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Syntheses and Characterization of New Styryl Fluorescent Dyes from DAMN. Part II

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ABSTRACT

*2,3-Bis(bromomethyl)-5,6-dicyanopyrazine (**3**) can be prepared more readily by the condensation of DAMN (**1**) and 1,4-dibromobutane-2,3-dione (**2**) than by direct bromination of 2,3-dimethyl-5,6-dicyanopyrazine. The Wittig reaction of **3** with arylaldehydes gave a new type of fluorescent styryl dyes (**6–8**). These styryl dyes have extended π-conjugation systems and strong intramolecular charge-transfer chromophoric systems. They have strong fluorescence in solution and some have fluorescence even in the solid state, which is very important to evaluate their electroluminescence (EL) property as the emitter for EL devices. Calculation of excitation energies using the PPP-MO method, and optimization of their structures using the MOPAC with the PM 3 method were conducted, and their spectral properties are discussed to correlate their functionalities with chemical structures. © 1997 Elsevier Science Ltd*

Keywords: styryl fluorescent dye, dicyanopyrazine, diaminomaleonitrile, solid state fluorescence, Wittig reaction, electroluminescence.

INTRODUCTION

It has recently been noted that 2,3-dichloro-5,6-dicyanopyrazine has become commercially available as a biologically active compound [1]. It has two

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strong electron withdrawing cyano groups on the pyrazine ring and the chlorine atoms are very reactive to various nucleophiles, such as amines, enamines, thiols, and phenols. The synthesis of diamino and vinylamino derivatives, and of dithiine derivatives of 2,3-dichloro-5,6-dicyanopyrazine, has been reported [2–4]. Pyrazine has two nitrogen atoms at the 1,4-positions in the ring, and pyrazine oriented coloring matters have additional functionalities compared with those of benzene analogues. These special characteristics are a stronger donor–acceptor chromophoric system, higher polarizability, higher melting point and higher solubility in polar solvents.

In a previous paper [5], we reported the synthesis and fluorescence behavior of new styryl dyes derived from diaminomaleonitrile (DAMN), which were shown to exhibit large differences in λ_{max} from solution to solid state resulting from strong intermolecular π–π interactions. These dyes are also very interesting since they produce a large dipole moment in the excited state, and consequently large induced dipole moment differences accompanying laser irradiation. These requirements are very necessary for nonlinear optical materials [6]. Strong fluorescence in the solid state is also of interest with respect to emitters for EL materials. We intend to synthesize and study the functionalities of these compounds.

RESULTS AND DISCUSSION

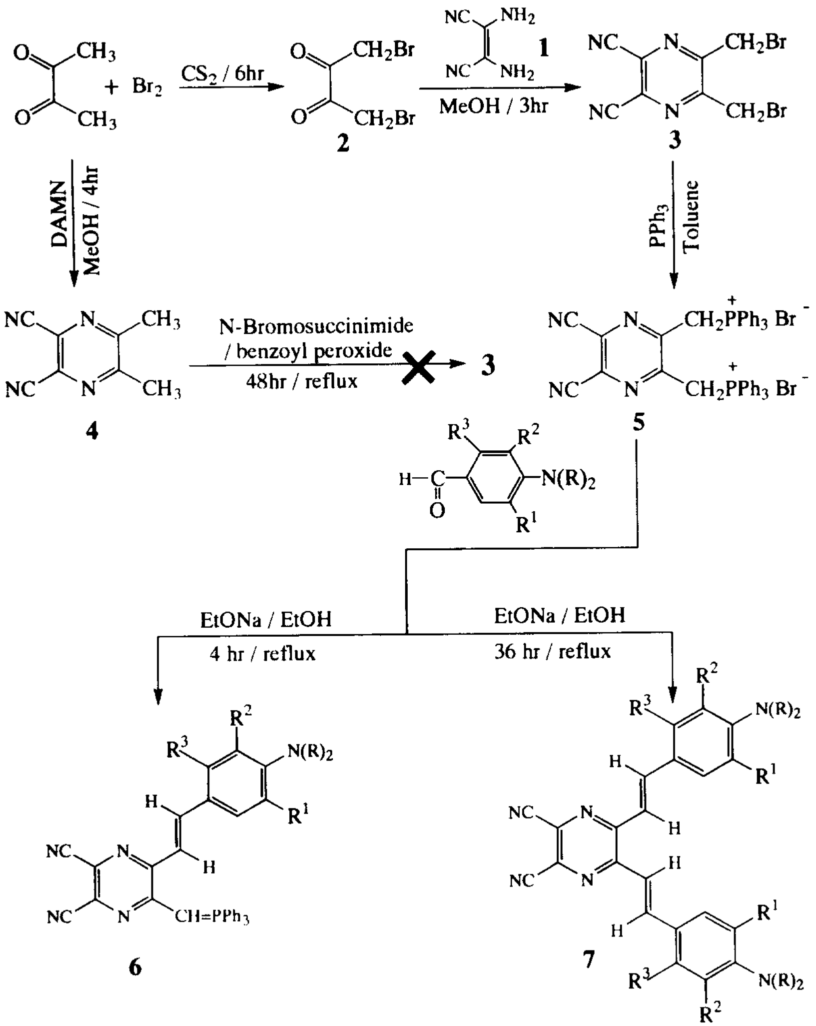
Wittig reaction of 3 with arylaldehydes

2,3-Bis(bromomethyl)-5,6-dicyano-pyrazine **3** was prepared by the condensation of DAMN **1** and 1,4-dibromobutane-2,3-dione **2**. Direct bromination of 2,3-dimethyl-5,6-dicyanopyrazine **4** hardly proceeded. Treatment of **3** with 2 equiv. of triphenylphosphine in toluene afforded 2,3-bis(triphenylphosphoniummethyl)-5,6-dicyanopyrazine dibromide **5** in good yield (78%). Reaction pathways are summarized in Scheme 1.

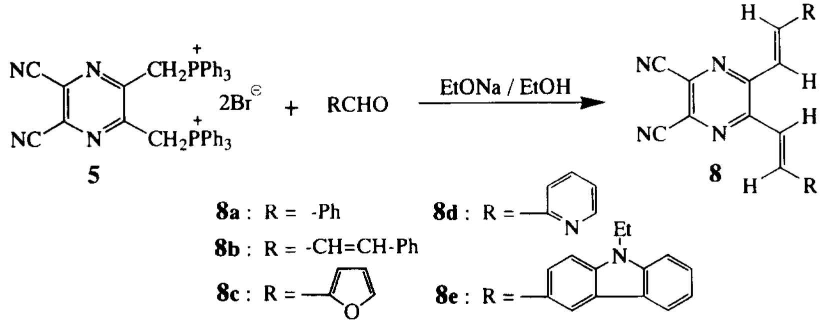
Reactions of **5** with 2 equiv. of N,N-dialkylaminobenzaldehydes in the presence of 2 equiv. of sodium ethoxide under reflux conditions gave the monostyryl derivatives **6**, and bis-styryl derivatives **7** under prolonged reaction time in low yield. On the other hand, treatment of **5** with 2 equiv. of arylaldehydes having lower electron donating substituents gave the bis-styryl derivatives **8** in higher yield. The results are summarized in Scheme 2 and Table 1.

Visible and fluorescence spectra

The PPP-MO calculation results revealed that the basic chromophore of the styryl dye **7** has a strong intramolecular charge-transfer chromophoric system



Scheme 1



Scheme 2

TABLE 1
Syntheses of Styryl Dyes

Compound	*R*	*R^1*	*R^2*	*R^3*	*Reaction time (h)*	*Yield (%)*
6a	Me	H	H	H	4	79
6b	Et	H	H	OH	4	75
6c			[a]		4	64
7	Me	H	H	H	36	16
8a					4	79
8b					4	69
8c					4	77
8d					4	77
8e					6	19

[a] $R,R^1 = R,R^2 = (CH_2)_3$.

in which the dialkylaminophenyl groups act as donor moieties and the dicyanopyrazine group acts as an acceptor moiety. The π-electron density changes accompanying the first excitation (HOMO–LUMO) of **7** are shown in Fig. 1. A large dipole moment of 27.1 debye was calculated in the first excited state, which is much larger than the 16.7 debye value of the ground state. The direction of the dipole moment oriented from the donor to the acceptor moiety, which was composed of the two donor–acceptor chromophoric systems in a lamda shape. This is important for second order nonlinear optical materials in the case of effective molecular packing to prevent dipole cancellation [7]. These large dipole moment differences accompanying the first excitation should be important in nonlinear optical materials.

The calculated λ_{max} of 457 nm was well in accordance with the observed value of 492 nm. The π-electron system of **7** was completely planar and no steric hindrances between the two styryl groups were observed from the results of the MOPAC with the PM 3 calculation (Fig. 2), and this was also observed in the case of **6**, except for the phosphorane moiety.

Table 2 shows the visible and fluorescence spectra of dyes **6**–**9**. The absorption and fluorescence maxima of these dyes were observed at 359–529 nm and 466–607 nm, respectively. Stoke's shifts were 78–114 nm, except of dye **8c** which showed a smaller value of 52 nm. The electron donating character of substituents in dyes **7** and **8** strongly reflect their absorption spectra in producing bathochromic shifts depending on their electron donating ability.

On the other hand, the mono-styryl dyes **6a**–**6c** showed two absorption maxima around 400 nm and 520 nm, respectively. The other mono-styryl dye **9** showed a single absorption maximum in the visible region and the two absorption maxima of **6** were resultant from the phosphorane group at the 3-position. Dyes **6** showed a large solvatochromism of 150–190 nm,

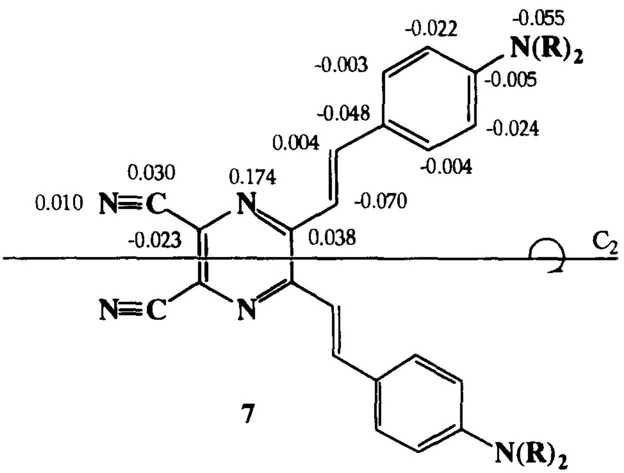


Fig. 1. π-Electron density changes accompanying the first excitation of styryl dye 7.

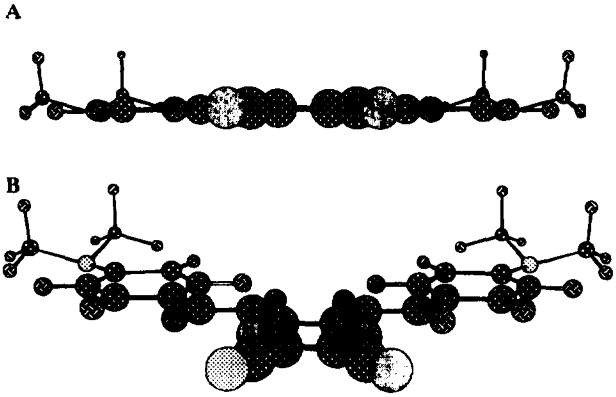


Fig. 2. Optimized structures of 7 by MOPAC with PM 3 calculations. (A) View from π-molecular plane; (B) rotated 15° from A site.

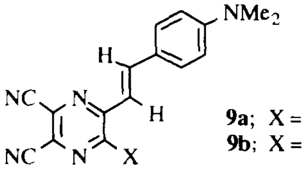
depending on the electrostatic interactions of triphenylphosphordiyl methyl group at the 3-position. The phosphorane group donates electrons to the dicyanopyrazine moiety, which may then cause a decrease of the electron withdrawing ability of the acceptor moiety of dye **6**, thus producing the hypsochromic shift of the λ_{max} value.

Alkylidene phosphorane can exist as a resonance hybrid of two equivalent structures **A** and **B**, but the canonical form **C** mainly contributes to the hypsochromic shift of dye **6** (Scheme 3). The two absorption maxima of **6** may be due to the hybrid mixtures of **A** to **C**. The reactivity of alkylidene phosphoranes is determined by the negative charge in the molecule, which in

TABLE 2
Visible and Fluorescence Spectra of Dyes **6**–**9**

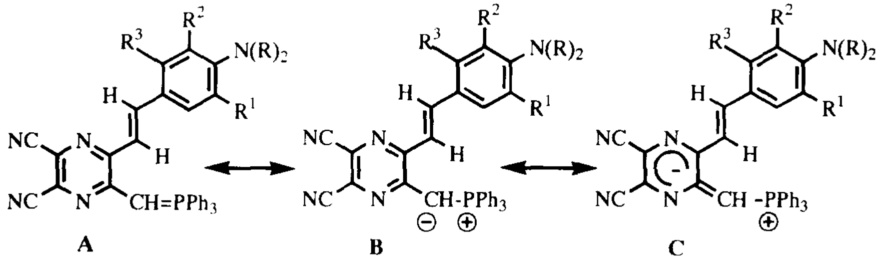
Compound	λ_{max} *(nm)*[a]	F_{max} *(nm)*[b]	*SS*[c]
6a	403, 518	602	84
6b	404, 523	605	82
6c	406, 529	607	78
7	492	595	103
8a	377	487	110
8b	419	523	114
8c	414	466	52
8d	359	470	111
8e	462	550	88
9a	498	598	99
9b	499	583	84

[a] In CHCl$_3$.
[b] Fluorescence maximum excited at λ_{max} value.
[c] Stoke's shift.



9

9a; X = H
9b; X = CH$_3$



Scheme 3

turn depends on the nature of the substituents on the alkylidene group as well as on the phosphorus group. It is possible to estimate the reactivity of the ylene from the pK_a value of its conjugate acid [8]. Thus the nucleophilic character of the phosphorane **C** is decreased because of delocalization of the negative charge into the dicyanopyrazine ring. The reactivity of the phosphorane moiety in dye **6** to give dye **7** was very low, and the yield for

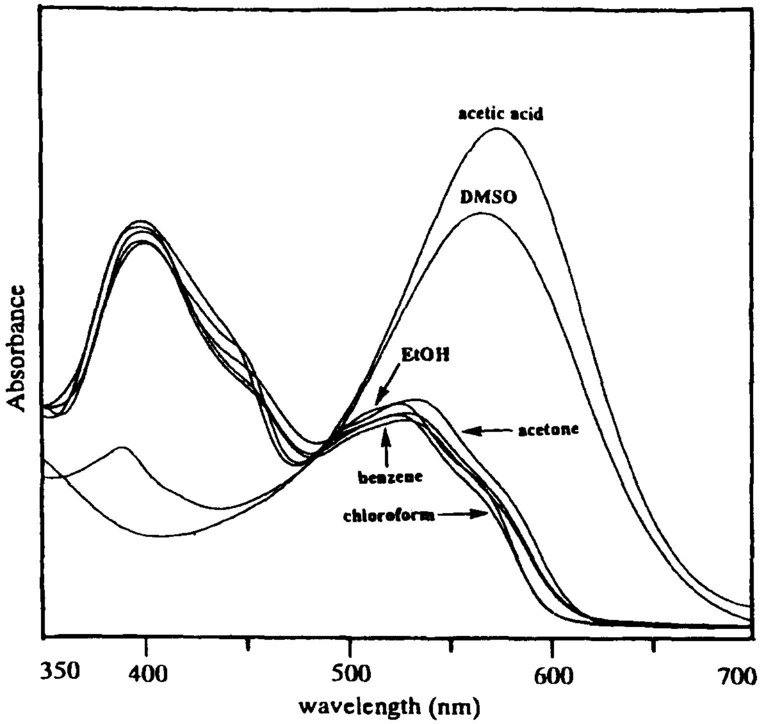


Fig. 3. The effects of solvent polarities on the absorption spectra of dye **6c**.

dye **7** was also very low in spite of prolonged reaction time and higher temperature (Scheme 1).

The ylide moiety of dye **6** greatly influenced their absorption spectra, which were also affected by the polarity of the solvent (Fig. 3). The color of **6** in solution changed dramatically from orange in nonpolar solvents to blue in polar solvents. The anionic delocalized form **C** was predominant in nonpolar solvents, while form **B** was predominant in polar solvents such as DMSO, in which electrostatic interactions stabilized and decreased the electron donating ability of the phosphorane moiety. The PPP-MO calculation revealed that substitution of the carbanion at the 3-position (X) of the parent chromophore **9** produced a hypsochromic shift of 95 nm compared with that of **9** (X = H). Addition of acetic acid to a chloroform solution of dye **6** produced a large bathochromic shift of λ_{max} from 400 to 600 nm, which is explicable by the addition of a proton to the ylide carbanion in the **B** form (Fig. 4). The same absorption spectra changes were also observed when one drop of hydrochloric acid or sulfuric acid was added to the solution of dye **6**.

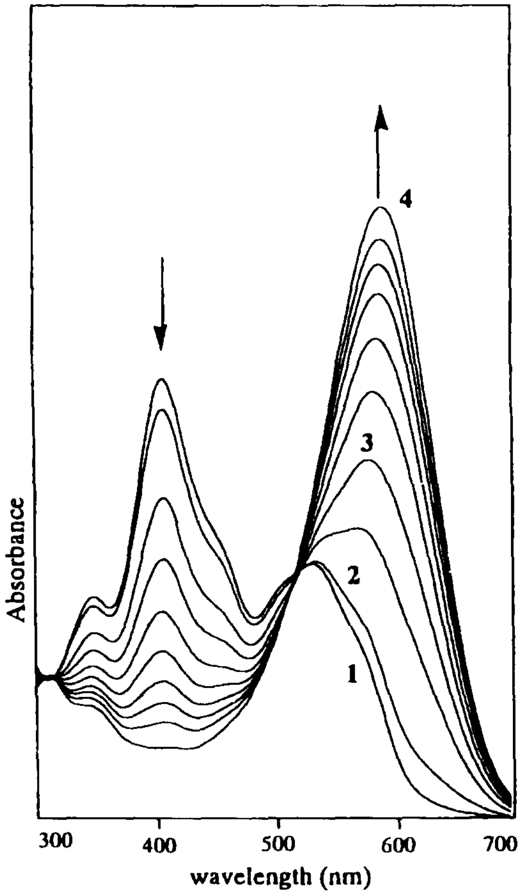


Fig. 4. The effects of acetic acid on the absorption spectra of **6c** in chloroform, AcOH/ **6c**, (mol/mol); **1.** (0/1), **2.** (10/1), **3.** (100/1), **4.** (1000/1).

EXPERIMENTAL

General

Melting points were determined on a Yanagimoto micro melting point apparatus without correction. The PMR spectra were taken on an FT-NMR QE 300 MHz Shimadzu spectrometer. The MS spectra were recorded on an M-80 B Hitachi mass spectrometer. The visible and fluorescence spectra were measured on a U-3410 Hitachi spectrophotometer and Shimadzu RF-5000 fluorescence spectrophotometer, respectively. Microanalysis was conducted with a Yanaco CHN MT-3 recorder. Geometry optimization of dyes was performed using the MOPAC 6.01 program [9] with the PM 3 Hamiltonians. All chemicals were of reagent grade and were used without further purification unless otherwise specified. 2-[2-(4-Dimethylaminophenyl)ethenyl]-5,6-pyrazines **9** were prepared by the established method [5].

Synthesis of compound 3

A solution of bromine (5.3 ml), in carbon disulfide (5 ml), was gradually added to a solution of the diaceyl (50 mmol) in the same solvent (20 ml). After refluxing for 3 h, the solvent was removed partially *in vacuo*. The residue was filtered and washed with petroleum ether. The crude 1,4-dibromo-2,3-butanedione was dissolved in EtOH (10 ml) and added to a solution of DAMN (50 mmol) in EtOH (20 ml). The reaction mixture was refluxed for 4 h and the solvent evaporated under reduced pressure. The residue was extracted with chloroform (200 ml) and concentrated under reduced pressure. The crude product was recrystallized from benzene. Yield 30%; m.p. 86–87°C; *m/z* 314 (M^+), 318 ($M^+ + 4$); ^1H NMR ($CDCl_3$) δ 4.75 (4H, s, $2CH_2Br$).

Anal. calcd. for $C_8H_4N_4Br_2$: C, 30.41; H, 1.28; N, 17.73. Found: C, 30.54; H, 1.35; N, 17.74.

Synthesis of compound 5

A solution of **3** (10 mmol) and triphenyl phosphine (20 mmol) in benzene (25 ml) was refluxed for 17 h and cooled to room temperature. The precipitated phosphonium salt was filtered, washed with benzene and recrystallized from benzene and acetonitrile. Yield 78%; m.p. 206°C (dec.); ^1H NMR (DMSO-d_6) δ 4.01 (4H, s, $2CH_2$), 7.63 (30H, m, $2PPh_3$).

Anal. calcd. for $C_{44}H_{34}N_4P_2Br_2$: C, 62.86; H, 4.05; N, 6.67. Found: C, 62.62; H, 4.17; N, 6.46.

General procedures for the Wittig reaction

A. Synthesis of compound 6

To a stirred suspension of **3** (1 mmol) and the dialkylaminoarylaldehyde (1 mmol) in EtOH (10 ml) under dry nitrogen at room temperature was added EtONa (2.6 mmol) in EtOH. The reaction mixture was refluxed as specified in Table 1 and then cooled to room temperature. The resulting precipitate was filtered, washed with EtOH and dried, to give the crude product of **6**.

*2-[2-(4-Dimethylaminophenyl)ethenyl]-5,6-dicyano-3-triphenylphosphordiylmethylpyrazine (**6a**).* The crude product was recrystallized from benzene to give **6a** as red crystals in 79% yield, m.p. 254–255°C; ^{1}H NMR ($CDCl_3$) δ 3.01 (6H, s, $N(CH_3)_2$), 4.02 (1H, b.s., CH=P), 6.67 (2H, d, *J* 9.0, ArH), 6.88 (1H, d, *J* 15.3, CH=CH–Ar), 7.51 (8H, m, ArH), 7.64 (9H, m, ArH), 7.72 (1H, d, *J* 15.3 Hz, CH=CH–Ar); *m/z* 549 (M^+).

Anal. calcd. for $C_{35}H_{28}N_5P_1$: C, 76.49; H, 5.13; N, 12.74. Found: C, 76.69; H, 5.36; N, 12.57.

*2-[2-(4-Diethylamino-3-hydroxyphenyl)ethenyl]-5,6-dicyano-3-triphenylphosphordiylmethylpyrazine (**6b**).* The crude product was recrystallized from benzene/acetonitrile to give **6b** as red crystals in 75% yield, m.p. 249°C (dec.); ^{1}H NMR (DMSO-d_6) δ 1.11 (6H, t, *J* 7.2, $2CH_3$), 3.23 (4H, q, *J* 7.2, $2CH_2$), 4.46 (1H, d, *J* 20.7, CH=P), 6.17 (1H, s, ArH), 6.24 (1H, d, *J* 11.1, ArH), 7.14 (1H, d, *J* 15.3, CH=CH–Ar), 7.61 (8H, m, ArH), 7.73 (8H, m, ArH), 7.93 (1H, d, *J* 15.3, CH=CH–Ar), 9.88 (1H, b.s, OH); *m/z* 593 (M^+).

Anal. calcd. for $C_{37}H_{32}N_5O_1P_1$: C, 74.85; H, 5.43; N, 11.80. Found: C, 74.64; H, 5.46; N, 11.75.

*2-[2-(4-Julolidinyl)ethenyl]-5,6-dicyano-3-triphenylphosphordiylmethylpyrazine (**6c**).* The crude product was recrystallized from benzene to give **6c** as red crystals in 64% yield, m.p. 233–234°C; ^{1}H NMR ($CDCl_3$) δ 1.96 (4H, t, *J* 6.3, CH_2), 2.75 (4H, t, *J* 6.3, $ArCH_2$), 3.21 (4H, t, *J* 6.3, NCH_2), 3.95 (1H, d, *J* 20.7, CH=P), 6.79 (1H, d, *J* 15.3, CH=CH–Ar), 7.04 (2H, s, ArH), 7.51 (8H, m, ArH), 7.64 (9H, m, ArH and CH=CH–Ar); *m/z* 601 (M^+).

Anal. calcd. for $C_{39}H_{32}N_5P_1$: C, 77.85; H, 5.36; N, 11.64. Found: C, 77.44; H, 5.25; N, 11.67.

B. Syntheses of compounds 7 and 8

To a stirred suspension of **4** (1 mmol) and the arylaldehyde (2 mmol) in EtOH (10 ml) under dry nitrogen at room temperature was added EtONa (2.6 mmol) in EtOH. The reaction mixture was refluxed as specified in Table 1 and then cooled to room temperature. The resultant precipitate was treated in accordance with method A.

2,3-Bis[2-(4-dimethylaminophenyl)ethenyl]-5,6-dicyanopyrazine (7). The crude product was purified by column chromatography on silica gel using benzene as an eluent. Compound **7** was obtained as red crystals (16%), m.p. 239–240°C; ^{1}H NMR ($CDCl_3$) δ 3.07 (12H, s, $N(CH_3)_2$), 6.70 (4H, d, *J* 9.0, ArH), 7.10 (2H, d, *J* 15.3, CH=CH–Ar), 7.54 (4H, d, *J* 9.0, ArH), 7.96 (2H, d, *J* 15.3, CH=CH–Ar); *m/z* 420 (M^+).

Anal. calcd. for $C_{26}H_{24}N_6$: C, 74.26; H, 5.75; N, 19.99. Found: C, 74.18; H, 5.74; N, 20.08.

2,3-Bis[2-phenylethenyl]-5,6-dicyanopyrazine (8a). The crude product was purified by column chromatography on silica gel using benzene as an eluent. Compound **8a** was obtained as yellow crystals (79%), m.p. 258–259°C; ^{1}H NMR ($CDCl_3$) δ 7.39 (2H, d, J 15.3, CH=CH–Ar), 7.46 (5H, m, ArH), 7.67 (5H, m, ArH), 8.08 (2H, d, J 15.3, CH=CH–Ar); m/z 334 (M^+).

Anal. calcd. for $C_{22}H_{14}N_4$: C, 79.04; H, 4.19; N, 16.77. Found: C, 78.53; H, 4.29; N, 16.69.

2,3-Bis[4-phenyl-1,3-butadienyl]-5,6-dicyanopyrazine (8b). The crude product was recrystallized from benzene to give **8b** as orange crystals in 69% yield, m.p. 246–247°C; ^{1}H NMR ($CDCl_3$) δ 6.91 (2H, d, J 14.7, CH=CH), 7.36 (7H, m, ArH), 7.51 (2H, d, J 14.7, CH=CH), 7.67 (5H, m, ArH), 7.86 (1H, d, J 10.2, CH=CH), 7.90 (1H, d, J 10.2, CH=CH); m/z 386 (M^+).

Anal. calcd. for $C_{26}H_{18}N_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.84; H, 4.83; N, 14.34.

2,3-Bis[2-(2-furanyl)ethenyl]-5,6-dicyanopyrazine (8c). The crude product was recrystallized from EtOH to give **8c** as orange crystals in 77% yield, m.p. 254–256°C; ^{1}H NMR ($CDCl_3$) δ 6.55 (2H, q, J 1.8 and 3.6, ArH), 6.74 (2H, d, J 3.6, ArH), 7.28 (2H, d, J 15.0, CH=CH–Ar), 7.58 (2H, d, J 1.8, ArH), 7.83 (2H, d, J 15.0, CH=CH–Ar); m/z 314 (M^+).

Anal. calcd. for $C_{18}H_{10}N_4O_2$: C, 68.79; H, 3.21; N, 17.83. Found: C, 68.54; H, 3.30; N, 17.58.

2,3-Bis[2-(2-pyridinyl)ethenyl]-5,6-dicyanopyrazine (8d). The crude product was recrystallized from EtOH/benzene to give **8d** as brown crystals in 77% yield, m.p. 261–262°C; ^{1}H NMR ($CDCl_3$) δ 7.39 (2H, q, J 1.8 and 4.5, ArH), 7.46 (2H, d, J 15.6, CH=CH–Ar), 7.98 (2H, d, J 7.8, ArH), 8.10 (2H, d, J 15.3, CH=CH–Ar), 8.66 (2H, d, J 3.3, ArH), 8.92 (2H, d, J 2.1, ArH); m/z 336 (M^+).

Anal. calcd. for $C_{20}H_{12}N_6$: C, 71.42; H, 3.60; N, 24.99. Found: C, 71.33; H, 3.65; N, 24.50.

2,3-Bis[2-(3-N-ethylcarbazolyl)ethenyl]-5,6-dicyanopyrazine (8e). The crude product was purified by column chromatography on silica gel using benzene as an eluent. Compound **8e** was obtained as orange crystals (19%), m.p. 287–288°C; ^{1}H NMR (DMSO-d_6) δ 1.31 (6H, t, J 7.2, $2CH_3$), 4.42 (4H, q, J 7.2, $2CH_2$), 7.24 (2H, t, J 7.5, ArH), 7.45 (2H, d, J 15.3, CH=CH–Ar), 7.64 (8H, m, ArH), 7.98 (2H, d, J 7.2, ArH), 8.14 (2H, d, J 15.3, CH=CH–Ar), 8.71 (2H, s, ArH); m/z 568 (M^+).

Anal. calcd. for $C_{38}H_{28}N_6$: C, 80.26; H, 4.96; N, 14.78. Found: C, 79.98; H, 4.95; N, 14.42.

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