SYNTHESIS AND CHARACTERIZATION OF NEW TYPES OF 4-[2-(2-HYDROXYARYL)ETHENYL]PYRIDINIUM BETAINE DYES†

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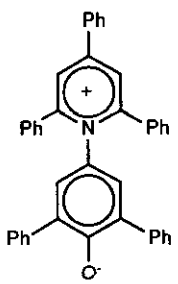
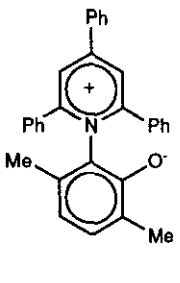
Abstract — Two types of pyridinium betaine dyes, 4-[4-(2-arylethenyl)-1-pyridinio]phenolates and 2-[2-(1-aryl-4-pyridinio)ethenyl]phenolates, which have a chromophore either of ET-30 type or the stilbazolium betaine type, have been synthesized. Both types of dyes show negative solvatochromism in various solvents, the intensity of chromism depending upon the polarity of the solvent. Betaines (**11a-c**) have the possibility of two betaine structures, the ET-30 or the stilbazolium betaine types. The transition energies of **11a-c** as well as **11g-i** are linear with the same slope against the E_T (30) scale of solvent polarity. Therefore, the stilbazolium betaine structure of **11a-c** contributes to the negative solvatochromism. The dyes prepared could be an indicator of solvent polarity.

2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)phenolate (**1**), called ET-30 or Reichardt's dye, is one of the most typical betaine dyes which show intense negative solvatochromic properties. Its absorption maxima in water and in diphenyl ether have been reported to be 453 and 810 nms, respectively, the absorption dependence upon



1 ET-30



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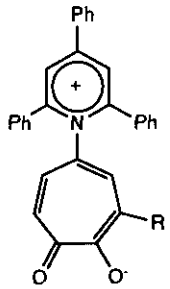
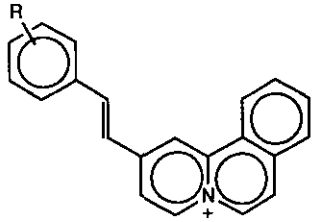


3a R=H
3b R= *i*-Pr



4a R=O⁻ at C-2
4b R=O⁻ at C-4

†Dedicated to Professor Edward C. Taylor on the occasion of his 70th birthday.

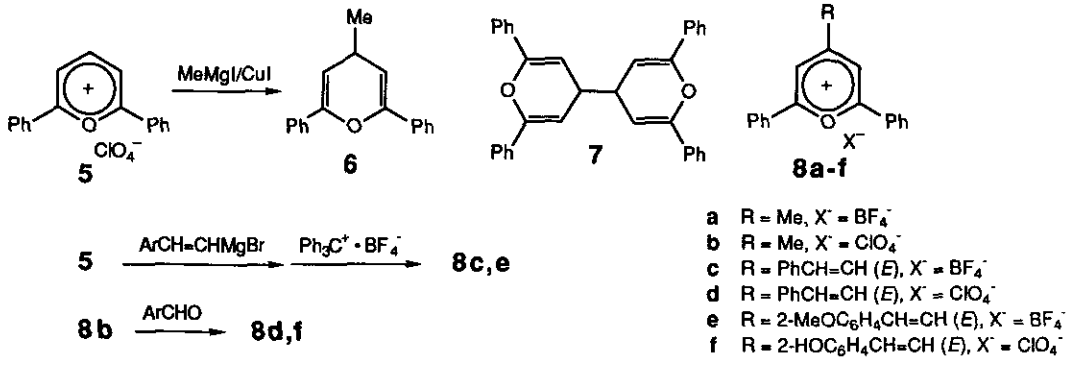
the solvent polarity being as large as 357 nm between these two solvents.[1]

Recently, some structural modifications of ET-30 were tried: Paley prepared the ortho-substituted betaine 2,5-dimethyl-6-(2,4,6-triphenyl-*N*-pyridinio)phenolate (**2**), of which the pyridine and phenolate rings are twisted out of plane by essentially 90° from the X-ray analysis.[2] We reported the synthesis of troponoid betaine dyes 5-(2,4,6-triphenyl-*N*-pyridinio)tropolonates (**3**), which showed the more blue-shifted absorption maxima than ET-30.[3] The crystal structure of **3a** shows the presence of two isomers, whose dihedral angles between the pyridinium and tropolonate rings are 74.6° and 67.9°. Much attention is recently paid on these betaine dyes for nonlinear optics such as second-harmonic generation.[4]

On the other hand, it was reported that stilbazolium betaine-type dyes (**4**) showed the remarkable negative solvatochromism.[5] We designed new solvatochromic dyes with two chromophores of the ET-30 and the stilbazolium betaine types in the molecule. In this paper, we report the preparation of new type of dyes and the characteristic behavior of the electronic spectra on solvent polarity.

RESULTS AND DISCUSSION

Synthesis. There are two possible routes to construct the skeletons of 4-[2-(2-hydroxyphenyl)ethenyl]-1-(4-hydroxyphenyl)pyridinium salts: 1) the initial synthesis of 4-[2-(2-hydroxyphenyl)ethenyl]pyryliums is followed by conversions to the pyridinium derivatives, and 2) the initial construction of 4-methyl-1-(4-hydroxyphenyl)pyridiniums is followed by condensations with 2-hydroxybenzaldehydes or synthetic equivalents. Since 4-methyl-2,6-diphenylpyryliums (**8a,b**) were expected to be one of the common and important starting compounds for the both synthetic routes, we first of all attempted to synthesize **8a,b** from the readily available 2,6-diphenylpyrylium perchlorate (**5**) (Scheme 1).

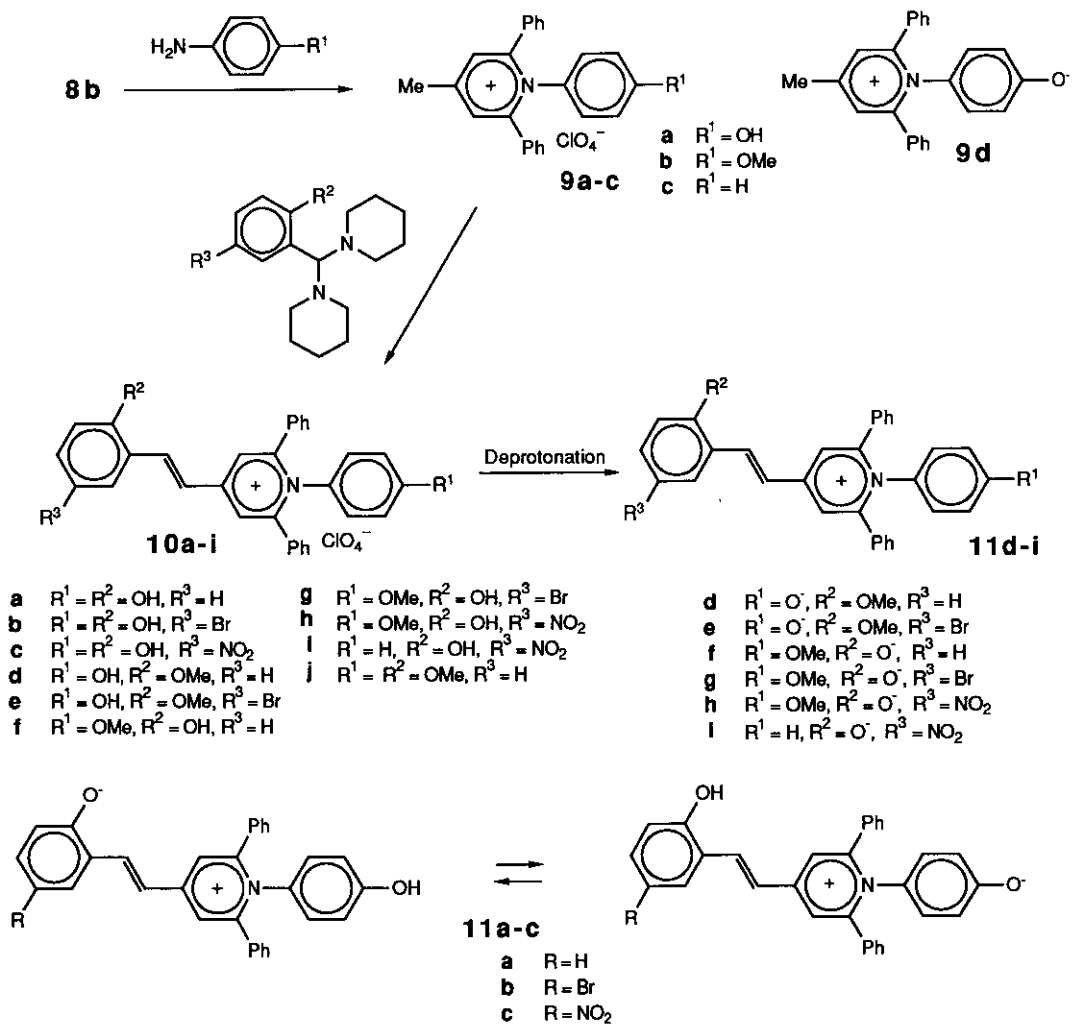


Scheme 1

The nucleophilic addition of a Grignard reagent to 2,6-disubstituted pyrylium salts followed by hydride abstraction is known to be an effective entry to 2,4,6-trisubstituted pyrylium derivatives.[6,7] Under the reported conditions as well as several other reaction conditions, the reaction of **5** with methylmagnesium iodide in dry ether resulted many products, from which a mixture of two major products was isolated after chromatography. The expected 4-methyl-4*H*-pyran (**6**) was accompanied by an inseparable product whose structure was deduced to

be **7** only on the basis of its partial ^{1}H-nmr spectrum (benzene-d_6): δ = 2.73 (t, J = 2.9 Hz) and 5.42 (d, J = 2.9 Hz). The dimeric product (**7**) was presumably formed through an electron transfer from the Grignard reagent to **5** and subsequent coupling reaction.[8] To avoid an electron transfer process, we performed this reaction in the presence of copper(I) iodide[9] to prepare 4-methyl-4*H*-pyran (**6**) quantitatively.

Compound (**6**) was converted to pyrylium (**8a**) with triphenylcarbenium tetrafluoroborate or with iron(III) chloride followed by the counter anion exchange to perchlorate (**8b**).[10] Styryl Grignard reagents, (*E*)-2-phenylethenylmagnesium and (*E*)-2-(2-methoxyphenyl)ethenylmagnesium bromides, could also be applied to **5** to directly construct 4-styrylpyrylium skeleton (**8c,e**). In these cases, no dimeric product (**7**) was formed even in the absence of the copper catalyst.



Scheme 2

Although 4-methylpyrylium perchlorate (**8b**) was converted easily with aldehydes to give (*E*)-4-(2-phenylethenyl)- (**8d**) and (*E*)-4-[2-(2-hydroxyphenyl)ethenyl]-2,6-diphenylpyrylium perchlorates (**8f**),[11] all attempts to convert the resulting 4-styrylpyrylium salts to the corresponding pyridinium derivatives, by the reaction with 4-aminophenol or 4-amino-2,6-diphenylphenol, were unsuccessful. The starting pyrylium salts were recovered. Therefore, the transformation of pyrylium perchlorate (**8b**) to the corresponding 4-methylpyridinium salts (**9**) was examined. Under reflux in ethanol, **8b** reacted smoothly with 4-aminophenol, 4-methoxyaniline, and aniline to give the corresponding pyridinium perchlorates (**9a-c**) in good yields (Scheme 2). However, due to the decreased reactivity, the use of 4-amino-2,6-diphenylphenol and 4-amino-2,6-diphenylanisole under the similar reaction conditions resulted in the partial recovery of the starting **8b**. With isopropylamine, an aliphatic amine, it formed a complex mixture. The reactions of 4-methylpyrylium tetrafluoroborate (**8a**) with 4-aminophenol and 4-amino-2,6-diphenylphenol gave no crystalline condensation product.

At the final step, the activated methyl moiety of 4-methylpyridinium compounds (**9a-c**) was condensed with aromatic aldehydes. Such reactivity of the 4-methyl substituent on pyrylium compounds was already demonstrated as in the condensation of **8b** with aromatic aldehydes to form **8d,f**. Although refluxing **9a** and 2-hydroxybenzaldehyde in acetic acid resulted in the quantitative recovery of the starting **9a**, the use of its aminal derivative,[12] 2-(bispiperidinomethyl)phenol, under reflux in ethanol produced the expected pyridinium salt (**10a**) in 81% yield. Employment of more than equimolar aminal is requisite for the smooth condensation, as the *in-situ* generation being ineffective. Thus, none of **10a** was obtained when **9a** was refluxed with 2-hydroxybenzaldehyde in ethanol in the presence of piperidine.

Although most of the condensation products were obtained as pale yellow to yellow solids, which were identified as pyridinium perchlorate structures (**10**) on the basis of elemental analyses, some products were obtained as deep-colored pyridinium betaines (**11**) by spontaneous elimination of perchloric acid under the reaction conditions. Such betaine formation was quite easy when the styryl moiety bears an electron-withdrawing substituent like a nitro group or a bromo atom as shown with the production of **11b,c,h**.

Since the pyridinium salts (**10**) were partly deprotonated with the piperidine liberated from the aminal reagent, the reaction mixtures were treated with either aqueous perchloric acid to complete the formation of pale-colored perchlorate (**10**) or with sodium ethoxide to complete the formation of deep-colored betaines (**11**). However, these procedures did not always work effectively; purification of the resulting salts and dyes was rather difficult. Accordingly, the deep-colored products were treated with sodium ethoxide in ethanol in prior to their purification, while the pale-colored products with perchloric acid.

Electronic Spectra and Solvatochromism. The pale-colored 4-styrylpyridinium perchlorates (**10b,c,i**) remained unchanged in color when dissolved in several different solvents (Table 1). On the other hand, the color of deep-colored pyridinium betaines (**11**) changed in solutions depending upon the polarity of the solvent used, indicating the intense solvatochromic properties. Such color change was also observed for the solution prepared from **10** and sodium ethoxide. When a drop of hydrogen perchlorate solution was added to a methanol solution of **11c**, a large blue shift from 488 to 376 nms was observed to indicate the protonation of the phenoxide. By an addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the above methanol solution of **11c**, the absorption maximum moved to 484 nm. The betaine structure was reproduced.

Table 1. Electronic Spectra (*nm*) of Pyridinium Perchlorates (**9**) and (**10**) in Various Solvents

	9a	**9c**	**10b**	**10c**	**10i**
Methanol	293	-	396	376	380
Ethanol	293	295	404	377	-
Acetonitrile	290	-	394	370	371
Acetone	-	-	394	-	373
Ethyl Acetate	288	-	-	-	-
Tetrahydrofuran	291	-	391	378	370
1,4-Dioxane	-	-	392	372	370

Table 2. Electronic Spectra [nm(ε)] and Transition Energies (kcal/mol) of Pyridinium Betaines (**11**) in Various Solvents

	ET-30	**11a**[a)]	**11b**[b)]	**11c**[b)]
Methanol	515.1, 55.5	530[c)], 53.9	516 (15300), 55.4	488 (24900), 58.6
Ethanol	550.9, 51.9	-	547 (16500), 52.3	506 (28700), 56.5
Acetonitrile	621.5, 46.0	-	606 (16500), 47.2	538 (39400), 53.1
Acetone	677.5, 42.2	640 (7300), 44.7	622 (5600), 45.9	522 (21300), 51.7
Ethyl Acetate	750.4, 38.1	-	-	591 (18600), 48.4
Tetrahydrofuran	764.5, 37.4	-	660 (11900), 43.3	592 (29800), 48.3
1,4-Dioxane	795, 36.0	-	670[c)], 42.7	620 (8900), 46.1

	11e[a,c)]	**11g**[a,c)]	**11h**[b)]	**11i**[a)]
Methanol	555 (11250), 51.5	525, 54.5	490[c)], 58.3	490 (17200), 58.3
Ethanol	-	553, 51.7	510[c)], 56.1	-
Acetonitrile	588 (3100), 48.6	615, 46.5	540 (44500), 52.9	539 (4400), 53.0
Acetone	593 (1900), 48.2	625, 45.7	555 (50800), 51.5	555 (22200), 51.5
Ethyl Acetate	-	664, 43.1	591[c)], 48.4	-
Tetrahydrofuran	-	667, 42.9	594, (29200), 48.1	597 (20900), 47.9
1,4-Dioxane	-	676, 42.3	622, (14500), 46.0	624[c)], 45.8

a) Prepared *in situ* from the corresponding perchlorates (**9**) or (**10**) and DBU (excess). b) Betaines (**11**) themselves were used. c) Molar extinction coefficient ε was not recorded because of the low solubility.

Based on the above observation, the solvatochromism was tested with the deep-colored betaines (**11b,c,h**), while other betaines (**11a,e,g,i**) were generated *in-situ* from the corresponding perchlorate (**10a,e,g,i**) and excess of DBU, and then submitted to the test. The results are summarized in Table 2.

All of betaines (**11**) in Table 2 showed the remarkable negative solvatochromism, i.e., 488~555 nm in methanol and 620~676 nm in 1,4-dioxane. It is apparent that betaines (**11e**) and (**11g-i**) have the 4-[4-(2-arylethenyl)-1-pyridinio]phenolate and 2-[2-(4-pyridinio)ethenyl]phenolate structures, respectively, **11e** belonging to the betaine dyes of ET-30, while the others have the merocyanine-type structure. Betaines (**11a-c**) are possible to occupy either 4-[4-(2-arylethenyl)-1-pyridinio)phenolate or 2-[2-(4-pyridinio)ethenyl]phenolate structures.
Plots of the transition energy for betaines (**11**) against the E_T (30) scale of solvent polarity are linear as shown in Figure 1. The slope of each lines except for **11e** is almost the same. This impies that the structure that actually contributed to the negative solvatochromism is the same in betaines (**11**) except for **11e**. It is concluded that the styryl moiety was more sensitive to solvent polarity than the phenolate one.

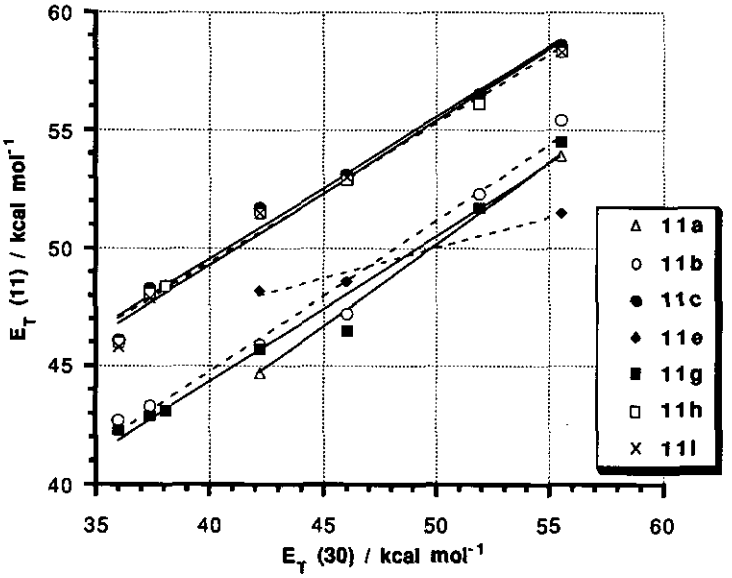


Figure 1. Correlation between E_T (30) and the transition energy of E_T (**11**).

The substituent in the styryl chromophore affected the absorption maximum. The electron-withdrawing nitro group shifted it to shorter wavelength [530 nm for **11a** (*p*-H), 516 nm for **11b** (*p*-Br), and 488 nm for **11c** (*p*-NO_2)]. Similar results were observed in **11g** (525 nm, *p*-Br) and **11h** (490 nm, *p*-NO_2), which have a methoxyl group on the phenyl ring on the nitrogen atom. The electron-withdrawing nitro group stabilizes the energy of the ground state more than that of the excited state with increasing solvent polarity. Since betaine (**11i**) showed an absorption maximum also at 490 nm, the electron-donating methoxyl group of **11g** and **11h** did not affect the absorption maximum.
Here, we like to note that the betaines (**11a-i**) retain fundamental features of ET-30 and that the styryl moiety in **11a-c** is responsible to the negative solvatochromism. Although **11a-i** showed no significant photochromic behaviors, it will be our next aim to design molecules having another function conjugated to ET-30 properties.

EXPERIMANTAL

Elemental analyses were performed by Mrs. M. Miyazawa of this Institute, Kyushu University. The mps were measured with a Yanagimoto Micro mp apparatus and are not corrected. The nmr spectra were measured by JEOL FX 100 and GSX 270H spectrometers, and the chemical shifts expressed were in δ units. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The ir spectra were taken using a JASCO IR-A 102 spectrophotmeter. The uv spectra were measured by the use of *Hitachi U-3200 and U-3410* spectrophotometers. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

4-Methyl-2,6-diphenyl-4*H*-pyran (6). *The solution of methylmagnesium* iodide, freshly prepared from metal magnesium (0.28 g, 11 mmol) and methyl iodide (0.747 ml, 12 mmol) in ether (30 ml), was added to the suspension of copper(I) iodide (0.342 g, 1.8 mmol) in ether (4 ml). The resulting mixture was slowly added, at –10 to –15 °C under dry nitrogen, to the cooled suspension of **5** (2 g, 6 mmol) in ether (25 ml). After stirring at the same temperature for a few minutes, the mixture was treated with saturated aqueous ammonium chloride and extracted with ether (25 ml x 2). The combined extracts were washed with water and dried over magnesium sulfate. The residue (**6**) (1.53 g, 100%) obtained by evaporation of the ether in vacuo was used without further purification [^{1}H-nmr (benzene-d_6) δ = 1.08 (3H, d, J = 8.1 Hz, Me), 3.03 (1H, dq, J = 3.8 and 8.1 Hz, H-4), 5.18 (2H, d, J = 3.8 Hz, H-3), and 7.0 - 7.8 (10H, m, Ph)].

4-Methyl-2,6-diphenylpyrylium Tetrafluoroborate (8a) and Perchlorate (8b). 1) To a solution of **6** (1.526 g, 6 mmol) in acetonitrile (30 ml) was added triphenylcarbenium tetrafluoroborate (2.2 g, 7 mmol) and the mixture was stirred at room temperature for 2.5 h. The precipitate was collected on a filter and washed with acetone - ether to give **8a** (1.67 g, 83%). Yellow crystals (acetic acid); mp 235 °C (lit.,[7] mp 234 °C). 2) To a solution of **6** (3.67 g, 14.8 mmol) in acetic acid (40 ml) was added little by little anhydrous iron(III) chloride (12 g, 75 mmol). The mixture was boiled for 5 min and then cooled down to room temperature to give dark green precipitate (1.37 g). This solid was dissolved in aqueous tartaric acid (40%) and the resulting solution was poured into aqueous perchloric acid (40%) to give **8b** (0.998 g, 75%). Pale yellow crystals (acetic acid); mp 271 - 272 °C (lit.,[10] mp 270 °C).

2,6-Diphenyl-4-[(*E*)-2-phenylethenyl]pyrylium Tetrafluoroborate (8c). To a solution of **5** (1.02 g, 3.59 mmol) in THF (13 ml) was slowly added, at –10 to –15 °C under dry nitrogen, the solution of styrylmagnesium bromide that had been freshly prepared from metal magnesium (0.14 g, 5.8 mmol) and (*E*)-1-bromo-2-phenylethene (0.722 ml, 5 mmol) in THF (6 ml). After stirring at the same temperature for 20 min, the reaction mixture was treated with saturated aqueous ammonium chloride and extracted with ether (20 ml x 2). The combined extract was washed with water twice, dried over magnesium sulfate, and then evaporated in vacuo. The red residual oil was dissolved in acetonitrile (15 ml) and the addition of triphenylcarbenium tetrafluoroborate (0.92 g) was followed. After stirring at room temperature for 3 h, the solvent was condensed in vacuo to give red solid of **8c** (0.732 g, 48% based on **5**). Red needles (acetone); mp 213 - 215 °C (decomp.); ir (Nujol) 1630, 1600, 1560, 1485, 1370, 1190, 1040, 880, and 770 cm^{-1}; ^{1}H-nmr (DMSO-d_6) δ = 7.6 - 7.7 (3H, m, Ph), 7.68 (1H, d, J_{trans} = 16.1 Hz, =Py$^+$), 7.8 - 7.9 (8H, m, Ph), 8.43 (4H, d, J = 7.0 Hz, *o*-H of 2- and 6-Ph of Py$^+$), 8.86 (1H, d, J_{trans} = 16.1 Hz, =CHPh), and 8.89 (2H, s, H-3 and H-5 of Py$^+$); ^{13}C-nmr

(DMSO-d_6) δ = 114.70, 123.61, 128.13, 129.02, 129.27, 129.53, 129.86, 132.44, 134.60, 134.70, 148.62, 163.12, and 168.69. Anal. Calcd for $C_{25}H_{19}OBF_4$: C, 71.12; H, 4.54. Found: C, 70.93; H, 4.71.

2,6-Diphenyl-4-[(*E*)-2-(2-methoxyphenyl)ethenyl]pyrylium Tetrafluoroborate (8e). A similar procedure using **5** (0.33 g, 1 mmol), (*E*)-2-(2-methoxyphenyl)ethenylmagnesium bromide (0.237 g, 1 mmol), and triphenylcarbenium tetrafluoroborate (0.23 g, 0.7 mmol) gave dark red solid of **8e** (0.142 g, 31% based on **5**). Red needles (acetone); mp 225 - 227 °C; ir (KBr) 1600, 1485, 1320, 1250, 1190, 1040, and 780 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ = 4.07 (3H, s, OMe), 7.15 (1H, t, J = 7.5 Hz, H-5 of Ar), 7.26 (1H, d, J = 8.8 Hz, H-3 of Ar), 7.63 (1H, br dd, J = 8.8 and 7.5 Hz, H-4 of Ar), 7.7 - 7.9 (7H, m, Ph and Ar), 7.97 (1H, d, J_{trans} = 16.1 Hz, =Py$^+$), 8.52 (4H, br, *o*-H of 2- and 6-Ph of Py$^+$), 8.84 (1H, d, J_{trans} = 16.0 Hz, =CHPh), 8.93 (2H, s, H-3 and H-5 of Py$^+$). Anal. Calcd for $C_{26}H_{21}O_2BF_4$: C, 69.05; H, 4.68. Found: C, 69.34; H, 4.53.

2,6-Diphenyl-4-[(*E*)-2-(2-hydroxyphenyl)ethenyl]pyrylium Perchlorate (8f). A mixture of **8b** (0.15 g, 0.43 mmol) and 2-hydroxybenzaldehyde (0.052 g, 0.43 mmol) was refluxed in acetic acid (1 ml) for 33 h. After cooled down to room temperature, the mixture was treated with ether to give violet solid of **8f** (0.15 g, 78%). mp 241 - 243 °C (lit.,[13] mp 243 - 244 °C).

1-(4-Hydroxyphenyl)-4-methyl-2,6-diphenylpyridinium Perchlorate (9a). A mixture of **8b** (3.47 g, 10 mmol) and 4-aminophenol (1.3 g, 11.9 mmol) in ethanol (20 ml) was heated under reflux for 8.5 h. After cooling to room temperature, the precipitate was collected on a filter and washed with small amount of acetic acid to give **9a** (2.8 g, 64%) after recrystallization from acetic acid. Colorless needles (AcOH); mp 235 - 237 °C; ir (KBr) 3450, 3020, 1680, 1610, 1550, 1500, 1440, 1350, 1225, 1060, 825, and 750 cm^{-1}; ^{1}H-nmr (CD_3OD) δ = 2.78 (3H, s, Me), 6.50 (2H, d, J = 8.8 Hz, H-2 and H-6 of Ar), 7.07 (2H, d, J = 8.8 Hz, H-3 and H-5 of Ar), 7.36 (10H, s, Ph), and 8.09 (2H, s, H-3 and H-5 of Py$^+$). Anal. Calcd for $C_{24}H_{20}NO_5Cl$: C, 65.83; H, 4.60; N, 3.20. Found: C, 65.89; H, 4.55; N, 2.92.

1-(4-Methoxyphenyl)-4-methyl-2,6-diphenylpyridinium Perchlorate (9b). A similar procedure (reflux for 5 h) using **8b** (0.346 g, 1 mmol) and *p*-anisidine (0.125 g, 1 mmol) in ethanol (3 ml) gave **9b** (0.29 g, 64%) after purification from ethanol. Pale yellow needles (methanol); mp 232 - 233 °C; ir (Nujol) 1550, 1500, 1370, 1180, 1060, 880, and 750 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ = 2.79 (3H, s, Me), 3.64 (3H, s, OMe), 6.55 (2H, d, J = 8.9 Hz, H-2 and H-6 of Ar), 7.08 (2H, d, J = 8.9 Hz, H-3 and H-5 of Ar), 7.2 - 7.4 (10H, m, Ph), and 7.81 (2H, s, H-3 and H-5 of Py$^+$); ^{13}C-nmr ($CDCl_3$) δ = 22.37 (Me), 55.04 (MeO), 113.92 (C-3 and C-5 of *N*-Ar), 128.39, 129.54, 129.72, 130.05, 131.43, 132.74 (Ph and Py$^+$, and *N*-Ar), 156.08, 159.94, and 160.11 (C-2 of Py+, C-1, and C-4 of *N*-Ar). Anal. Calcd for $C_{25}H_{22}NO_5Cl$: C, 66.45; H, 4.91; N, 3.10. Found: C, 65.95; H, 5.17; N, 3.10.

4-Methyl-1,2,6-triphenylpyridinium Perchlorate (9c). A similar procedure (reflux for 7 h) using **8b** (0.173 g, 0.5 mmol) and aniline (0.045 ml, 0.5 mmol) in ethanol (3 ml) gave **9c** (0.18 g, 85%) after purification from ethanol. Pale yellow needles (ethanol); mp 229 - 232 °C (decomp.); ir (Nujol) 1600, 1360, 1230, 1060, and 750 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ = 2.87 (3H, s, Me), 7.1 - 7.4 (15H, m, Ph) , and 7.89 (2H, s, H-3 and H-5 of Py$^+$); ms (rel intensity, %) *m/z* 323 (M$^+$ + 1, 24), 322 (M$^+$, base peak), and 321 (62). Anal. Calcd for $C_{24}H_{20}NO_4Cl$: C, 68.33; H, 4.78; N, 3.32. Found: C, 67.80; H, 4.86; N, 2.76.

General Procedure for the Condensations of 5 with Arylaldehyde Aminals Leading to 10 or 11. The reaction of **9a** with *o*-(dipiperidinomethyl)phenol leading to **10a** is described as a typical example. A mixture of **9a** (0.437 g, 1 mmol) and *o*-(dipiperidinomethyl)phenol (0.274 g, 1 mmol) was heated under reflux in ethanol (5 ml) for 3 h. The mixture was cooled down to room temperature, treated with aqueous perchloric acid (30%, 1 ml), and then allowed to stand in a refrigerator for about half a day. The precipitate of **10a** (0.44 g, 81%) was collected on a filter and washed with ethanol. The yields of other examples are: **10d**: 86%; **10e**: 70%; **10f**: 76%; **10g**: 80%; **10i**: 90%.

10a: Pale yellow prisms (ethanol); mp 305 - 308 °C; ir (Nujol) 1590, 1550, 1275, 1090, 870, 840, and 750 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ = 6.46 (2H, d, *J* = 9.2 Hz, H-3 and H-5 of *N*-Ar), 6.67 (1H, t, *J* = 7.5 Hz, H-5 of Ar), 6.76 (1H, d, *J* = 8.0 Hz, H-3 of Ar), 6.85 (1H, d, *J* = 7.5 Hz, H-6 of Ar), 6.93 (2H, d, *J* = 9.2 Hz, H-2 and H-6 of *N*-Ar), 6.98 (1H, dd, *J* = 8.0 and 7.5 Hz, H-4 of Ar), 7.1 - 7.4 (10H, m, Ph), 7.63 (1H, d, J_{trans} = 16.1 Hz, =CHPy$^+$), 8.16 (2H, s, H-3 and H-5 of Py$^+$), and 8.27 (1H, d, J_{trans} = 16.1 Hz, =CHAr). ms (rel intensity, %) *m/z* 338 (41), 337 (base peak), and 94 (32). Anal. Calcd for $C_{31}H_{24}NO_6Cl \cdot 1.5H_2O$: C, 65.44; H, 4.78; N, 2.46. Found: C, 65.88; H, 4.48; N, 2.56.

10g: Pale yellow prisms (ethanol); mp 297 - 300 °C; ir (KBr) 1530, 1355, 1300, 1220, 1080, 810, 755, and 700 cm^{-1}; ^{1}H-nmr (CD_3OD) δ = 3.66 (3H, s, OMe), 6.67 (2H, d, *J* = 9.1 Hz, H-3 and H-5 of *N*-Ar), 6.72 (1H, d, *J* = 8.8 Hz, H-3 of Ar), 7.12 (2H, *J* = 9.1 Hz, H-2 and H-6 of *N*-Ar), 7.27 (1H, dd, *J* = 8.8 and 2.6 Hz, H-4 of Ar), 7.3 - 7.4 (10H, m, Ph), 7.49 (1H, d, J_{trans} = 16.1 Hz, =CHPy$^+$), 7.77 (1H, d, *J* = 2.6 Hz, H-6 of Ar), 8.14 (2H, s, H-3 and H-5 of Py$^+$), and 8.31 (1H, d, J_{trans} = 16.1 Hz, =CHAr). Anal. Calcd for $C_{32}H_{25}NO_6BrCl$: C, 60.54; H 3.97; N, 2.21. Found: C, 60.89; H, 4.17; N, 2.21.

10i: Yellow needles (methanol); mp 139 - 142 °C; ir (KBr) 1590, 1230, 1160, 1060, 830, 750, and 690 cm^{-1}; ^{1}H-nmr (CD_3OD) δ = 3.63, 3.89 (each 3H, s, OMe), 6.56 (2H, d, *J* = 9.0 Hz, H-3 and H-5 of *N*-Ar), 7.13 (2H, s, H-2 and H-6 of *N*-Ar), 6.9 - 7.6 (16H, m, Ph, Ar, =CH, and OH), 7.89 (2H, s, H-3 and H-5 of Py$^+$), and 8.04 (1H, d, J_{trans} = 16.4 Hz, =CH); ^{13}C-nmr (CD_3OD) δ = 55.40, 55.62, 111.35, 113.93, 121.06, 123.18, 123.68, 128.30, 128.43, 128.69, 129.60, 129.69, 129.80, 129.90, 131.70, 132.36, 133.19, 137.52, 154.60, 156.11, 158.50, and 159.84. Anal. Calcd for $C_{33}H_{28}NO_6Cl \cdot 2H_2O$: C, 65.40; H 5.32; N, 2.31. Found: C, 65.86; H, 4.89; N, 2.51.

Other pyridinium perchlorates (**10d-f**) were characterized by elemental analyses: **10d**: Pale yellow prisms (ethanol); mp 298 - 300 °C; Anal. Calcd for $C_{32}H_{26}NO_6Cl$: C, 69.13; H, 4.71; N, 2.52. Found: C, 68.81; H, 4.92; N, 2.43. **10e**: Yellow crystals (ethanol); mp 274 - 278 °C; Anal. Calcd for $C_{32}H_{25}NO_6BrCl$: C, 60.54; H 3.97; N, 2.21. Found: C, 61.29; H, 4.18; N, 2.27. **10f**: Pale yellow prisms (ethanol); mp 310 °C; Anal. Calcd for $C_{32}H_{26}NO_6Cl$: C, 69.13; H, 4.71; N, 2.52. Found: C, 68.95; H, 4.86; N, 2.32.

A mixture of **9a** (0.12 g, 0.25 mmol) and 4-bromo-2-(bispiperidinomethyl)phenol (0.176 g, 0.5 mmol) in ethanol (3 ml) was refluxed for 30 min. The condensed mixture was cooled down to room temperature and kept in a refrigerator to give violet solid of **11b** (0.105 g, 81%). The yields in the other cases are: **11c**: 95%; **11h**: 80%.

11b: Deep violet solid (ethanol); mp 263 - 265 °C; ir (KBr) 1560, 1490, 1370, 1240, 1100, 960, 810, and 750 cm^{-1}; ^{1}H-nmr (CD_3OD) δ = 6.54 (2H, d, *J* = 9.2 Hz, H-3 and H-5 of *N*-Ar), 6.64 (1H, d, *J* = 8.8 Hz, H-3 of Ar), 6.93 (2H, d, *J* = 9.2 Hz, H-2 and H-6 of *N*-Ar), 7.18 (1H, dd, *J* = 8.8 and 2.6 Hz, H-4 of Ar), 7.2 -

7.4 (12H, m, Ph, =CHPy$^+$, and OH), 7.71 (1H, d, J = 2.6 Hz, H-6 of Ar), 8.07 (2H, s, H-3 and H-5 of Py$^+$), and 8.36 (1H, J_{trans} = 16.5 Hz, =CHAr). ms (rel intensity, %) m/z 519 (M$^+$, 6), 427 (31), 425 (31), 347 (37), and 94 (base peak). Anal. Calcd for $C_{31}H_{22}NO_2Br \cdot H_2O$: C, 69.15; H 4.49; N, 2.60. Found: C, 69.59; H, 4.37; N, 2.44.

11c: Deep red prisms (ethanol); mp 273 - 275 °C; ir (Nujol) 1580, 1230, 1125, 820, 750, and 690 cm^{-1}; ^{1}H-nmr (CD_3OD) δ = 6.49 (2H, d, J = 8.8 Hz, H-3 and H-5 of *N*-Ar), 6.56 (1H, d, J = 9.2 Hz, H-3 of Ar), 6.99 (2H, d, J = 8.8 Hz, H-2 and H-6 of *N*-Ar), 7.3 - 7.4 (10H, m, Ph), 7.61 (1H, d, J_{trans} = 16.2 Hz, =CHPy$^+$), 7.97 (1H, dd, J = 9.2 and 3.1 Hz, H-4 of Ar), 8.13 (2H, s, H-3 and H-5 of Py$^+$), 8.35 (1H, d, J_{trans} = 16.2 Hz, =CHAr), and 8.53 (1H, d, J = 3.1 Hz, H-6 of Ar). Anal. Calcd for $C_{31}H_{22}N_2O_4$: C, 76.53; H 4.56; N, 5.76. Found: C, 76.52; H, 4.76; N, 5.63.

11h: Deep red powders (ethanol); mp 287 - 290 °C (decomp.); ^{1}H-nmr (CD_3OD) δ = 6.77 (1H, d, J = 9.5 Hz, H-3 of Ar), 7.1 - 7.4 (15H, m, Ph), 7.71 (1H, d, J_{trans} = 16.1 Hz, =CHPy$^+$), 8.06 (1H, dd, J = 9.2 and 2.8 Hz, H-4 of Ar), 8.24 (2H, s, H-3 and H-5 of Py$^+$), 8.34 (1H, d, J_{trans} = 16.1 Hz, =CHAr), and 8.58 (1H, d, J = 2.8 Hz, H-6 of Ar); Anal. Calcd for $C_{31}H_{22}N_2O_3 \cdot 3H_2O$: C, 70.98; H, 5.30; N, 5.34. Found. C, 71.21; H, 4.65; N, 5.18.

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