HETEROCYCLES, Vol. 61, 2003, pp. 433 - 447
Received, 7th August, 2003, Accepted, 8th September, 2003, Published online, 2nd October, 2003

A NEW SYNTHESIS OF FUNCTIONAL DYES FROM 2-ACENAPHTHO[1,2-*c*]PYRROLE

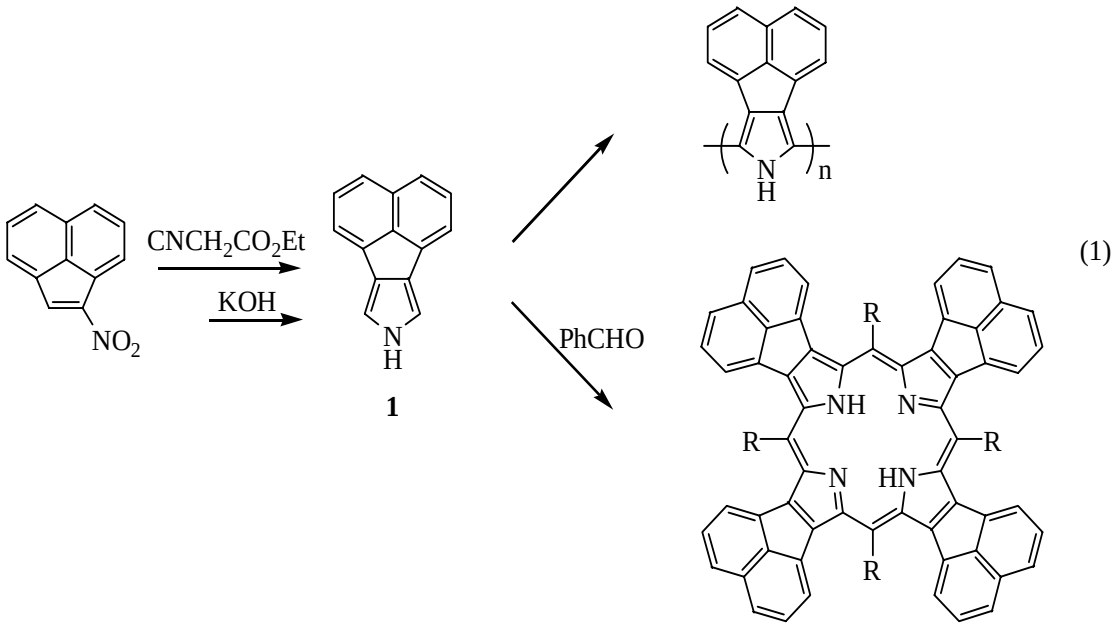
Noboru Ono,* Takanori Yamamoto, Naomi Shimada, Kenji Kuroki, Mitsuo Wada, Ryouhei Utsunomiya, Tomoko Yano, Hidemitsu Uno, [a] and Takashi Murashima [b]

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, 790-8577, Japan: E-mail ononbr@dpc.ehime-u.ac.jp. [a] Integrated Center for Science, Ehime University, Matsuyama, Japan; [b] Department Chemistry, Konan University, Kobe, Japan

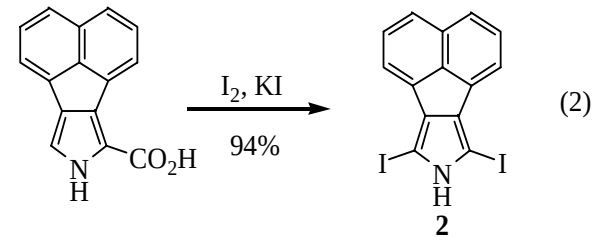
Abstract –Incorporation of acenaphtho[1,2-*c*]pyrrole units into the π-conjugated systems is very effective to get the narrow HOMO-LUMO gap materials, and the absorption spectra of π-conjugated polymers, porphyrins, and boron dipyrromethene dyes fused with acenaphthene rings are extensively red-shifted.

The reaction of nitroalkenes with ethyl isocyanoacetate in the presence of a base gives ethyl 3, 4-substituted pyrroles (Barton-Zard reaction),[1] which provide useful precursors for synthesis of porphyrins or biologically active pyrroles.[2] This reaction has been extended to aromatic nitro compounds, and pyrroles fused with various aromatic rings such as benzene, naphthalene, phenanthrene, phenanththroline, quinoline, isoquinoline, fluoranthene, and acenaphthene have been prepared.[3,4] Smith has found that nitro- porphyrins also undergo the Barton- Zard reaction to give pyrrolo-fused porphyrins.[5] Such pyrroles are readily converted into the corresponding porphyrins. In 1996, we reported that the UV-VIS absorption spectra of tetraacenaphthoporphyrins were extremely red-shifted (Soret band: 525 nm).[3b] Lash reported that the introduction of phenyl ring at the *meso* position of tetraacenaphthoporphyrins induced the further red-shift of absorption (Soret band: 560 nm).[4a] Typical porphyrins such as octaethylporphyrin or *meso*-tetraphenylporphyrin absorb at about 400 nm (Soret band), and λ max is not much affected by the change of substituents on these porphyrins. Lash has claimed that fused acenaphthene rings induce large bathochromic shifts in the UV-VIS spectra of porphyrins, contrasting with the minimal influence of fused benzenoid aromatic systems.[6] It is important to confirm whether the effect of acenaphthene is limited to porphyrins or not. In order to answer this question, π-conjugated oligomers, polymers, and cyclic

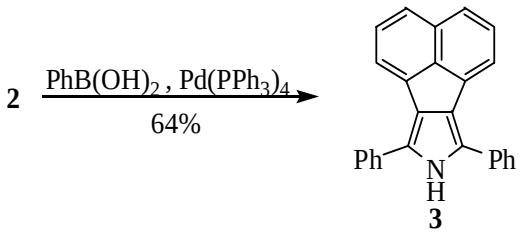
oligomers containing acenaphthene rings are prepared, and their UV-VIS spectra are compared with those of other π-conjugated molecules.



(1)

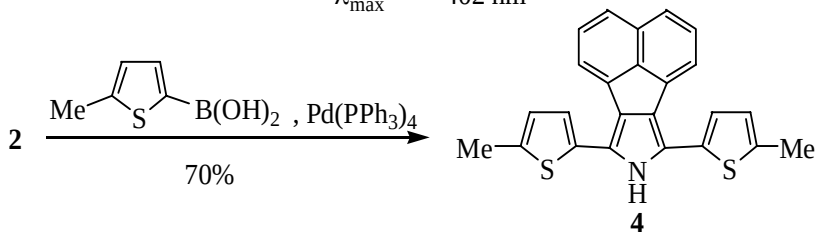


(2)



(3)

λ_{max}^{abs} = 402 nm

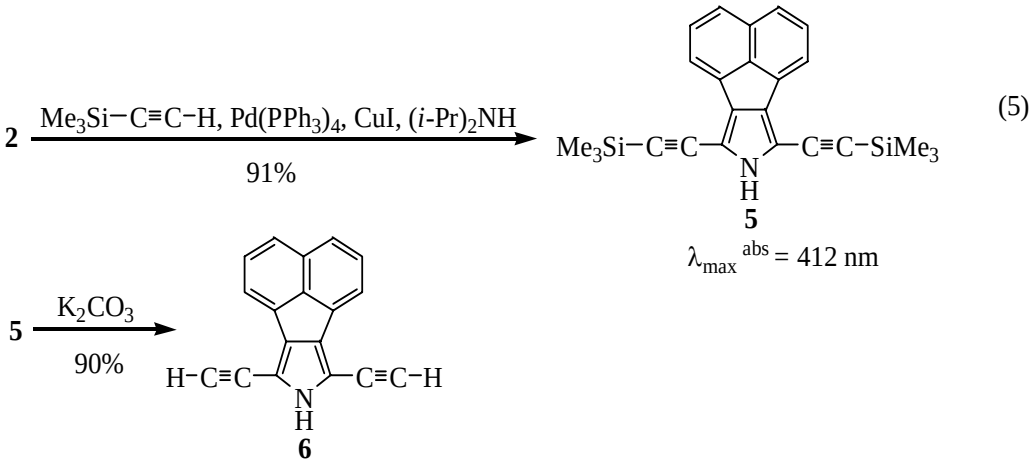


(4)

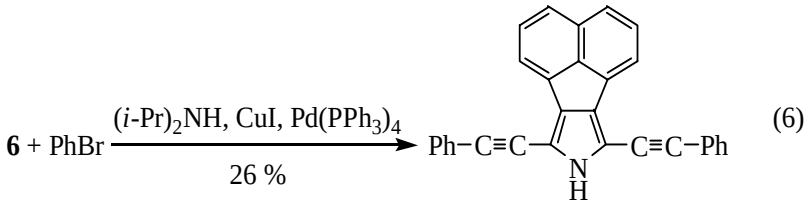
λ_{max}^{abs} = 428 nm

α-Free pyrrole (**1**) was prepared by deethoxycarbonylation of ethyl acenaphtho[1,2-*c*]pyrrole-7-carboxylate by heating with KOH in ethylene glycol.[3a] α,α‘-Diiodopyrrole (**2**) was prepared in 94 %

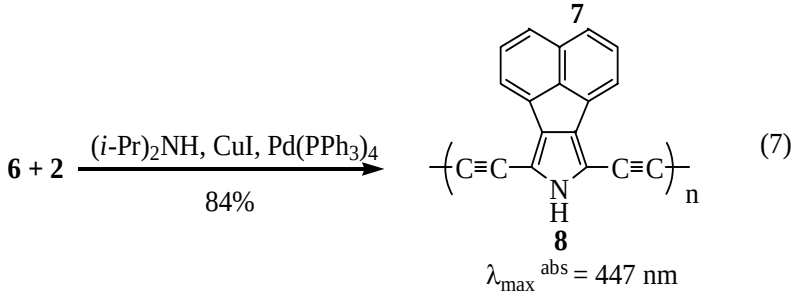
yield on treatment acenaphtho[1,2-*c*]carboxylic acid with KI and I_2 in the presence of $NaHCO_3$. Suzuki coupling of **2** with phenyllboronic acid or 2-(5-methylthiophene)boronic acid gave the coupling product (**3**) or (**4**), respectively. The UV-VIS absorption can be changed by the choice of aryl groups; λ_{max} of **1**, **3**, and **4** are 353, 402, and 428 nm, respectively. Polycyclic aromatic compounds such as anthracenes are generally highly fluorescent, and they have been used in various fields of science.[7] Photophysical properties of isoindole and its benzo[*f*]- and dibenzo[*e*,*g*]-derivatives were reported, where fluorescence quantum yields were 0.88, 0.70, and 0.99, respectively.[8] So, it is expected that isoindoles (**1**), (**3**), and (**4**) are also highly fluorescent. In fact, they emit at 442, 460, and 502 nm with quantum yield of 0.5-0.7, respectively. It is not simple to compare electronic properties of **4** with those of other systems, for their absorption and emission λ_{max} are affected by various factors. Terthiophenes are selected as standard, though it is very rough, the absorption λ_{max} (428 nm) and emission λ_{max} (502 nm) of **4** are considerably red-shifted than those of terthiophene (absorption λ_{max}: 350 nm, emission λ_{max}: 430 nm).[9] Although the estimation is very rough, the HOMO-LUMO energy gap of **4** is smaller than that of terthiophenes.



(5)



(6)



(7)

Oligomer (**7**) or polymer (**8**) were prepared, where acenaphtho[1,2-*c*]pyrroles are linked with acetylene bonds. Organic compounds with aromatic groups that are linearly conjugated thorough acetylene linkages

have been the center of much attention in the past few years.[10] Poly(*p*-phenylenethynylene)s or poly(*p*-phenylenebutadiynylene)s have been prepared from their potential in a wide variety of applications including organic EL materials.[11] Reaction of **2** with trimethylsilyll acetylene using Pd (0), CuI and diisopropylamine gave **5** in 91% yield, and subsequent deprotection with base provided **6** in 90% yield. Compound (**6**) is a good precursor for constructing π-conjugated systems which contain acenaphtho[1,2-*c*]pyrrole unit. For example, a palladium catalyzed coupling reaction of **6** with bromobenzene gave **7** in 26 % yield. The absorption spectra of **7** (λ_{max} 428 nm) are highly red-shifted compared to those of 1,4-bis(phenylethynyl)benzene (λ_{max} 320 nm).[11b] A palladium catalyzed coupling reaction of **2** with **6** gave polymer (**8**) in 84 % yield. This polymer is insoluble in most organic solvents and it is a little soluble in DMF. The UV-VIS of **8** shows broad absorption (λ_{max} 447 nm, band edge is near 600 nm). Due to the low solubility of **8**, further characterization of **8** was not done. Thus, π-extended analogs of **1** linked with acetylene units provide a new class of materials whose absorption spectra are extremely red shifted.

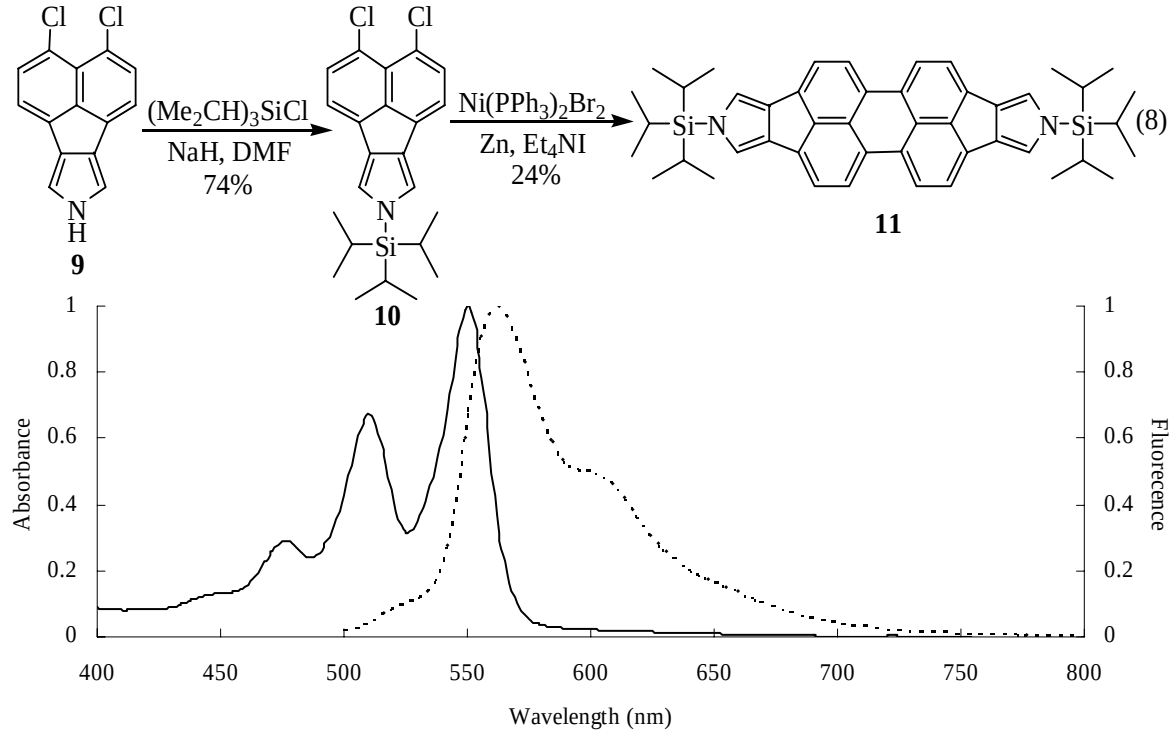
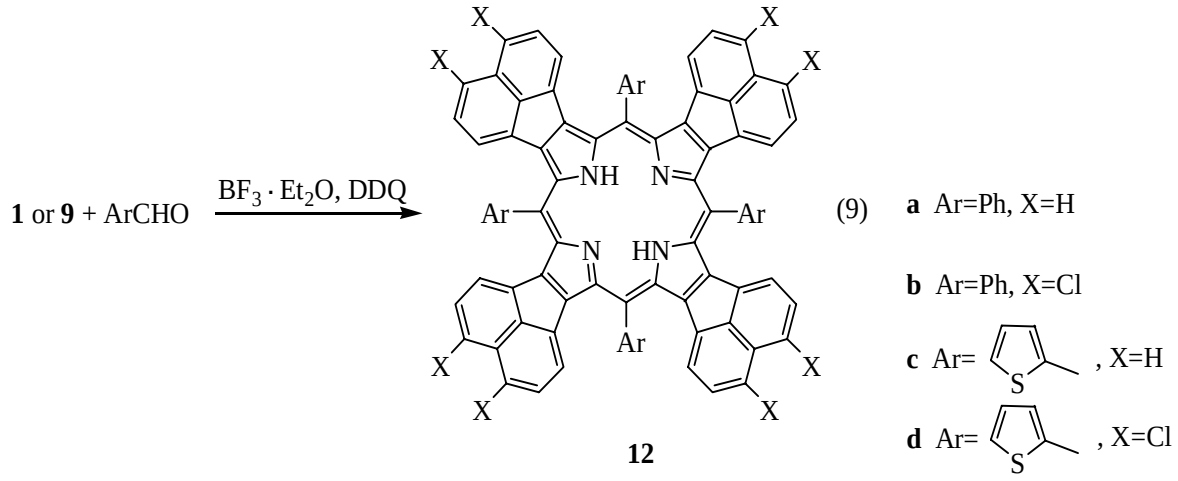


Figure 1. Absorption (solid line) and fluorecence (dotted line) spectra of **11**.

As another π-extended molecules containing acenaphtho[1,2-*c*⌋pyrrole units, perylene type of compound (**11**) was prepared. 5,6-Dichloroacenaphthopyrrole (**9**) was prepared from 5,6-dichloroacenaphthene as previously reported.[12] Pyrrole (**9**) was converted into *N*-silyl derivative (**10**), and the Ni-catalyzed coupling reaction of **10** affords a new dye (**11**) in 24% yield. The absorption and emission spectra of **11** are shown in Figure 1, which are very similar to those of perylene dyes. Very strong red emission was observed in the solution of **11**. Dyes containing perylene framework are very important as pigments

and fluorescent dyes.[13] So, a new perylene dye containing fused pyrrole rings was prepared, which may be useful as a functional dye with a narrow HOMO-LUMO energy band. Furthermore, pyrrole units can be further converted into other dyes such as porphyrins. Such work is in progress in our laboratory. The absorption λ_{max} 550 nm of **11** is red shifted by *ca.* 100 nm compared to that of perylene.



12

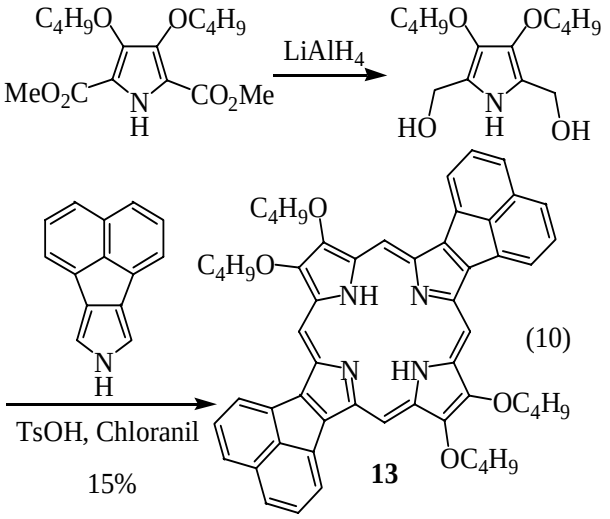
Table 1. Yield of **12** and their absorption λ_{max}

Ar	X	**12**	yield (%)	λ_{max}, nm (log ε)
Ph	H	**12a**	40	555(5.13), 636(4.23), 704(3.92) [a] 568(5.40), 693(4.36), 764(4.21) [b]
Ph	Cl	**12b**	34	571(5.18), 646(4.55), 715(4.30) [a] 583(5.40), 700(4.61), 775(4.32) [b]
	H	**12c**	40	564(5.17), 651(4.14), 720(4.00) [a] 585(5.36), 722(4.13), 802(4.42) [b]
	Cl	**12d**	30	579(5.22), 663(4.27), 730(4.11) [a] 603(5.39), 732(4.32), 817(4.45) [b]

a) $CHCl_3$
b) $CHCl_3$+1%TFA

The present study has started from the observation of unusual red shifted absorption of tetraacenaphtho-porphyrins. Porphyrin systems with strong absorption in the far red/near-infrared are important for various applications in nonlinear optics, sensitizers for photodynamic therapy (PDT) for cancer, or in other optical materials. Several approaches have been reported for this purpose.[14] Lash has found that the presence of arylethynyl groups at the *meso* position induced larger red shift of the absorption to bring the Soret band at 560-600 nm.[4b] Introduction of *meso*-arylethynyl groups is very effective to increase π-conjugation of porphyrins, but the yields for the introduction of arylethynyl groups are very poor (2-3 %). We proposed that the introduction of *meso*-2-thienyl groups is also effective to increase the π-conjugation of porphyrins. [15] The introduction of the *meso*-2-thienyl groups is much simpler than that of arylethylnyl groups. The reaction of pyrrole (**1**) with thiophene-2-carboxyaldehyde in the presence of $BF_3 \cdot Et_2O$ and subsequent oxidation with DDQ gave porphyrin (**12c**) in 40 % yield. Compared to **12a**,

the absorption λ_{max} of **12c** is considerably red-shifted (10-20 nm). When **11** was used, octachlorinated porphyrins (**12b**) and (**12d**) were prepared. The absorption λ_{max} of them is red shifted by *ca.* 10 nm compared to λ_{max} of nonchlorinated ones. Thus, the absorption λ_{max} of **12d** is red shifted by about 20 nm compared to that of **12a**. Thus, the absorption λ_{max} of porphyrins (**12)** can be finely tuned by changing *meso* aryl groups and substituents on acenaphthene rings. This strategy is very useful to provide the porphyrin type of dyes, which have strong absorption at the region of 500-600 nm.



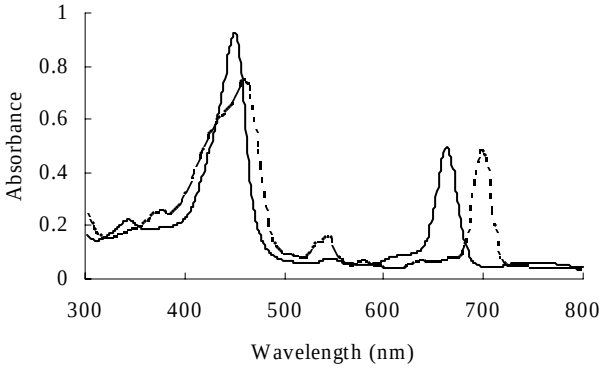
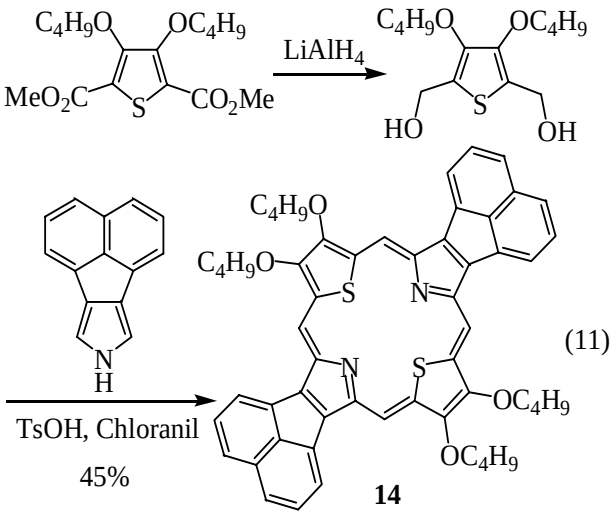


Figure 2. Absoption spectra of **13** (solid line) and Zn complex of **13** (dotted line).



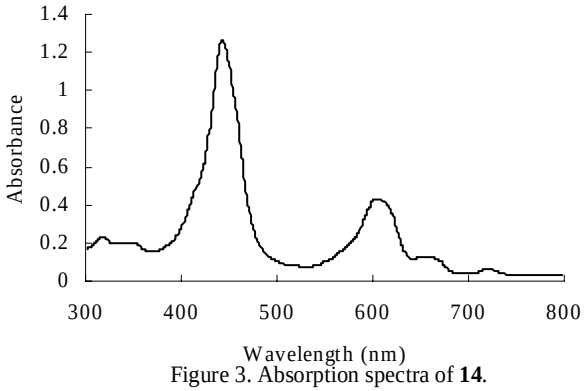
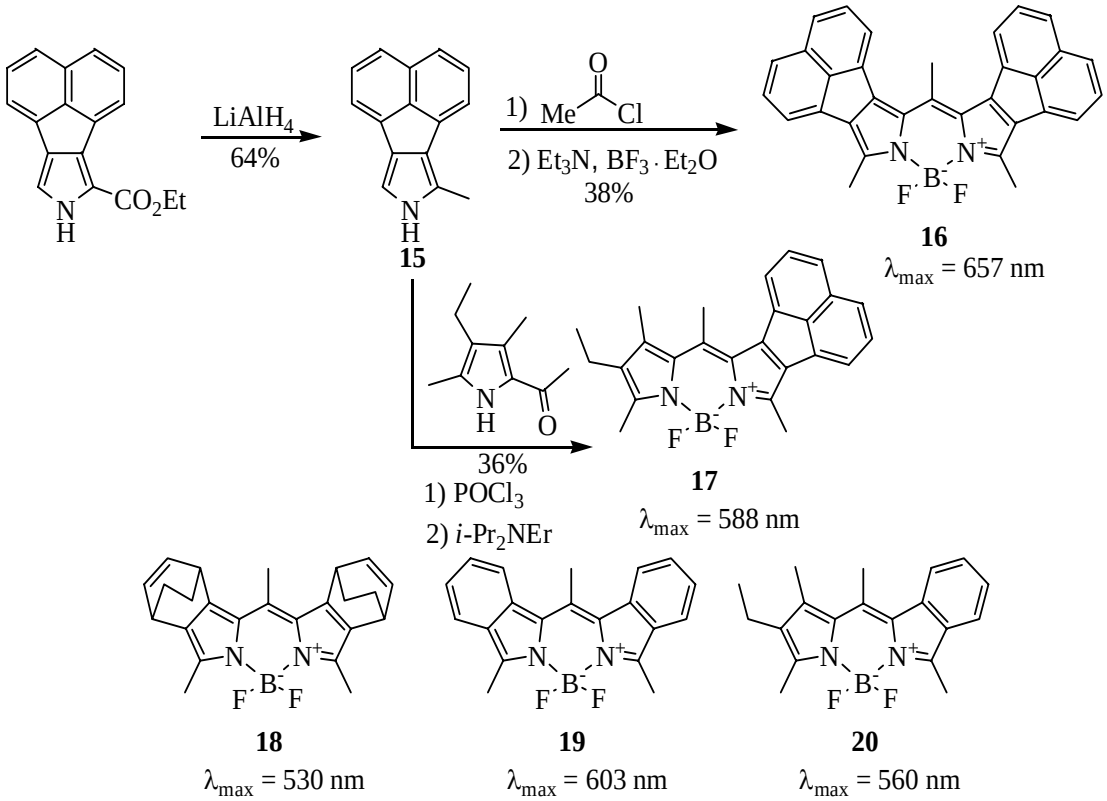


Figure 3. Absorption spectra of **14**.

We have studied another approach for the modification of electronic properties of porphyrins or related macrocycles. The reaction of pyrrole (**1**) with 3,4-dialkoxy-2,5-bis(hydroxymethyl)pyrroles or 3,4-dialkoxy-2,5-dialkoxythiophenes gave porphyrin (**13)** or thiaporphyrin (**14)**, respectively. This method is very useful, because the fused aromatic rings can control the conjugation and the alkoxy groups can control the chemical and physical properties of porphyrins. Another important point of this method is simple operation and ready availability of starting materials.[16] 3,4-Dialkoxy-2,5-bis(dihydroxy-methyl)pyrroles or thiophenes were readily prepared by the reduction of the corresponding esters with

$LiAlH_4$. The requisite esters were prepared by alkylation of the 3,4-dihydroxypyrroles or thiophenes with alkyl halides. 3,4-Alkylenedioxypyrroles and 3,4-alkylenedioxythiophenes are very useful as monomers for new electron rich conductive polymers.[17] Combination of these pyrroles and thiophenes with acenaphtho[1,2-*c*]pyrrole may afford a new strategy for adjustment of the HOMO-LUMO energy levels of π-extended molecules. The absorption spectra of **13** and **14** are shown in Figures 2 and 3, respectively. Porphyrin (**13**) is a good candidate for application to PDT, for the strong Q band at 700 nm is desirable for it.



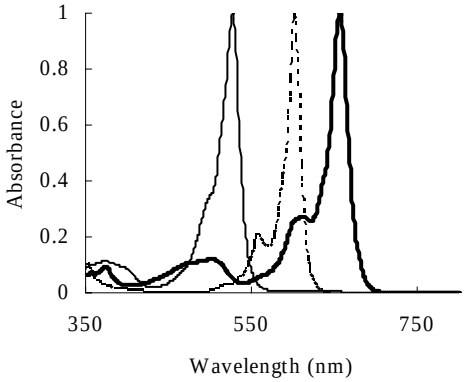


Figure 4. Absorption spectra of **18** (solid line), **19** (dotted line) and **16** (bold line).

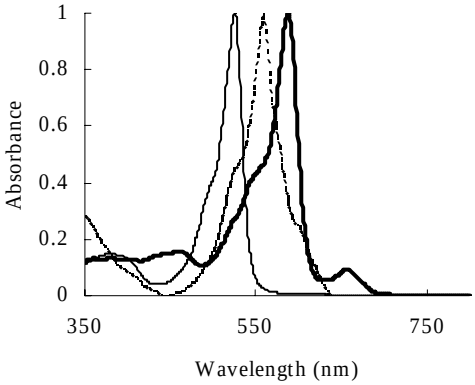


Figure 5. Absorption spectra of **18** (solid line), **20** dotted line) and **17** (bold line).

Boron dipyrromethene (BDP) dyes are highly fluorescent materials and have been used in various fields of science, for example, for laser dyes, molecular probes for biochemical research, sensors, other optical devices.[18] In order to the control the properties of BDP, variously substituted BDP dyes have been

prepared. We prepared BDP dyes fused with bicyclo[2.2.2]octadiene (BCOD) units, which were converted into benzo BDP dyes *via* a retro Diels-Alder reaction.[19] As shown in Figure 4, absorption of BDP dye (**18**) fused with BCOD is observed at 530 nm, and that of benzo BDP (**19**) is red shifted to 603 nm. BDP dyes have merits of sharp absorption and emission spectra. They show strong fluorescence at 540 nm (green) and 618 nm (red), respectively. BDP dyes derived from acenaphtho[1,2-*c*]pyrrole are interesting, for electronic properties are effectively altered by acenapthopyrrole. BDP dyes with mono- and di-acenaphthopyrroles (**16**) and (**17**) were prepared. The absorption spectra of these dyes are shown in Figures 4 and 5. The absorption λ_{max} of **16** is 657 nm, which is the longest wavelength for BDP dyes. The absorption of BDP dyes can be finely controlled from 530 nm to 657 nm by introduction of acenaphthopyrroles or benzopyrroles into BDP.

In conclusion, several new dyes containing acenaphtho[1,2-*c*]pyrrole have been prepared, and their absorption and emission spectra are considerably red-shifted compared to those of dyes derived from alkyl substituted pyrroles or thiophenes. Electrochemical and photophysical properties of these new dyes are being studied in our laboratory and they will be reported later.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a JEOL-JNM-GSX 270 or JNM-EX 400 specrometer using tetramethylsilane as an internal standard. IR and UV-VIS spectra were obtained with a Hitachi 270-30 and a Shimadzu UV-2200 spectrophotometer, respectively. MS spectra were measured with a Hitachi M80B spectrometer. FAB Ms spectra of porphyrins were measured with a JEOL JMS-DX 300 or JMS-LX 2000 spectrometer; samples were dissolved in *m*-nitrobenzyl alcohol was used as a matrix. Elemental analysis was performed with a Yanako MT-5.

Preparation of 7, 9-diiodoacenaphtho[1, 2-c]pyrrole (2)

A mixture of ethyl acenaphtho[1,2-*c*]pyrrole-7-carboxylate (2.1 g, 8.0 mmol) and 0.63 N NaOH solution (320 mL) was heated at 60-70 ˚C for 1 h, and cooled to rt. Dilute HCl was added to precipitate white solid. The collected solid was dissolved in ethyl acetate, and the organic layer was dried over $MgSO_4$, and concentrated to give 1.8 g (96 %) of the acid. A mixture of the acid (1.78 g, 7.67 mmol) and $NaHCO_3$ (5.34 g) in EtOH (50 mL) and water (50 mL) was heated at 50 ˚C. A mixture of I_2 (3.84 g, 15 mmol) and KI (7.5 g, 45 mmol) in water (840 mL) was added slowly to this solution for 30 min. The mixture was stirred at 45 ˚C for 90 min and cooled to rt. The precipitate solid was washed with water and dried to give **2** as a brown powder (3.2 g, 94 %) This sample was pure enough to use for the next coupling step: mp >250˚C; ^{1}H NMR ($CDCl_3$) δ 7.98 (br s, 1H), 7.77 (d, 2H, *J* = 7.6), 7.70 (d, 2H, *J* = 7.6), 7.56 (dd, 2H, *J* = 6.7, 8.2); UV-VIS (CH_2Cl_2) λ_{max} (ε) 376, 428 nm; EI/MS 443 (M^+).

Preparation of coupling materials (3) and (4)

A solution of **2** (0.44 g, 1 mmol), $PhB(OH)_2$ (0.37 g, 3.0 mmol), $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol), and Na_2CO_3 (0.63 g, 6.0 mmol) in DMF (15 mL) was heated at 100 ˚C for 7 h. The reaction mixture was poured into water, and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel, CH_2Cl_2:hexane=1:1) to give **3** as a yellow solid (0.22 g, 64 %): mp 223-224˚C (from CH_2Cl_2-hexane); ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1H); UV-VIS (CH_2Cl_2) λ_{max} (ε) 350 (4.22), 402 (4.11) nm; EI/MS 343 (M^+). Anal. Calcd for $C_{26}H_{17}N$: C, 90.86; H, 5.18; N, 4.01 Found: C, 90.93; H, 4.99; N, 4.08

A solution of **2** (0.44 g, 1 mmol), 5-methyl-2-thiophene boronic acid (0.43 g, 3.0 mmol), $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol), and Na_2CO_3 (0.63 g, 6.0 mmol) in DMF (15 mL) was heated at 100 ˚C for 7 h. The reaction mixture was poured into water, and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel, CH_2Cl_2:hexane=3:7) to give **4** as a yellow solid (0.27 g, 70 %): mp 185-187 ˚C (CH_2Cl_2-hexane); ^{1}H NMR (C_5D_5N) δ 12.31 (s, 1H), 8.39 (d, 2H, *J* = 7.0), 7.80 (d, 2H, *J* = 7.6), 7.66 (dd, 2H, *J* = 6.9, 8.3), 7.47 (d, 2H, *J* = 3.4), 6.75-6.78 (m, 2H), 2.40 (s, 6H); UV-VIS (CH_2Cl_2) λ_{max} (ε) 376 (4.34), 428 (4.14) nm; EI/MS 383 (M^+). Anal. Calcd for $C_{24}H_{17}NS_2$: C, 75.16; H, 4.47; N, 3.65. Found: C, 75.16; H, 4.47; N, 3.65.

Preparation of alkynes (5), (6) and (7)

A flask containing $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol) and CuI (0.05, 0.025 mmol) was degassed and charged with Ar. To this flask were added diisopropylamine (0.21 mL, 1.5 mmol), trimethylsilylacetyrene (0.16 mL, 1.1 mmol), and **2** (0.22 g, 0.5 mmol) in 10 mL of THF. The resulting mixture was stirred at rt for 24 h, and poured into water, and extracted with $CHCl_3$. The organic layer was washed with water and brine. After drying over $MgSO_4$, concentration and column chromatography (silica gel, $CHCl_3$: hexane=1:1) gave **5** as pale yellow solid (0.174 g, 91 %): mp 165-168 ˚C ($CHCl_3$-hexane); ^{1}H NMR ($CDCl_3$) δ 8.21 (s, 1H), 7.71 (d, 2H, *J* = 6.7), 7.69 (d, 2H, *J* = 8.2), 7.54 (dd, 2H, *J* = 6.7, 8.2), 0.31 (s, 18H); UV-VIS (CH_2Cl_2) λ_{max} 316, 340, 390, 416 nm; EI/MS 383(M^+). Anal. Calcd for $C_{24}H_{25}NSi$: C, 75.14; H, 6.67: N. 3.65. Found: C, 75.10; H, 6.39; N, 3.71. Replacement of Me_3Si by hydrogern was carried out by stirring a mixture of **5** and K_2CO_3 in MeOH-CH_2Cl_2 to give **6** as a pale yellow crystal in 88 % yield.

Coupling reaction of **6** with bromobenzene using $Pd(PPh_3)_4$, diisopropylamime and CuI gave **7** as a yellow crystal in 26 % yield: mp 228-230 ˚C (CH_2Cl_2-hexane); ^{1}NMR ($CDCl_3$) δ 8.34 (br s, 1H), 7.83 (d, 2H, *J* = 7.0), 7.72 (d, 2H, *J* = 7.6), 7.53-7.62 (m, 6H), 7.38–7.44 (m, 6H); UV-VIS (CH_2Cl_2) λ_{max} (ε) 364 (4.59), 378 (4.61), 428 (4.14) nm; EI/MS 391 (M^+). Anal. Calcd for $C_{30}H_{17}N$: C, 92.04; H, 4.38; N, 3.58.

Found: C, 92.01, H, 4.51; N, 3.43.

Preparatiuon of polymer (8)

A mixture of Pd $(PPh_3)_4$ (0.035 g, 0.0031 mmol), CuI (0.0006 g, 0.003 mmol), **2** (0.044 g, 0.1 mmol), **6** (0.024 g, 0.1 mmol), and diisopropylamine (0.48 mL) in THF (5 mL) was heated at 70 ˚C under Ar for 1 h. The reaction mixture was poured into water containing diluted HCl. The precipitate was collected and washed repeatedly with MeOH and Et_2O to give **8** as black solid (0.024 g, 84 %): UV-VIS (DMF) λ_{max} 447 nm. Due to poor solubility, further characterization of **8** was not done.

Preparation of *N*-(Triosopropylsilyl) -6,7-dichloroacenaphtho[1,2-*c*⌋pyrrole (10)

Under Ar, NaH (60 %, 0.04 g, 0.75 mmol) was placed in a flask and washed twice with dry hexane. DMF (2 mL) was added to the flask and the mixture was cooled at 0 ˚C. To this reaction mixture was added a solution of pyrrole (**9**) (0.13 g, 0.5 mmol) in DMF (3 mL), and the whole was stirred at 0 ˚C for 30 min. Then triisopropylsilylchloride (0.13 mL, 0.6 mmol) was added to the reaction mixture, and the mixture was stirred at rt for 4 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was washed with water, dried over $MgSO_4$ and concentrated. The residue was subjected to a column chromatography (silica gel, $CHCl_3$:hexane=1:1) to give **10** as a pale yellow solid (0.153 g, 74 %): mp 160-162 ˚C ($CHCl_3$-hexane); ^{1}H NMR δ 7.51 (d, 2H, *J* = 7.6), 7.39 (d, 2H, *J* = 7.2), 6.91 (s, 2H), 1.40-1.56 (m, 3H), 1.16 (d, 18H, *J* = 7.3), UV-VIS (CH_2Cl_2) λ_{max} 380 nm. Anal. Calcd for $C_{23}H_{27}NCl_2Si$: C, 66.33; H, 6.53; N, 3.36. Found: C, 66.26; H, 6.61; N, 3.26.

Preparation of coupling material (11)

A flask containing $NiBr_2(PPh_3)_2$ (0.45 g, 0.6 mmol), activated Zn dust (0.078 g, 1.2 mmol), and Et_4NI (0.077 g, 0.3 mmol) was degassed and filled with Ar gas. To this flask was added dry THF (15 mL) and stirred at rt for 30 min. The color of the solution was turned to red, and to this solution was added **11** (0.13 g, 0.3 mmol) in THF (5 mL). The reaction mixture was stirred at 50 ˚C for 20 h, and then poured into water. Extraction with $CHCl_3$ followed by washing with water, dried over $MgSO_4$, and concentration gave the dark red solid, which was purified by column chromatography (silica gel, $CHCl_3$:hexane=1:1) and recrystallization from CH_2Cl_2-hexane to give pure **11** as a dark red solid (0.025 g, 24 %): mp >250 ˚C (CH_2Cl_2-hexane); ^{1}H NMR ($CDCl_3$) δ 8.12 (d, 4H, *J* = 7.6), 7.56 (d, 4H, *J* = 7.6), 6.93 (s, 4H), 1.40-1.59 (m, 6H), 1.19 (d, 36H, *J*= 7.3); m/z (EI) 690 (M^+); UV-VIS (CH_2Cl_2) λ_{max} 477, 51, 551 nm; Anal. Calcd for $C_{46}H_{54}N_2Si_2$: C, 79.94; H, 7.88; N, 4.05. Found: C, 79.76; H, 7.66; N, 3.86.

Preparation of Porphyrin (12)

Porphyrin (**12a**) was prepared by the procedure of Lash in 40 % yield. Porphyrin (**12b**) was also prepared in 34 % yield by the same procedure using pyrrole (**9**) and benzaldehyde. **12a**: mp >250 ˚C (CH_2Cl_2-MeOH); ^{1}H NMR ($CDCl_3$ + TFA) δ 9.00 (d, 8H, *J* = 7.3), 8.15 (t, 4H, *J* = 7.3), 8.05 (t, 8H, *J* = 7.3), 7.80 (d, 8H, *J* = 8.5), 7.26 (t, 3H, *J* = 7.3), 6.11 (d, 8H, *J* = 6.7); FAB/MS 1111 (M + 1); UV-VIS ($CHCl_3$) λ_{max} (log ε) 704 (3.92), 636 (4.23), 555 (5.13) nm; UV-VIS ($CHCl_3$ + 1% TFA) λ_{max} (log ε) 764 (4.21), 693 (4.36), 568 (5.40) nm. These data were in good agreement of those of literature.[4b] **12b**: mp >250 ˚C (CH_2Cl_2-MeOH); ^{1}H NMR ($CDCl_3$ + TFA) δ 8.88 (d, 8H, *J* = 7.8), 8.14 (t, 4H, *J* = 7.3), 8.02 (t, 8H, *J* = 7.3), 5.88 (d, 8H, *J* = 7.8); UV-VIS ($CHCl_3$) λ_{max} (log ε) 715 (4.30), 646 (4.55), 571 (5.40) nm; UV-VIS ($CHCl_3$ + 1 % TFA) λ max (log ε) 775 (4.32), 700 (4.61), 583 (5.40) nm. Anal. Calcd for $C_{84}H_{38}N_4Cl_8 \cdot H_2O$; C, 71.81; H, 2.76; N, 3.98. Found: C, 71.58; H, 3.06; N, 3.90.

Preparation of 5, 10, 15, 20-Tetrakis(2-thienyl)traacenaphthoporphyrins (12c) and (12d)

To a stirred solution of **1** (0.22 g, 1.2 mmol) and 2-thiophenecarboxyaldehyde (0.14 mL, 1.2 mmol) in $CHCl_3$ (120 mL) was added $BF_3 \cdot Et_2O$ (0.029 mL, 0.23 mmol), and the resulting solution was stirred for 2 h under Ar at rt. Then DDQ (0.20 g, 0.86 mmol) was added to the reaction mixture, and the whole was stirred for 1 h. Triethylamine (one drop) was added and poured into water. The organic layer was washed with aqueous saturated $NaHCO_3$ and brine. Concentration followed by column chromatography (silica gel, $CHCl_3$ containing 1% Et_3N) gave **12c**. Recrystallization from $CHCl_3$-MeOH gave pure **12c** as a dark green solid (0.13 g, 40 %): mp >250 ˚C (CH_2Cl_2-MeOH); ^{1}H NMR ($CDCl_3$ + TFA) δ 8.60 (m, 4H), 8.36 (m, 4H), 7.82 (m, 12H), 7.36 (m, 8H), 6.42 (m, 4H), 6.35 (m, 4H); UV-VIS ($CHCl_3$) λ_{max} (log ε) 720 (4.00), 646 (4.14), 564 (5.17) nm; UV-VIS ($CHCl_3$ + 1 % TFA) λ_{max} (log ε) 802 (4.42), 722 (4.13), 585 (5.36). Anal. Calcd for $C_{76}H_{38}N_4S_2 \cdot 2H_2O$: C, 77.93; H, 3.61; N, 4.78. Found: C, 78.11; H, 3.46; N, 4.85. Porphyrin (**12d**) was prepared in the same way, recrystallization from EtOH-$CHCl_3$ gave pure **12d** in 30%: mp >250 ˚C (CH_2Cl_2-MeOH); ^{1}HNMR ($CDCl_3$ + TFA) δ 8.56 (m, 4H), 7.84 (m, 4 H), 7.45 (m, 8H), 6.23 (m, 4H), 6.16 (m, 4H); UV-VIS ($CHCl_3$) λ_{max} (log ε) 730 (4.11), 663 (4.27), 479 (5.22) nm; UV-VIS ($CHCl_3$ + 1% TFA) λ_{max} (log ε) 817 (4.45), 732 (4.22), 603 (5.39) nm. Anal. Calcd for $C_{76}H_{30}N_4Cl_8S_4 \cdot 2C_2H_5OH$: C, 64.30; H, 2.49; N, 3.85. Found: C, 64.36; H, 2.82; N, 3.84.

Preparation of Porphyrin (13)

To a solution of dimethyl 3,4-dibutoxypyrrole-2,5-dicarboxylate (0. 32 g, 1 mmol) in dry THF (15 mL) was added $LiAlH_4$ (0.19 g, 5 mmol) slowly at 0 ˚C, and the mixture was stirred for 1 h. The reaction mixture was poured into water, and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, dried and filtered. To the filtrate was added pyrrole **(1)** (0.19 g, 1 mmol) and *p*-TsOH (0.05 g). The

resulting solution was stirred at rt for 24 h, and *p*-chloranil (0.1 g, 0.41 mol) was added and the mixture was stirred for additional 24 h. After the usual work-up, column chromatography (silica gel, $CHCl_3$) followed by recrystallization from MeOH-$CHCl_3$ gave **13** as a green solid (0.127 g, 15 %): mp >250 ˚C (CH_2Cl_2-MeOH); ^{1}H NMR ($CDCl_3$) δ 10.24 (s, 4H), 8.80 (d, 4H, *J* = 6.4), 8.02 (d, 4H, *J* = 8.1), 7.90 (m, 4H), 4.96 (t, 8H, *J* = 6.6), 2.37-2.47 (m, 8H), 1.80-1.92 (m, 8H), 1.60-1.78 (m, 8H), 1.04 (t, 12H, *J* = 6.8), –3.08 (s, 2H); UV-VIS ($CHCl_3$) λ_{max} (log ε) 698 (4.38), 460 (5.09). Anal. Calcd for $C_{56}H_{54}N_4O_4 \cdot 0.5H_2O$: C, 77.69; H, 6.40; N, 6.47. Found: C, 77.75; H, 6.52; N, 6.48.

Preparation of dithiaporphyrin (14)

To a solution of dimethyl 3,4-dibutoxythiophene-2,5-dicarboxylate (0.34 g, 1 mmol) in dry THF (20 mL) was added $LiAlH_4$ (0.19 g, 5 mmol) slowly at 0 ˚C, and the mixture was stirred at 0 ˚C for 1 h. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and filtered. To the $CHCl_3$ solution (100 mL) were added pyrrole **(1)** (0.19 g, 1 mmol) and *p*-TsOH (0.05 g). The resulting solution was stirred at rt for 24 h, and then *p*-chloranil (0.25 g, 0.1 mmol) was added and the mixture was stirred for additional 24 h. After the usual work up, column chromatography (silica gel, $CHCl_3$) gave **14** followed by recrystallization from $CHCl_3$-MeOH gave pure **14** as a green solid (0.397 g, 45 %): mp >250 ˚C (CH_2Cl_2-MeOH); ^{1}HNMR ($CDCl_3$) δ 11.04 (s, 4H), 8.92 (d, 4H, *J* = 6..2), 8.12 (d, 4H, *J* = 8.1), 8.01 (m, 4H), 5.02 (t, 8H, *J* = 6.7), 2.45-1.57 (m, 8H), 1.92-2.02 (m, 8H), 1.15 (t, 12H, *J* = 6.7); UV-VIS (CH_2Cl_2) λ_{max} (log ε) 443 (5.34), 604 (4.35). Anal. Calcd for $C_{56}H_{52}N_2S_2O_4 \cdot 2H_2O$: C, 73.33; H, 6.15; N, 3.04. Found: C, 73.63; H, 5.82; N, 3.04.

Preparation of 7-methylacenaphtho[1, 2-*c*]pyrrole (15)

To a solution of ethyl acenaohtho[1,2-*c*]pyrrole-7-carboxylate (1.32 g, 5 mmol) in THF (200 mL) was added $LiAlH_4$ (2.85 g, 45 mmol) slowly. The resulting mixture was refluxed for 6 h and cooled to rt. The reaction mixture was poured into water carefully, and extracted with $CHCl_3$. The organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by column chromatography (silica gel, $CHCl_3$:hexane=1:1) gave **15** as a yellow crystal (0.65 g, 64 %): ^{1}H NMR ($CDCl_3$) δ 7.75 (s, 1H), 7.58-7.52 (m, 3H), 7.51-7.43 (m, 3H), 6.84 (d, 1H), 2.51 (s, 3H); EI/MS 205 (M^+). Anal. Calcd for $C_{15}H_{11}N$: C, 85.77; H, 5.40; N, 6.82. Found: C, 85.59; H, 5.39; N, 6.23.

Preparation of pyrromethene-BF_2-complexes (16) and (18)

Pyrromethene dyes were prepared by the method of Boyer.[18] As a general method, preparation of dye (**18**) was described here. To a solution of 4,7-dihydro-4,7-ethano-1-methyl-2*H*-isoindole (0.57 g, 3.6 mmol) in CH_2Cl_2 (100 mL) was added acetyl chloride (0.57 mL, 6.6 mmol). The solution was heated at reflux for 3

h, then hexane was added to form the precipitation. The precipitate was washed with hexane and was dissolved in toluene (200 mL). To this solution was added Et_3N (1.31 mL, 9.86 mmol) and the mixture was stirred at rt for 15 min, then $BF_3 \cdot Et_2O$ (1.74 mL, 10.95 mmol) was added. The resulting solution was heated at 80 ˚C with stirring for 30 min. After cooling to rt and filtration, the filtrate was washed with brine and dried over $MgSO_4$. Concentration followed by column chromatography (silica gel, $CHCl_3$) gave **18** as a orange crystal (0.377 g, 54 %): mp 182 ˚C (decomp), (CH_2Cl_2-hexane); ^{1}H-NMR ($CDCl_3$) δ 6.51 (m, 2H), 6.42 (m, 2H), 4.34 (m, 2H), 3.88 (m, 2H), 2.73 (s, 3H), 2.49 (s, 6H), 1.60-1.26 (m, 8H); EI/MS 391 (M^+); UV-VIS ($CHCl_3$) λ_{max} (log ε) 530 (4.89), 390 (4.07) nm. Anal. Calcd for $C_{24}H_{25}N_2BF_2 \cdot 0.5H_2O$: C, 71.48; H, 7.50; N, 6.95. Found: C, 71.25; H, 7.22; N, 6.73.

Pyrromethene dye (**16**) was prepared from **15** as a deep green crystal in 38 % yield by the same way: mp >350 ˚C (CH_2Cl_2-hexane); EI/MS 482 (M^+); UV-VIS ($CHCl_3$) λ_{max} (log ε) 657 (5.15), 612 (4.35), 603 (4.27). Anal. Calcd for $C_{32}H_{21}N_2BF_2$: C, 79.68; H, 4.36; N, 5.81. Found: C, 79.54; H, 4.21; N, 5.67.

Preparation of Unsymmetrical Pyrromethene Dyes (17)

To a solution of 7-methylacenaphto[1,2-*c*]pyrrole (0.37 g, 1.78 mmol) and 2-acetyl-4-ethyl-3,5-dimethylpyrrole (0.35 g, 1.85 mmol) in $CHCl_3$ (100 mL) was added $POCl_3$ (0.18 mL, 1.85 mmol). The resulting solution was refluxed for 12 h. Ethyldiisopropylamine (1.32 mL, 7.49 mmol) was added and the reflux was continued for additional 2 h, and then $BF \cdot Et_2O$ (0.96 mL, 8.32 mmol) was added and the mixture was refluxed for 7 h. After the usual work up, column chromatography (silica gel, $CHCl_3$) gave **17** as a deep blue solid (0.26 g, 36 %): mp 285-287 ˚C (CH_2Cl_2-hexane); ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 1H, *J* = 7.3), 7.80 (d, 1H, *J* = 7.8), 7.67-7.65 (m, 2H), 7.58-7.55 (m, 2H), 2.90 (s, 3H), 2.58 (s, 3H), 2.41-2.38 (m, 5H), 1.07 (t, 3H, *J* = 7.5); EI/MS 400 (M^+); UV-VIS ($CHCl_3$) λ_{max} (log ε) 588 (5.01). Anal. Calcd for $C_{25}H_{23}N_2BF_2$: C, 75.02; H, 5.79; N, 7.00. Found: C, 74.74; H, 5.68; N, 6.89.

Preparation of 19

Compound (**18**) (0.039 g, 0.1 mmol) was placed in a flask and heated at 230 ˚C (1 mmHg) for 2 h to give pure **19** as a golden crystal (0.034 g, 100 %): ^{1}H NMR ($CDCl_3$) δ 8.12 (d, 2H, *J* = 8.3), 7.93 (d, 2H, *J* = 8.3), 7.50 (t, 2H, *J* = 7.5), 7.30 (t, 2H, *J* = 7.3), 3.07 (s, 3H), 2.87 (s, 6H); EI/MS 334 (M^+); UV-VIS ($CHCl_3$) λ_{max} (log ε) 603 (5.19), 558 (4.52), 335 (4.32) nm. Anal. Calcd for $C_{20}H_{17}N_2BF_2$: C, 71.88; H, 5.13; N, 8.38. Found: C, 71.76; H, 5.20; N, 8.44.

ACKNOWLEDGEMENTS

The work was supported by Grants-in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

REFERENCES

1. D. H. R. Barton, J. Kervagoret, and S. Zard, *Tetrahedron*, 1990, **46**, 7587.
2. N. Ono, H. Kawamura, M. Bougauchi, and K. Maruyama, *Tetrahedron*, 1990, **46**, 7483; Y. Fumoto, T. Eguchi, H. Uno, and N. Ono, *J. Org. Chem*., 1999, **64**, 6518; M. Adamzyk, D. D. Johnson, and R. E. Reddy, *Angew. Chem., Int. Ed*., 1999, **38**, 3537; N. Ono, The Nitro Group in Organic Synthesis, Wiley-VCH, New York, 2001, pp. 330-338.
3. (a) N. Ono, H. Hironaga, K. Simizu, K. Ono, K. Kuwano, and T. Ogawa, *J. Chem. Soc., Chem. Commun.*, 1994, 1019; (b) N. Ono, H. Hironaga, K. Ono, S. Kaneko, T. Murashima, T. Ueda, C. Tsukamura, and T. Ogawa, *J. Chem. Soc., Perkin Trans. 1*, 1996, 417; (c)T. Murashima, R. Tamai, K. Fujita, H. Uno, and N. Ono, *Tetrahedron Lett*., 1996, **37**, 8391; (d) T. Murashima, R. Tamai, K. Nishi, K. Nomura, K. Fujita, H. Uno, and N. Ono, *J. Chem. Soc., Perkin Trans 1*, 2000, 995.
4. (a) T. D. Lash and P. Chandraseker, *J. Am. Chem. Soc*., 1996, **118**, 8767; (b) J. D. Spence and T. D. Lash, *J. Org. Chem*., 2000, **65**, 1530; (c) T. D. Lash, T. M. Werner, M. L. Thompson, and J. M. Manley, *J. Org. Chem*., 2001, **66**, 3152 and references therein.
5. L. Jaquinod, C. Gros, M. M. Olmstead, and K. M. Smith, *Chem. Commun*., 1996, 1475.
6. T. D. Lash, The Porphyrin Handbook, ed. by K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, **2**, 2000, pp. 157-230 and references therein.
7. B. Valeur, Molecular Fluorescence, Wiley-VCH, Weinheim, 2002.
8. W. Rettig and J. Wirz, *Helv. Chim. Acta*, 1976, **59**, 1054.
9. L. deWitt, G. J. Blanchar, E. LeGoff, M. E. benz, J. H. Liao, and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1993, **115**, 12158.
10. R. E. Martin and F. Diederich, *Angew. Chem., Int. Ed*., 1999, **38**, 1350.
11. (a) A. Pelter and D. E. Jones, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2289; (b) T. M. Swager, C. J. Gil, and M. S. Wrighton, *J. Phys. Chem*., 1995, **99**, 4886 and references therein.
12. N. Ono, C. Tsukamura, Y. Nomura, H. Hironaga, T. Murashima, and T. Ogawa, *Adv. Mater*., 1997, **9**, 149.
13. K. Mullen and G. Wegner, Electronic Materials: The Oligomer Approach, Wiley-VCH, Weinheim, 1998; B. Valeur, Molecular Fluorescence, Wiley-VCH, Weimheim, 2001 and references therein
14. T. E. O. Screen, J. R. G. Thorme, R. G. Denning, D. G. Bucknall, and H. L. Anderson, *J. Am. Chem. Soc*., 2002, **124**, 9712; A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79; H. L. Anderson, *Chem. Commun*., 1999, 2323 and many references therein.
15. N. Ono, H. Miyagawa, T.Ueta, T. Ogawa, and H. Tani, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1595.
16. T. Murashima, N. Wakamori, Y. Uchihara, T. Ogawa, H. Uno, and N. Ono, *Mol. Cryst. Liq. Cryst*., 1996, **278**, 165; A. Merz, R. Schropp, and E. Dotterl, *Synthesis*, 1995, 795.

17. K. Zong and J. R. Reynolds, *J. Org. Chem*., 2001, **66**, 6873 and references therein.
18. A. Burghart, H. Kim, M. B. Welch, L. H. Thoresen, J. Reibenzpies, K. Burgstorm, and L. B. A. Johansson, *J. Org. Chem*., 1999, **64**, 7813; J. Chen, A. burghart, A. D. kovac, and K. Burgess, *J. Org. Chem*., 2000, **65**, 2900; K. rurack, M. kollmannsberger, and J. Daub, *Angew. Chem., Int. Ed*., 2001, **40**, 385 and references therein.
19. M. Wada, S. Ito, H. Uno, T. Murashima, N. Ono, T. Urano, and Y. Urano, *Tetrahedron Lett*., 2001, **42**, 6711.
20. M. Shah, K. Thangaraji, M. L. Soong, L. T. Wolford, J. H. Boyer, I. R. Politer, and T. G. Pavlopoulos, *Heteroatom Chemistry*, 1990, **1**, 389.