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Synthesis and characteristics of dicyanopyrazine dyes containing spiropyran group

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Abstract

2,3-Dicyano-5-(4-ethynyl phenyl)-6-(4-alkoxy phenyl) pyrazines (**10**) were synthesized by the condensation reaction of diaminomaleonitrile(DAMN) with 1-(4-alkoxy phenyl)-2-(4-ethynyl phenyl) ethanediones (**9**). And the coupling reaction of 1,3,3-trimethyl-6′-iodo-spiro [2*H*-benzopyran-2,2′-indoline] (**14**) with **10** gave the novel 2,3-dicyanopyrazine dyes (**15**) containing a spiropyran group. Compounds **15** had emission at 484 nm in chloroform solution as well as photochromic properties under UV irradiation. Their characteristics were evaluated by DSC, UV–visible and fluorescence spectroscopy. The combination of different functional dyes such as 2,3-dicyanopyrazines and spiropyran was successfully synthesized.

Keywords: Dicyanopyrazine; DAMN; Spiropyran; Ethynylation; Fluorescence; Photochromism

1. Introduction

The importance of functional dyes has increased with the rapid progress of information and communication industries in recent years. A large number of functional dye molecules have been known for many years and many researchers have reported on synthetic methods, mechanisms, and specific properties [1–3]. Furthermore, a great deal of interest has been focused on the synthesis and characteristics of multi-functional dyes, because of their applications to various technical fields. The multi-functional dyes could be generally synthesized by link to different functional dyes each other [4–7].

We successfully synthesized multi-functional dye combining spiropyrans and dicyanopyrazines, which could exhibit photochromic and fluorescent properties in one molecule. The spiropyrans are popular classes of photochromic compounds because they exhibit two forms, colorless closed spiro form and colored open merocyanine form. It is easy to control their physical and chemical properties by modifying their molecule structures, so they are used for data storage, electronic devices and optical filters and so on [8–11]. Dicyanopyrazine derivatives are valuable in a broad range of chemistry fields for their application to dyestuff, nonlinear optical materials (NLO) etc. [12–14]. Because dicyanopyrazine derivates have specific properties resulting from the two strong electron withdrawing cyanogroups on the pyrazine ring.

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In this investigation, 2,3-dicyano-5-{4-[2-(1,3,3-trimethyl spiro [2*H*-benzopyran-2,2′-indoline]-6′-yl)ethynyl phenyl]-6-(4-alkoxy phenyl) pyrazine (**15**) were designed and synthesized by the direct coupling reaction of 6-iodospiropyran (**14**) with 2,3-dicyanopyrazine derivatives (**10**) including the terminal acetylene group. We demonstrated their characteristic properties correlated to their own moiety by UV–visible and fluorescent spectroscopy.

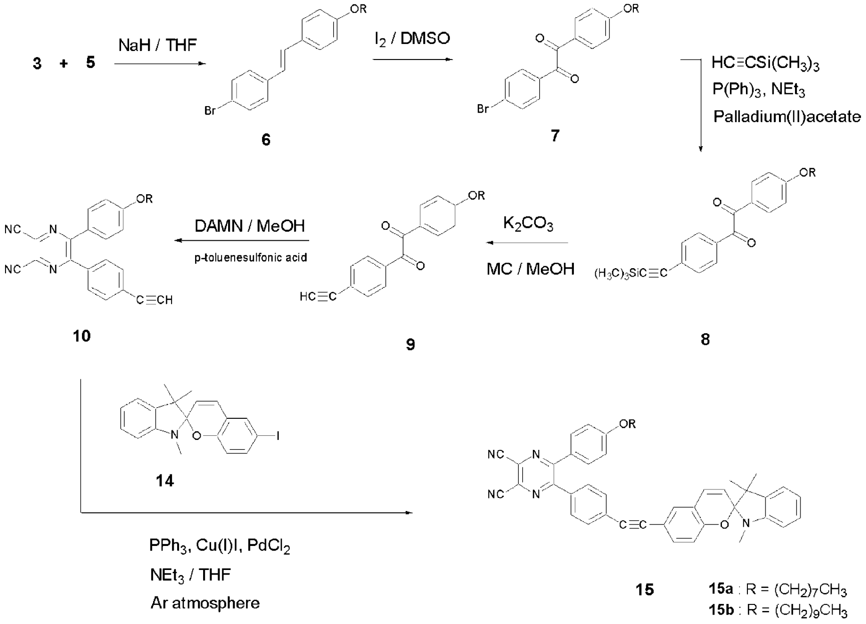
2. Results and discussion

2.1. Reaction of the 2,3-dicyanopyrazines containing spiropyran

Wittig reaction of 4-bromobenzyl-phosphonic acid diethylester (**3**) and 4-alkoxybenzaldehydes (**5**) in tetrahydrofuran using sodium hydride as base under refluxing condition gave 1-(4-alkoxy phenyl)-2-(4-bromophenyl) ethenes (**6**) in good yield. 1-(4-Alkoxy phenyl)-2-(4-bromophenyl)-ethanediones (**7**) were prepared by refluxing **6** in DMSO with 0.5 equiv of iodine in moderate yield. These products were purified by column chromatography. 1-(4-Alkoxy phenyl)-2-(4-trimethylsilyl ethynyl phenyl) ethanediones (**8**) were synthesized by palladium-catalyzed ethynylation in triethylamine in the presence of triphenylphosphine. Treatment of **8** with potassium carbonate using mixture of dichloromethane and methanol under mild condition resulted in a very high conversion to 1-(4-alkoxy phenyl)-2-(4-ethynyl phenyl) ethanediones (**9**) [15]. 2,3-Dicyano-5-(4-ethynyl phenyl)-6-(4-alkoxy phenyl) pyrazines (**10**) were obtained by the condensation reaction of diaminomaleonitrile (DAMN) with compound **9** in the presence of catalytic amount of *p*-toluenesulfonic acid.

1,3,3-Trimethyl-6′-iodo-spiro [2*H*-benzopyran-2,2′-indoline] (**14**) was prepared by literature process [9]. The palladium-catalyzed coupling reaction of **14** with **10** in tetrahydrofuran in the presence of triphenylphosphine, CuI and triethylamine gave 2,3-dicyano-5-{4-[2-(1,3,3-trimethyl spiro [2*H*-benzopyran-2,2′-indoline]-6′-yl) ethynyl phenyl]-6-(4-alkoxy phenyl) pyrazine (**15**) in moderate yield. The reaction routes were summarized in Scheme 1. All products were identified by ^{1}H NMR, MS, FT-IR spectra and microanalyses.

The ^{1}H NMR spectra of **6** indicated that ethylene protons appeared two doublets at 7.07 and 6.91 ppm ($J = 16.2$ Hz). According to coupling



Scheme 1.

constant, compound **6** should exist in *trans*-configuration. Terminal-CH_3 protons of long alkyl chain group appeared as triplet at 0.89 ppm, and O-CH_2 protons split as triplet at 3.97 ppm. In the case of compound **15**, N-CH_3 of spiropyran appeared as singlet at 2.17 ppm and two-CH_3 signals partially overlapped at the range 1.45–1.26 ppm with long alkyl chain group of the 2,3-dicyanopyrazine moiety.

From the FT-IR spectra **6**, we noticed the band of ethylene stretching absorption at 1707 cm^{-1}. These bands disappeared upon **7** and new absorption bands at 1678–1651 cm^{-1} were characteristic of the diketone. In the case of **9** and **10**, terminal acetylene absorption band at 3301 cm^{-1} were observed and disappeared internal acetylene absorption band of compound **8**. Stretching vibrations of cyano groups for all of the **10** and **15** were observed appearing at 2227 cm^{-1}. In the case of **15**, C-O and C-N of the spiropyran group stretching band appeared at 955 and 1258 cm^{-1}, respectively.

2.2. Absorption and fluorescence properties

Fig. 1 shows the fluorescent and UV-visible absorption curves of compound **6, 10** and **15**. Their spectral properties were compared with chemical structures. The absorption maximum of compound **10** was 370 nm, a bathochromic shift of 46 nm from compound **6** was due to the strong electron withdrawing effect of the cyano group in **10**. Compound **15** showed bathochromic shift of 28 nm compared with **10**, which was caused by the expended π-conjugation system. The fluorescent maxima of compound **10** and **15** in chloroform solution were observed at 482 and 484 nm and their Stokes' shifts were 112 and 86 nm, respectively. From these results, it is considered that a substituted spiropyran group does not seriously affect the fluorescent property of compounds **15**.

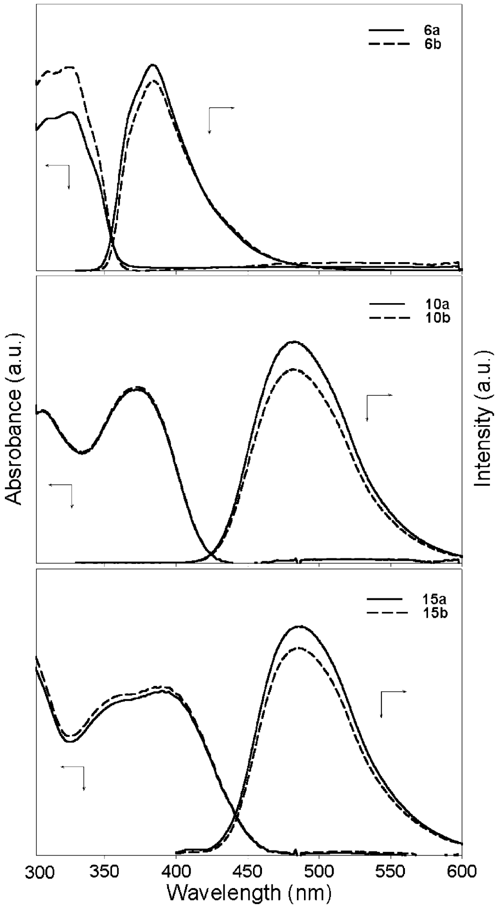


Fig. 1. Absorption and fluorescence spectra of **6**, **10** and **15** in chloroform.

Absorption and fluorescence spectral changes of **15a** in o-dichlorobenzene are shown in Fig. 2. The original yellow solution became orange solution under UV light (254 nm) irradiation for a few minutes at at 273K. The new absorption band at around 500 nm was observed with an isosbestic point at 452 nm due to the ring opening reaction of spiropyran moiety, and the fluorescence intensity excited at 398 nm was increased with UV light irradiation time due to the extension π-conjugation system of the ring opening form of spiropyran moiety. However, the fluorescent spectral change was not observed by the excitation of new absorption band (500 nm). It is expected that the energy of new absorption band is not of sufficient intensity. While the same solution was irradiated at room temperature, absorption spectrum did not change. During visible light (> 400 nm) irradiation, the colored solution returned to original yellow solution within 5 min and a small amount of fading was observed by the photodecomposition.

Fig. 3 shows the effect of concentration of *p*-toluenesulfonic acid on absorption spectra of **15a**

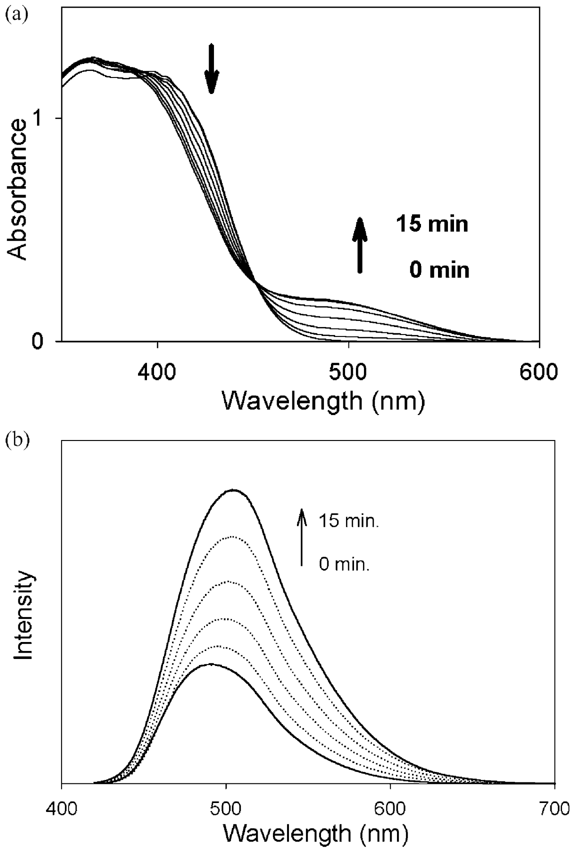


Fig. 2. Spectral change of a 2.5×10^{-4} mol/l of **15a** in *o*-dichlorobenzene during irradiation of UV light (254 nm) at 273 K; (a) absorbance (b) fluorescence excited at 400 nm.

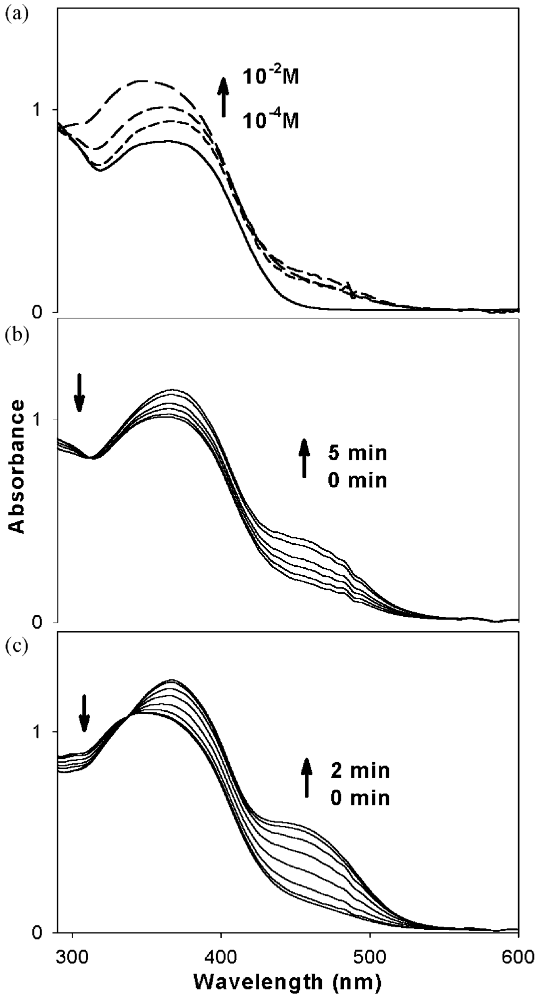


Fig. 3. Absorption spectral change of a 2.5×10^{-4} mol/l of **15a** in methanol/chloroform (1/10) at room temperature: (a) absence and presence of *p*-toluenesulfonic acid (*p*-TSA): 1×10^{-2}, 1×10^{-3}, 1×10^{-4} mol/l; (b) irradiation of UV light (254 nm) in the presence of 1×10^{-3} mol/l of *p*-TSA; (c) irradiation of UV light (254 nm) in the presence of 1×10^{-2} mol/l of *p*-TSA.

at room temperature. As the acidity of solution increased, optical density was increased and conversion time was shortened. It is considered that spiropyran group in the **15a** opened by acid induced ring opening reaction. These intermediates exhibit protonated *cis*-form and can be changed *trans*-form by UV irradiation [16,17]. Consequently, we demonstrated that novel compounds (**15**) accompanied two characteristics of photochromic and fluorescent property.

2.3. Thermal properties

Differential scanning calorimetric analysis (DSC) of **10** shows melting endotherm and a polymerization exotherm at the heating rate of 10 °C/min in nitrogen flow (Fig. 4). A broad exotherm started at ca. 202 °C and the transition energy of **10a** and **10b** was calculated to be 387 and 351 J/g, respectively. The transition is thought to be characteristic of the thermal polymerization of the terminal triple bond. The reactivity of **10b** is lower compared with **10a** due to the long chain alkyl group. The weight losses were observed at 234 and 429 °C, the former was due to the polymerization and the latter was degradation temperature by TGA.

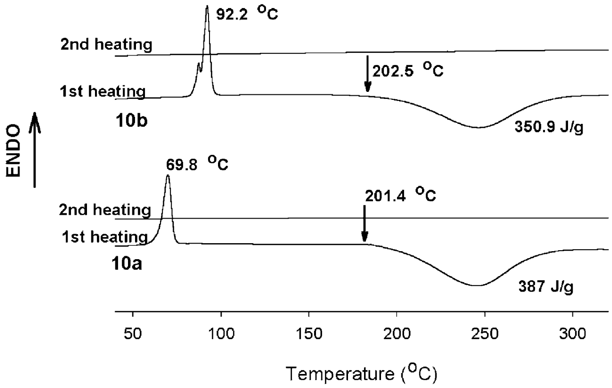


Fig. 4. DSC curves of **10a** and **b**: heating rate, 10 °C/min; under nitrogen flow.

In addition, various acetylene substituted organic compounds are very useful materials for preparing conjugated polymers [18]. These 2,3-dicyanopyrazine substituted internal or terminal acetylene group should be very interesting compounds, and further detailed studies will be reported.

3. Experimental

3.1. General procedure

^{1}H NMR spectra were taken on a Bruker DRX-300 FT-NMR Spectrometer in chloroform-d_6. Infrared spectra were taken on a MAGNA-IR 760 spectrometer using KBr pellets. Melting points were determined on a JISICO melting point apparatus without correction. Mass spectra were obtained using a JEOL JMS-DX303 Mass Spectrometer. Differential scanning calorimetry (DSC) was obtained using a TA Instrument 2100, under nitrogen flow at a heating rate of 10 °C/min. Elemental analyses were performed on a CE instruments EA-1110 Elemental Analyzer. The visible and fluorescence spectra were measured on UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometer, respectively. All chemicals were reagent grade and used without further purification.

3.2. Synthesis of **6**

To a solution of 4-alkoxybenzaldehyde (5) 0.1 mol and 4-bromobenzylphosphonic acid diethylester (3) 30.7 g (0.1 mol) in toluene (30 ml) at 0 °C was added 60% sodium hydride 4.4 g (0.11 mol). The ice bath was removed after 10 min and the reaction mixture was refluxed until all of **5** were disappeared by TLC. After reaction was complete, solvent was removed under reduced press. Methanol was added to the residue and precipitate was filtered off. The crude product was recrystallized from carbon tetrachloride as ivory powder.

3.2.1. 1-(4-Octyloxy phenyl)-2-(4-bromophenyl) ethene (**6a**)

Yield: 82%; m.p.: 158–162 °C; *m/z* 386 (M^+), 388 ($[M+2]^+$); ^{1}H NMR ($CDCl_3$-d_6): 7.46 (d+d, J=8.4 Hz, 4H, phenyl protons), 7.35 (d, J=8.4 Hz, 2H, phenyl protons), 7.07 (d, J=16.2 Hz, 1H, ethene proton), 6.91 (d, J=16.2 Hz, 1H, ethene proton), 6.90 (d, J=9 Hz, 2H, phenyl protons), 3.97 (t, J=6.6 Hz, 2H, O-$\mathbf{CH_2}$$CH_2$), 1.81–1.76 (m, 2H, O-$CH_2$$\mathbf{CH_2}$), 1.46–1.29 (m, 10H, alkyl protons), 0.89 (t, J=6.6 Hz, 3H, –$CH_2$$\mathbf{CH_3}$).

Anal. calcd. for $C_{22}H_{27}BrO$: C, 68.22; H, 7.03. Found: C, 67.98; H, 7.06.

3.2.2. 1-(4-Decyloxy phenyl)-2-(4-bromophenyl) ethene (**6b**)

Yield: 85%; m.p.: 154–157 °C; *m/z*: 414 (M^+), 416 ($[M+2]^+$); ^{1}H NMR ($CDCl_3$-d_6): 7.47 (d+d, J=8.4 Hz, 4H, phenyl protons), 7.37 (d, J=8.4 Hz, 2H, phenyl protons), 7.07 (d, J=16.5 Hz, 1H, ethene proton), 6.91 (d, J=16.2 Hz, 1H, ethene proton), 6.90 (d, J=8.7 Hz, 2H, phenyl protons), 3.97 (t, J=6.6 Hz, 2H, O-$\mathbf{CH_2}$$CH_2$), 1.82–1.76 (m, 2H, O-CH$_2$**CH$_2$**), 1.43–1.28 (m, 14H, alkyl protons), 0.91 (t, $J=6.9$ Hz, 3H,-CH$_2$**CH$_3$**).

Anal. calcd. for $C_{24}H_{31}BrO$: C, 69.39; H, 7.52. Found: C, 69.14; H, 7.61.

3.3. Synthesis of 7

A Dean–Stark trap was fitted with a reflux condenser, a solution of **6** (50 mmol) and iodine 6.4 g (25 mmol) in dimethylsulfoxide (20 ml) was heated at reflux for 5 h. After reaction was complete, the resulting mixture was cooled at room temperature and then methanol was added to the residue and precipitate was filtered off. The crude product was purified by column chromatograph in silica gel, eluting with hexane–ethylacetate (5:1).

3.3.1. 1-(4-Octyloxy phenyl)-2-(4-bromophenyl)-ethanediones (7*a*)

Yield: 45%; m.p.: 64–65 °C; *m*/*z*: 417 (M^+), 419 ($[M+2]^+$); ^{1}H NMR(CDCl$_3$-d_6): 7.93(d, $J=8.7$ Hz, 2H), 7.86 (d, $J=8.7$ Hz, 2H), 7.67 (d, $J=9$ Hz, 2H), 6.98 (d, $J=9$ Hz, 2H), 4.06 (t, $J=6.6$ Hz, 2H), 1.85–1.76 (m, 2H), 1.46–1.25 (m, 10H), 0.91 (t, $J=6.6$ Hz, 3H).

Anal. calcd. for $C_{22}H_{25}BrO_3$: C, 63.31; H, 6.04. Found: C, 62.97; H, 6.00.

3.3.2. 1-(4-Decyloxy phenyl)-2-(4-bromophenyl)-ethanediones (7*b*)

Yield: 47%; m.p.: 63–64 °C; *m*/*z*: 445 (M^+), 447 ($[M+2]^+$); ^{1}H NMR(CDCl$_3$-d_6): 7.93 (d, $J=8.7$ Hz, 2H), 7.86 (d, $J=8.7$ Hz, 2H), 7.67 (d, $J=8.7$ Hz, 2H), 6.98 (d, $J=8.7$ Hz, 2H), 4.06 (t, $J=6.3$ Hz, 2H), 1.85–1.76 (m, 2H), 1.46-1.25 (m, 14H), 0.91 (t, $J=6.3$ Hz, 3H).

Anal. calcd. for $C_{24}H_{29}BrO_3$: C, 64.72; H, 6.56. Found: C, 64.44; H, 6.54.

3.4. Synthesis of 8

7 (20 mmol), 1.5 equiv. of (trimethylsilyl)acetylene 2.95 g (30 mmol), 1.2 mol% palladium(II) acetate, 2 mol% triphenylphosphine in triethylamine (10 ml) were placed under an argon atmosphere in a sealed flask and heated at 65–70 °C for 4 hr. The reaction mixture was cooled and poured into dilute hydrochloric acid solution. The brown organic layer was extracted with methylene chloride. The methylene chloride solution was washed with dilute hydrochloric acid aqueous solution and water (×3), dried over MgSO$_4$. Methanol was added and precipitate was filtered off.

3.4.1. 1-(4-Octyloxy phenyl)-2-(4-trimethylsilyl ethynyl phenyl) ethanediones (8*a*)

Yield: 89%; m.p.: 53–55 °C; *m*/*z*: 434 (M^+); ^{1}H NMR(CDCl$_3$-d_6): 7.94–7.89 (d+d, $J=8.7$ Hz, 4H), 7.57 (d, $J=8.7$ Hz, 2H), 6.97 (d, $J=9.3$ Hz, 2H), 4.06 (t, $J=6.3$ Hz, 2H), 1.83–1.78 (m, 2H), 1.45–1.29 (m, 10H), 0.91 (t, $J=6.3$ Hz, 3H), 0.26 (s, 9H,-Si**(CH$_3$)$_3$**).

Anal. calcd. for $C_{27}H_{34}O_3Si$: C, 74.61; H, 7.88. Found: C, 74.26; H, 7.90.

3.4.2. 1-(4-Decyloxy phenyl)-2-(4-trimethylsilyl ethynyl phenyl) ethanediones (8*b*)

Yield: 92%; m.p.: 46–47 °C; *m*/*z*: 462 (M^+); ^{1}H NMR(CDCl$_3$-d_6): 7.94–7.89 (d+d, $J=8.7$ Hz, 4H), 7.57 (d, $J=8.4$ Hz, 2H), 6.97 (d, $J=9$ Hz, 2H), 4.06 (t, $J=6.6$ Hz, 2H), 1.83–1.78 (m, 2H), 1.45–1.27 (m, 14H), 0.90 (t, $J=6.6$ Hz, 3H), 0.26 (s, 9H,-Si**(CH$_3$)$_3$**).

Anal. calcd. for $C_{29}H_{38}O_3Si$: C, 75.23; H, 8.28. Found: C, 74.93; H, 8.29.

3.5. Synthesis of 9

To a solution of **8** (15 mmol) in a mixture of O$_2$-free methanol (10 ml) and methylene chloride (20 ml) was added potassium carbonate 0.8 g (5 mmol) under an argon atmosphere. The reaction mixture was stirred for 1 h below 40 °C. The reaction mixture was cooled and poured into dilute hydrochloric acid solution. The brown organic layer was extracted with methylene chloride. The solution was washed with dilute hydrochloric acid aqueous solution and water (×3), dried over MgSO$_4$. Methanol was added and precipitate was filtered off.

3.5.1. 1-(4-Octyloxy phenyl)-2-(4-ethynyl phenyl) ethanediones (9*a*)

Yield: 98%; m.p.: 55–57 °C; *m*/*z*: 362 (M^+); ^{1}H NMR (CDCl$_3$-d_6): 7.95–7.91 (d+d, $J=8.7$ Hz, 4H), 7.61 (d, $J=8.7$ Hz, 2H), 6.98 (d, $J=8.7$ Hz, 2H), 4.06 (t, $J = 6.3$ Hz, 2H), 3.30 (s, 1H, C≡**CH**), 1.83–1.78 (m, 2H), 1.46–1.29 (m, 10H), 0.91 (t, $J = 6.3$, 3H).

Anal. calcd. for $C_{24}H_{26}O_3$: C, 79.53; H, 7.23. Found: C, 79.24; H, 7.21.

*3.5.2. 1-(4-Decyloxy phenyl)-2-(4-ethynyl phenyl) ethanediones (**9b**)*

Yield: 97%; m.p.: 49–50 °C; *m/z*: 390 (M^+); ^1H NMR ($CDCl_3$-d_6): 7.95–7.89 (d + d, $J = 8.7$ Hz, 4H), 7.61 (d, $J = 8.7$ Hz, 2H), 6.98 (d, $J = 9.3$ Hz, 2H), 4.06 (t, $J = 6.6$ Hz, 2H), 3.30 (s, 1H, C≡**CH**), 1.83–1.78 (m, 2H), 1.45–1.27 (m, 14H), 0.90 (t, $J = 6.3$ Hz, 3H).

Anal. calcd. for $C_{26}H_{30}O_3$: C, 79.97; H, 7.74. Found: C, 79.42; H, 7.79.

*3.6. Synthesis of **10***

A solution of **9** (10 mmol), diaminomaleonitrile 1.3 g (12 mmol) and a catalystic amount of *p*-toluenesulfonic acid in methanol (10 ml) was refluxed for 4 h. After reaction was complete, the mixture was cooled. The precipitate was filtered off and washed with methanol. The crude product was recrystallized from *n*-hexane as yellow powder.

*3.6.1. 2,3-Dicyano-5-(4-ethynyl phenyl)-6-(4-octyloxy phenyl) pyrazines (**10a**)*

Yield: 77%; m.p.: 61–64 °C; *m/z*: 434 (M^+); ^1H NMR ($CDCl_3$-d_6): 7.57–7.48 (d + d + d, $J = 8.7$ Hz, 6H), 6.87 (d, $J = 8.7$ Hz, 2H), 4.01 (t, $J = 6.6$ Hz, 2H), 3.23 (s, 1H), 1.82–1.77 (m, 2H), 1.45–1.29 (m, 10H), 0.91 (t, $J = 6.3$ Hz, 3H).

Anal. calcd. for $C_{28}H_{26}N_4O$: C, 77.39; H, 6.03; N 12.89. Found: C, 77.78; H, 6.02; N 12.56.

*3.6.2. 2,3-Dicyano-5-(4-ethynyl phenyl)-6-(4-decyloxy phenyl) pyrazines (**10b**)*

Yield: 81%; m.p.: 89–93 °C; *m/z*: 462 (M^+); ^1H NMR($CDCl_3$-d_6): 7.57–7.48 (d + d + d, $J = 8.7$ Hz, 6H), 6.87 (d, $J = 8.7$ Hz, 2H), 4.01 (t, $J = 6.6$ Hz, 2H), 3.23 (s, 1H), 1.82–1.76 (m, 2H), 1.45–1.29 (m, 14H), 0.90 (t, $J = 6.3$ Hz, 3H).

Anal. calcd. for $C_{30}H_{30}N_4O$: C, 77.89; H, 6.54; N 12.11. Found: C, 77.45; H, 6.57; N 11.89.

*3.7. Synthesis of **15***

A mixture of **14** (5 mmol), $PdCl_2$ (5 mol%), $P(Ph)_3$ (10 mol%), CuI (2.5 mol%), and triethylamine (15 mmol) in THF (10 mL) was refluxed. To the refluxing solution was added a **10** (5 mmol) over 10 min. After the solution was refluxed for 2 hr, the precipitate was filtered off. The crude product was purified by column chromatograph in silica gel, eluting with hexane–ethylacetate (5:1).

*3.7.1. 2,3-Dicyano-5-{4-[2-(1,3,3-trimethyl spiro [2H-benzopyran-2,2′-indoline]-6′-yl)ethynyl phenyl]}-6-(4-octyloxy phenyl) pyrazine (**15a**)*

Yield: 50%; m.p.: 77–83 °C; *m/z*: 709 (M^+); ^1H NMR ($CDCl_3$-d_6): 7.58–7.47 (d + d + d, 6H), 7.29–7.25 (d + s, 2H), 7.21 (t, $J = 7.8$ Hz, 1H), 7.09 (d, $J = 7.2$ Hz, 1H), 6.88–6.83 (d + d + t, 4H), 6.71 (d, $J = 8.1$ Hz, 1H), 6.55 (d, $J = 7.8$ Hz, 1H), 5.77 (d, $J = 10.2$ Hz, 1H), 4.01 (t, $J = 6.3$ Hz, 2H), 2.17 (s, 3H, N-$\mathbf{CH_3}$), 1.82–1.77 (m, 2H), 1.45–1.26 (m + s, 13H, alkyl protons + –$\mathbf{CH_3}$), 1.31 (s, 3H, –$\mathbf{CH_3}$), 0.89 (t, $J = 7.2$ Hz, 3H).

Anal. calcd. for $C_{47}H_{43}N_5O_2$: C, 79.52; H, 6.11; N 9.87. Found: C, 79.04; H, 6.09; N 9.76.

*3.7.2. 2,3-Dicyano-5-{4-[2-(1,3,3-trimethyl spiro [2H-benzopyran-2,2′-indoline]-6′-yl)ethynyl phenyl]}-6-(4-decyloxy phenyl) pyrazine (**15b**)*

Yield: 45%; m.p.: 108–119 °C; *m/z*: 737 (M^+); ^1H NMR ($CDCl_3$-d_6): 7.58–7.47 (d + d + d, 6H), 7.28–7.25 (d + s, 2H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 6.9$ Hz, 1H), 6.88–6.83 (d + d + t, 4H), 6.72 (d, $J = 8.4$ Hz, 1H), 6.56 (d, $J = 7.5$ Hz, 1H), 5.77 (d, $J = 10.2$ Hz, 1H), 4.01 (t, $J = 6.3$ Hz, 2H), 2.17 (s, 3H, N-$\mathbf{CH_3}$), 1.82–1.77 (m, 2H), 1.45–1.26 (m + s, 17H, alkyl protons + –$\mathbf{CH_3}$), 1.31 (s, 3H, –$\mathbf{CH_3}$), 0.89 (t, $J = 7.2$ Hz, 3H).

Anal. calcd. for $C_{49}H_{47}N_5O_2$: C, 79.75; H, 6.42; N 9.49. Found: C, 79.97; H, 6.45; N 9.14.

Acknowledgements

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