, C6, 6'-H) and 3.83 (J = 6.3 Hz, C5, 5'-H). The absorption spectrum of **1d** exhibited the λ_{max} at 641 nm. As shown in Figure 1, the dye (**2d)** indicates large bathochromic shift compared with **1d**. The conjugation effect of the C5 = C6 double bond in **2d** is + 109 nm (λ_{max} / 2 = (858 – 641) / 2 = 108.5 nm). Conjugation effect of double bonds was also examined for another chromophore. The λ_{max} of a dye (**7**) is reported to be 438 nm.[4] Subsequently, the dehydro-type dye (**8**) was prepared from a compound (**9**),[4] an isomer of **5a.** On aminolysis with 2-aminoacetaldehyde dimethyl acetal, followed by cyclization with TFA, and then by treatment with $AlCl_3$, **9** yielded the dye (**8**), which showed the λ_{max} at 514 nm. As shown in Figure 2, the conjugation effect of the double bond in **8** is +38 nm (λ_{max} / 2 = (514 – 438) / 2 = 38 nm). Hence, such large bathochromic shift (109 nm) observed in **2d** suggests that the intrinsic chromophore of the dyes (**2c** — **2e**) is different from that of the dyes (**1a** and **1d)**.



7



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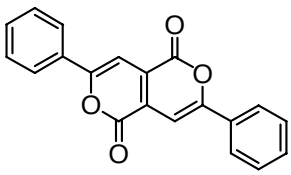
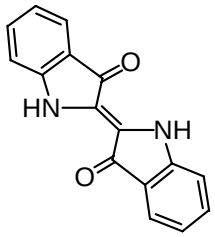
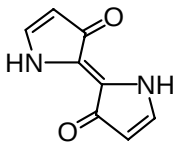


9

The intrinsic chromophore of indigo (**10**) is discussed on the basis of theoretical and experimental evidence, and a structure (**11**) is proposed for it.[9,10] The intrinsic chromophore of the dyes (**1a** and **1d**) will be a structure (**12)**. In a previous paper, we reported that the λ_{max} of a tetramethyl derivative (**13**) would be close to that of **14** (522 nm), because the 2,4,6-trimethylphenyl rings in **14** were twisted by 71°



indigo (10)



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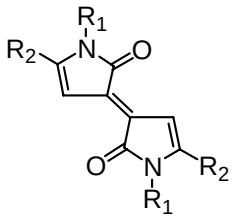
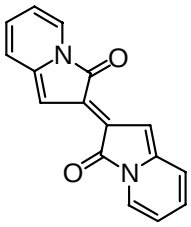


12 $R_1 = R_2 = H$
13 $R_1 = R_2 = CH_3$
14 $R_1 = CH_3$ $R_2 = 2,4,6\text{-}(CH_3)_3\text{-}C_6H_2$



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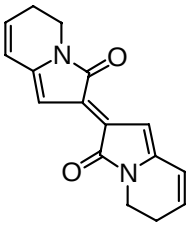

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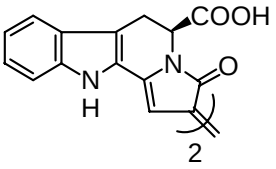
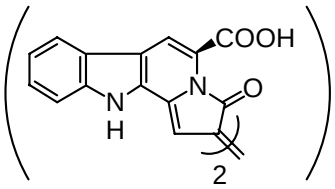


trichotomine (17)



dehydrotrichotomine (18)

and their effect on the λ_{max} would be similar to that of methyl groups.[4] The intrinsic chromophore of the dehydro dyes (**2c** —**2e**) will be a structure (**15**), which is the dehydro-type of a chromophore (**16**). In order to estimate the λ_{max} of these chromophore, molecular orbital calculation was carried out using Discrete-Variational (DV)-Xα method.[11] The calculation was performed for the ground electronic state and the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied MO (HOMO) is taken to be the first absorbing band. All the species calculated in the present study have the HOMO with *ungerade* symmetry and the LUMO with *gerade* symmetry, thus the transitions from the HOMO to the LUMO are allowed. The calculation for indigo (**10**) showed the first absorbing band at 605 nm, which was in good agreement with the observed band at 605 nm.[9] The calculated λ_{max} is as follows: **11** (544 nm), **12** (569nm), **13** (582 nm), **15** (855 nm), and **16** (670 nm). Hence, the MO calculation indicates that dyes with the chromophore (**15**) will exhibit the λ_{max} in NIR region.

The intrinsic chromophore (**12**) is found in natural pigment, trichotomine (**17**, λ_{max} 660 nm).[12] Accordingly, the dyes (**1a** and **1d**) are regarded as trichotomine-type dyes. Dehydrotrichotomine (**18**) with the chromophore (**15**) is not yet found in nature, but the dyes (**2c** — **2e**) can be regarded as dehydrotrichotomine-type dyes. Pechmann dyes (**5a** — **5d**) belong to an indigoid,[13] and there is a structural resemblance between indigo (**10**) and **15**. The dehydrotrichotomine-type dyes (**2c** — **2e**) composed of the intrinsic chromophore (**15**) and two benzene rings are regarded as a new indigoid.

EXPERIMENTAL

All melting points are uncorrected. UV-VIS spectra were measured on a HITACHI-U3000 or SHIMADZU UV-1650PC in $CHCl_3$. IR spectra were recorded on a JASCO FT/IR 460 plus in KBr. ^1H NMR spectra were measured on a Bruker AC300 (300 MHz) in $CDCl_3$, using a $CHCl_3$ signal (δ_H = 7.26) as an internal standard. HRMS were obtained on a JEOL-DX303 by the FAB method. Column chromatography was performed with silica gel 60 (70−230 mesh, Merck) and $CHCl_3$.

Preparation of 4a — 4d. A typical procedure is described for the preparation of **4a**. A mixture of **5a**[4] (330 mg, 1.00 mmol), 2-aminoacetaldehyde dimethyl acetal (0.48 g, 4.6 mmol), and CH_2Cl_2 (4 mL) was stirred at rt overnight. To the solution was added 10% HCl (10 mL). The mixture was stirred at rt overnight and extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was separated by column chromatography to give **4a** (246 mg, 48%): mp 195 — 197 °C (MeOH); UV-VIS 302 (ε 23300) and 555 nm (19400); ^1H NMR δ = 3.30 (6H × 2, s), 3.78 (2H × 2, d, J = 5.7 Hz), 4.55 (1H × 2, t, J = 5.7 Hz), 6.92 (1H × 2, s), and 7.42 — 7.65 (5H × 2, m). *Anal*. Calcd for $C_{28}H_{30}N_2O_6$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.31; H, 6.23; N, 5.60. **4b (**32%): mp 179 — 180 °C (MeOH); UV-VIS 289 (ε 15000) and 532 nm (14800); ^1H NMR δ = 2.34 (3H × 2, s), 3.19 (6H × 2, s), 3.52 (2H × 2, d, J = 5.6 Hz), 4.36 (1H × 2, t, J = 5.6 Hz), 6.77 (1H × 2, s), and 7.23 — 7.38 (4H × 2, m). *Anal.* Calcd for $C_{30}H_{34}N_2O_6$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.18; H, 6.65, N, 5.35. **4c** (41%): mp 209 — 210 °C (EtOAc); UV-VIS 307 (ε 23800) and 564 nm (22100); ^1H NMR δ = 1.35 (9H × 2, s), 3.33 (6H × 2, s), 3.78 (2H × 2, d, J = 5.6 Hz), 4.59 (1H × 2, t, J = 5.6 Hz), 6.91 (1H × 2, s), 7.48 (2H × 2, d, J = 8.5 Hz), and 7.59 (2H × 2, d, J = 8.5 Hz). *Anal.* Calcd for $C_{36}H_{46}N_2O_6$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.62; H, 7.73; N, 4.63. **4d** (35%): mp 117 — 119 °C (MeOH); UV-VIS 308 (ε 25800) and 563 nm (24300); ^1H NMR δ = 0.89 (3H × 2, t, J = 6.7 Hz), 1.20 — 1.70 (12H × 2, m), 2.65 (2H × 2, t, J = 7.7 Hz), 3.31 (6H × 2, s), 3.78 (2H × 2, d, J = 5.6 Hz), 4.56 (1H × 2, t, J = 5.6 Hz), 6.70 (1H × 2, s), 7.25 (2H × 2, d, J = 8.2 Hz), and 7.54 (2H × 2, d, J = 8.2 Hz). HRMS Calcd for $C_{44}H_{63}N_2O_6$: M + H, 715.4686. Found: 715.4684.

Attempts to prepare 2a and 2b. A typical procedure is described for **2b**. A mixture of **4b** (103 mg, 0.20 mmol), $AlCl_3$ (0.50 g, 3.8 mmol), and CH_2Cl_2 (10 mL) was stirred at rt overnight. To the mixture were added 10% HCl and $CHCl_3$ under stirring. The resulting solid was collected by filtration to give **2b** (47 mg as a powder, 60%): UV-VIS 295 (ε 27800) 796 (13500), and 866 nm (14800); IR 1677, 1630 and 1510 cm^{-1}. **2a** (as a powder, 44%): UV-VIS 289 (ε 29200), 787 (sh, 16500), and 850 nm (19400); IR 1662, 1577, 1557 cm^{-1}.

Preparation of 5c and 5d. A typical procedure is described for the preparation of **5c**. A mixture of 4-[4-(1,1-dimethylethyl)phenyl]-4-oxo-2-butenoic acid (2.32 g, 10 mmol), cuprous chloride (0.60 g,

6.0 mmol), ammonium chloride (1.00 g, 19 mmol), and acetic anhydride (15 mL) was heated under reflux for 2 h. The mixture was cooled and the resulting solid was collected. Using Soxhlet's extractor, the solid was extracted with toluene to give **5c** (0.54 g, 25%): mp > 300 °C ($CHCl_3$); UV-VIS 294 (ε 28800), 521 (53900), and 555 nm (55100); ^{1}H NMR δ = 1.36 (9H × 2, s), 7.50 (1H × 2, s), 7.51 (2H × 2, d, J = 8.6 Hz), and 7.77 (2H × 2, d, J = 8.6 Hz). *Anal.* Calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59. Found: C, 78.36; H, 6.66. **5d** (36%): mp 258 — 262 °C ($Cl_2CHCHCl_2$); UV-VIS 299 (ε 28900), 522 (54200), and 556 nm (55100); ^{1}H NMR δ = 0.88 (3H × 2, t, J = 6.6 Hz), 1.20 — 1.70 (12H × 2, m), 2.67 (2H × 2, t, J = 7.6 Hz), 7.29 (2H × 2, d, J = 8.2 Hz), 7.49 (1H × 2, s), and 7.74 (2H × 2, d, J = 8.2 Hz). *Anal.* Calcd for $C_{36}H_{44}O_4$: C, 79.96; H, 8.20%. Found: C, 79.69; H, 8.25.

Preparation of 2c and 2d. A typical procedure is described for the preparation of **2c**. To a solution of **5c** (300 mg, 0.50 mmol) in CH_2Cl_2 (10 mL) was added TfOH (1.7 g, 11 mmol). The solution was stirred at rt overnight, neutralized with aqueous $NaHCO_3$, and extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was treated with $CHCl_3$ to give a powder of **2c** (140 mg, 59%): UV-VIS 292 (ε 30500), 317 (31000), 373 (21800), 790 (sh, 22500), and 857 nm (26600); IR 1674, 1624, and 1532 cm^{-1}; ^{1}H NMR δ = 1.35 (9H × 2, s), 6.11 (1H × 2, d, J = 7.0 Hz), 7.13 (1H × 2, s), 7.22 (1H × 2, d, J = 1.9 Hz), 7.27 (1H × 2, d, J = 7.0 Hz), 7.37 (1H × 2, dd, J = 8.4 and 1.9 Hz), and 7.72 (1H × 2, d, J = 8.4 Hz). HRMS Calcd for $C_{32}H_{31}N_2O_2$: M + H, 475.2385. Found: 475.2389. Similarly, **2d** was obtained by treating the residue with $ClCH_2CHCl_2$ (as a powder, 41%): UV-VIS 298 (ε 23900), 319 (23900), 373 (17400), 789 (16200), and 858 nm (19500); IR 1677, 1625, and 1537 cm^{-1}; ^{1}H NMR δ = 0.88 (3H × 2, t, J = 7.0 Hz), 1.20 — 1.70 (12H × 2, m), 2.62 (2H × 2, t, J = 7.4 Hz), 6.10 (1H × 2, d, J = 7.6 Hz), 7.04 (1H × 2, s), 7.13 (1H× 2, s), 7.15 (1H × 2, d, J = 8.3 Hz), 7.27 (1H × 2, d, J = 7.6 Hz), and 7.69 (1H × 2, d, J = 8.3 Hz). HRMS Calcd for $C_{40}H_{47}N_2O_2$: M + H, 587.3637. Found: 587.3642.

Preparation of 6e. A mixture of **5c** (430 mg, 1.0 mmol), propargylamine (0.40 g, 7.3 mmol), and CH_2Cl_2 (7 mL) was stirred at rt overnight. To the solution was added *p*-TsOH·H_2O (1.5 g, 7.9 mmol). The mixture was stirred at rt for 3 h, neutralized with aqueous $NaHCO_3$, and extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Crystallization of the residue from MeOH gave **6e** (220 mg, 44%): mp 235 — 236 °C; UV-VIS 305 (ε 27400) and 561 nm (24200); ^{1}H NMR δ = 1.37 (9H × 2, s), 2.28 (1H × 2, t, J = 2.4 Hz), 4.40 (2H × 2, d, J = 2.4 Hz), 6.99 (1H × 2, s), 7.50 (2H × 2, d, J = 8.5 Hz), and 7.63 (2H × 2, d, J = 8.5 Hz). *Anal.* Calcd for $C_{34}H_{34}N_2O_2$: C, 81.24; H, 6.82; N, 5.57. Found: C, 80.87; H, 684, N, 5.40.

Preparation of 2e. A mixture of **6e** (100 mg, 0.20 mmol), $AlCl_3$ (0.53 g, 4.0 mmol), and CH_2Cl_2 (5 mL) was stirred at rt for 29 h. The mixture was worked up as described above to give an oily product,

which was treated with hot MeOH to yield a powder of **2e** (15 mg, 15%): UV-VIS 323 (ε 27000), 377 (18900), 810 (sh, 17600), and 881 nm (20700); ^{1}H NMR δ = 1.37 (9H × 2, s), 2.18 (3H × 2, s), 7.12 (1H × 2, s), 7.15 (1H × 2, s), 7.36 (1H × 2, d, J = 1.8 Hz), 7.40 (1H × 2, dd, J = 8.4 and 1.8 Hz), and 7.76 (1H × 2, d, J = 8.4 Hz). HRMS Calcd for $C_{34}H_{35}N_2O_2$: M + H, 503.2698. Found: 503.2695.

Preparation of 3d. A mixture of **5d** (541 mg, 1.0 mmol), 2-aminoethanol (0.40 g, 6.6 mmol), and CH_2Cl_2 (10 mL) was stirred at rt for 1 d. To the solution was added 10% HCl (10 mL). The mixture was stirred at rt for 3 h and extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. A mixture of the residue, Ph_3P (1.0 g, 3.8 mmol), CCl_4 (30 mL) and CH_2Cl_2 (30 mL) was stirred at rt for 1 d, and concentrated under reduced pressure. Crystallization of the residue from MeOH gave **3d** (222 mg, 33%): mp 152 — 154 °C; UV-VIS 306 (ε 24000) and 557 nm (22200); ^{1}H NMR δ = 0.89 (3H × 2, t, J = 6.9 Hz), 1.20 — 1.75 (12H × 2, m), 2.66 (2H × 2, t, J = 7.4 Hz), 3.56 (2H × 2, t, J = 6.8 Hz), 4.02 (2H × 2, t, J = 6.8 Hz), 6.90 (1H × 2, s), 7.28 (2H × 2, d, J = 8.2 Hz), and 7.43 (2H × 2, d, J = 8.2 Hz). *Anal.* Calcd for $C_{40}H_{52}Cl_2N_2O_2$: C, 72.38; H, 7.90; N, 4.22. Found: C, 71.97; H, 7.86, N, 4.16.

Preparation of 1d. A mixture of **3d** (68 mg, 0.10 mmol), $AlCl_3$ (0.20 g, 1.5 mmol), and 1-chloro-4-fluorobenzene (1.5 mL) was heated under reflux and stirring for 30 min. To the mixture was added ice and 10% HCl. The mixture was extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was separated with thin layer chromatography (SiO_2 – $CHCl_3$) to give **1d** (11 mg as an oil, 19%): UV-VIS 315 (ε 19600), 596 (15900), and 641 nm (14000); ^{1}H NMR δ = 0.88 (3H × 2, t, J = 6.2 Hz), 1.20 — 1.80 (12H × 2, m), 2.62 (2H × 2, t, J = 7.3 Hz), 3.02 (2H × 2, t, J = 6.3 Hz), 3.83 (2H × 2, t, J = 6.3 Hz), 7.06 (1H × 2, br s), 7.14 (1H × 2,d, J = 8.0 Hz), 7.22 (1H × 2, s), and 7.71 (1H × 2, d, J = 8.0 Hz). HRMS Calcd for $C_{40}H_{51}N_2O_2$: M + H, 591.3950. Found: 591.3906.

Preparation of 8. A mixture of **9**[4] (95 mg, 0.30 mmol), 2-aminoacetaldehyde dimethyl acetal (0.19 g, 1.8 mmol), and DMF (1 mL) was heated under reflux for 1 h. To the solution was added TFA (0.45 g, 3.9 mmol). The solution was stirred at rt for 1 h and diluted with EtOAc. The solution was washed with water and then with saturated aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. A mixture of the residue, $AlCl_3$ (0.50 g, 3.8 mmol) and CH_2Cl_2 (5 mL) was stirred at rt for 1 h. The mixture was worked up as described above to give an oily residue, which was treated with hot MeOH to yield a powder of **8** (10 mg, 9%): UV-VIS 295 (ε 31300), 450 (22600), 479 (39000), and 514 nm (47500); ^{1}H NMR δ = 7.02 (1H × 2, d, J = 7.9 Hz), 7.55 — 7.65 (3H × 2, m), 8.36 (1H × 2, s), 8.52 (1H × 2, m), and 8.78 (1H × 2, d, J = 7.9 Hz). HRMS Calcd for $C_{24}H_{14}N_2O_2$: M, 362.1055. Found: 362.1054.

REFERENCES

1. (a) M. Ookawara, M. Matsuoka, T. Hirashima, and T. Kitao, 'Kinousei Shikiso,' Koudansha, Tokyo, 1992. (b) 'Application of Functional Dyes,' ed. by M. Irie, CMC Publishing, Tokyo, 1996.
2. (a) H. Langhals, *Angew. Chem., Int. Ed*., 2003, **42**, 4286. (b) J. Fabian, H. Nakazumi, and M. Matsuoka, *Chem. Rev*., 1992, **92**, 1197.
3. R. Gompper, K. Hartmann, R. Kellner, and K. Polborn, *Angew. Chem., Int. Ed. Engl*., 1995, **34**, 464.
4. H. Irikawa and N. Adachi, *Heterocycles*, 2000, **53**, 135.
5. (a) C. S. Fang and W. Bergmann, *J. Org. Chem*., 1951, **16**, 1231. (b) E. Klingsberg, *Chem. Rev*., 1954, **54**, 59.
6. C. Kohl, S. Becker, and K. Müllen, *Chem. Commun*., **2002**, 2778.
7. G. Seybold and G. Wagenblast, *Dyes and Pigments*, 1989, **11**, 303.
8. F. K. Kirchner, J. H. Bailey, and C. J. Cavallito, *J. Am. Chem. Soc*., 1949**, 71**, 1210.
9. E. Wille and W. Lüttke, *Angew. Chem., Int. Ed. Engl*., 1971, **10**, 803.
10. N. Tyutyulkov, G. Olblich, and F. Dietz, *J. Inf. Rec. Mater*., 1988, **16**, 431.
11. H. Adachi, M. Tsukada, and C. Satoko, *J. Phys. Soc. Jpn.*, 1978, **45**, 875.
12. S. Iwadare, Y. Shizuri, K. Sasaki, and Y. Hirata, *Tetrahedron*, 1974, **30**, 4105.
13. M. Sainsbury, 'Rodd's chemistry of carbon compounds,' 2nd ed., Vol. IV, Part B, ed. by S. Coffey, Elsevier, New York, 1977, pp. 341 — 367.