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# Synthesis of new porphyrins with dicyanopyrazine moiety and their optical properties

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**Abstract**

5,10,15,20-Tetra[5-{2-(4-alkoxyphenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyano-pyrazino]-porphyrin (**5**) was prepared by the condensation reaction of pyrrole and a bis-styryl derivative (**4**) containing 2,3-dicyanopyrazine. The existence of a strong intramolecular charge-transfer chromophoric system was confirmed for dyes **5**, and its large Stokes shift of over 200 nm resulted in the emission of red fluorescence. The chromophoric systems of these dyes were studied from the viewpoint of the protonation and deprotonation effects on their absorption and fluorescence spectra in solution.


*Keywords:* 2,3-Dicyanopyrazine; *meso*-Porphyrin; Absorption spectra; Q band

## 1. Introduction

The basic structure of porphyrin consists of four pyrrole units linked by four methine bridges. This indicates that the 16-atom cyclic structure is the preferred cyclic system for π-electron delocalization since this pathway exhibits the highest degree of bond equalization. Fig. 1(a) shows the 16-center system, which is the chromogen of the porphyrins and which allows the 18π-electron delocalization that causes this molecule to have aromatic characteristics [1]. Porphyrins and related tetrapyrrolic pigments occur widely in nature, and play very important roles in various biological processes. Fig. 1(b) and (c) shows the structures of the two most important porphyrins. 'Heme' is the prosthetic group in hemoglobins and myoglobins, which is responsible for oxygen transport and storage in living tissues, respectively. 'Heme' can also be found in the enzyme peroxidase, which catalyzes the oxidation of substrates by hydrogen peroxide. Certain heme-containing proteins serve as one-electron carriers in the electron transport chain. The reduction of one of the pyrrole units on the porphyrin ring leads to the formation of a class of porphyrin derivatives called 'Chlorins' which is found abundantly in green plants [2].

A large number of porphyrin derivatives have been synthesized for the purpose of molecular recognition [3–5]. There are two general approaches to obtain the desired porphyrin, viz. modification of natural porphyrins and total synthesis. Although convenient, the modification of naturally occurring porphyrins places severe limitations on the choice of the peripheral substituents, because some of them cannot be easily modified. In most cases, such limitations can be overcome by the use of total synthesis, which involves the synthesis of the pyrrole having the required substituents. As mentioned above, the size and symmetry of monomeric structures can be relatively easily controlled [6,7].

Among the great diversity of porphyrins with a specific pattern of substituents, *meso*-substituted porphyrins have recently been the subject of a great deal of attention. The most popular method of synthesizing *meso*-substituted porphyrins is by the reaction of dipyrrolmethanes with aldehydes [8]. These compounds have proven their usefulness in many fields, such as energy transfer (solar cells), biomedical applications, chemical sensors, and photodynamic therapy [9–13].

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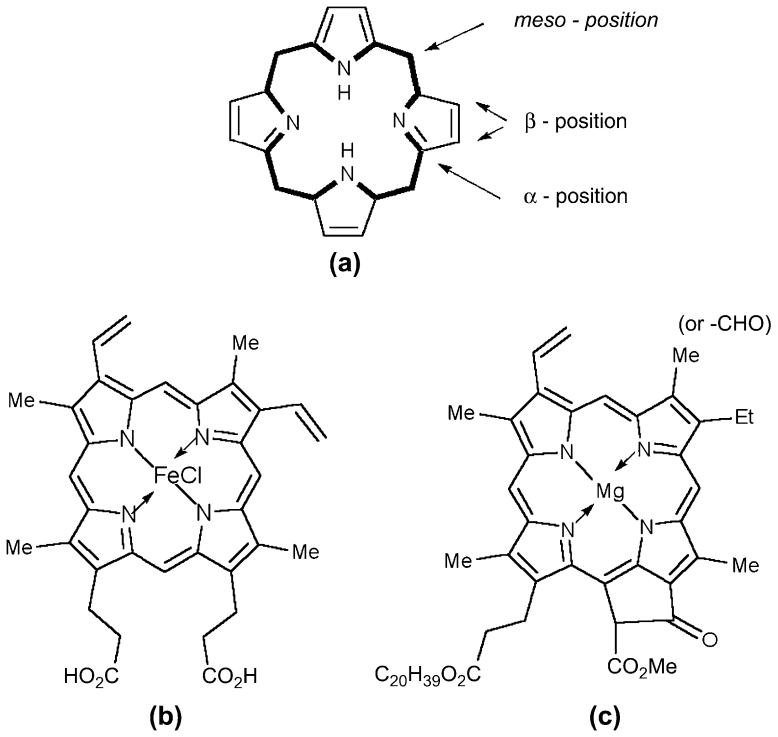



Fig. 1. Chemical structures of natural porphyrins.

Recently, the combination of porphyrins with another large organic molecule has become an interesting route to new materials [14]. In this study, pyrazine-linked porphyrins were synthesized and their characteristics were investigated. The chromophoric systems of these dyes were studied from the viewpoint of the protonation and deprotonation effects on their absorption and fluorescence spectra in solution.

## 2. Results and discussion

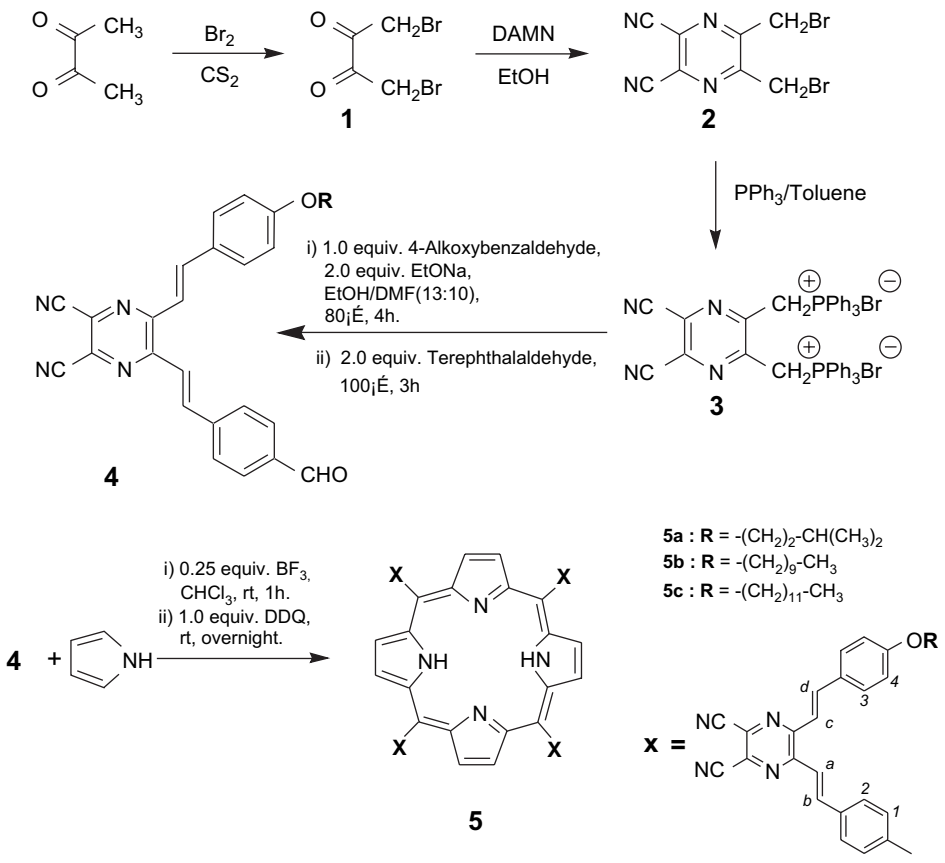
### *2.1. Synthesis of 2,3-dicyanopyrazine derivatives and meso-[5-{2-(4-dodecyloxy phenyl)-ethenyl}-6-{2-(4-phenyl)-ethenyl}-2,3-dicyanopyrazino]dipyrrolmethanes*

The treatment of 1,4-dibromobutane-2,3-dione (**1**) and diaminomaleonitrile (DAMN) in the presence of a catalytic amount of *p*-toluenesulfonic acid in ethanol under reflux conditions afforded 2,3-bis(bromomethyl)-5,6-dicyanopyrazine (**2**). The reaction of compound **2** with two equivalents of triphenylphosphine in toluene afforded 2,3-bis(triphenylphosphonium methyl)-5,6-dicyanopyrazine dibromide (**3**) with a good yield of 78% [15]. 4-Alkoxybenzaldehyde was synthesized by the reaction of 4-hydroxybenzaldehyde with various alkylbromides in the presence of excess potassium carbonate in acetone to afford high yields of more than 90%. The linear long alkyl ether moiety was chosen to improve the solubility of the resulting styryl and porphyrin fluorescent dyes in common organic solvents.

The reaction of compound **3** with one equivalent of 4-alkoxybenzaldehyde in the presence of two equivalents of sodium ethoxide gave the mono-styryl intermediate. This crude product was used in the next step without purification. An excess of terephthalaldehyde was added to the reaction mixture to give the 2,3-dicynopyrazine styryl dyes (**4**). The $^1$H NMR spectrum of compound **4** indicated that the ethylene protons appeared as doublets at 7.43 ppm ($J = 15.6$ Hz) and 7.82 ppm ($J = 15.3$ Hz). According to the coupling constant, compound **4** should exist in the *trans*-configuration.

Rothemund synthesized *meso*-tetraphenylporphyrin by condensation between pyrrole and benzaldehyde. Since this report, *meso*-substituted porphyrin derivatives have been synthesized using arylaldehydes. The compound 5,10,15,20-tetra[5-{2-(4-alkoxyphenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyanopyrazino]-porphyrin (**5**) was prepared by the condensation reaction of pyrrole and the bis-styryl derivative of **4** containing the dicyanopyrazine moiety in the presence of boron trifluoride ($BF_3$) in chloroform to afford a moderate yield of 15–27%. The reaction pathways are summarized in Scheme 1.

The synthesized porphyrins were characterized by UV–visible spectroscopy, MALDI-TOF-MS (matrix-assisted laser desorption ionization time-of-flight mass spectroscopy) and $^1$H NMR spectroscopy. The MALDI-TOF-MS spectra of the porphyrins confirmed their high purity (Fig. 2). Fig. 3 shows the spectrum of **5b** in $CDCl_3$ at 25 °C, which provides structural information. In the aliphatic region, a sharp triplet resonance corresponding to the *O*-methylene protons (O–$CH_2$) is observed. The proton resonances in the aromatic region of **5b** are distinguishable and assignable, as shown in Fig. 3. The proton resonance of the phenyl units near the porphyrin core is shifted downfield compared with that of the exterior phenyl units. Due to the anisotropic effect resulting from the porphyrin ring current, the NMR signals for the deshielded β-protons




Scheme 1.

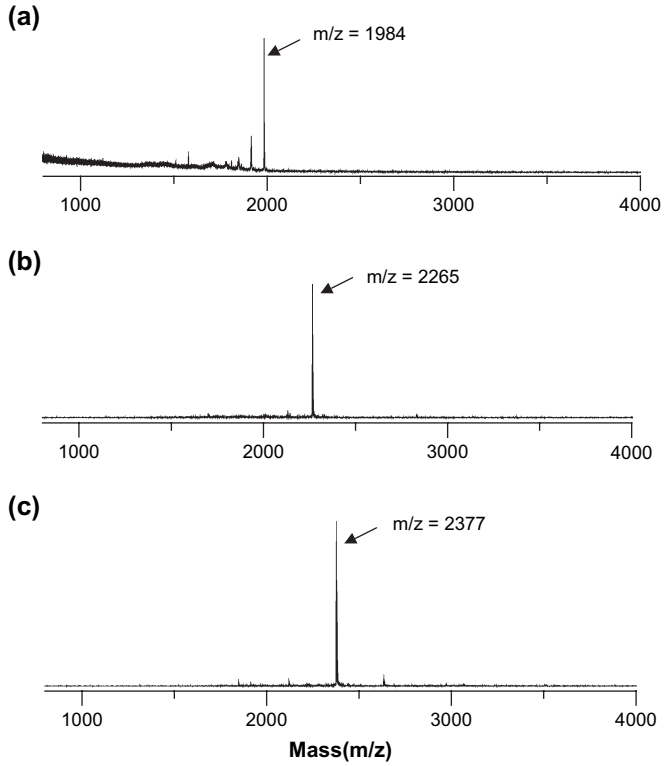



Fig. 2. MALDI-TOF mass spectra of (a) **5a**, (b) **5b** and (c) **5c**.

show up at low field (8–9 ppm), whereas the signals for the shielded protons on the inner nitrogen atoms show up at high field (−2.86 ppm).

### 2.2. Optical properties (absorption and emission spectra)

Strong intramolecular charge-transfer chromophoric systems are observed for dyes **4** and **5**. Their visible and fluorescent spectra are summarized in Table 1. Two absorption peaks of **4** were observed at 340 and 412 nm in chloroform. The absorption band at around 412 nm was attributed to the $\pi-\pi^*$ transition due to the strongly electron withdrawing cyano group. The fluorescence maximum was observed at 532 nm excited at 412 nm. The Stokes shift value was about 120 nm, which indicated the energy loss in the excited state. This may be observed when a molecule in the first excited state adopts a more coplanar configuration than in the ground state.

Porphyrins generally display absorption spectra with Q (visible range) and B (near UV range) bands which are comparable in terms of their relative intensity and wavelength [16]. In the UV–visible absorption spectrum, the highly conjugated porphyrin macrocycles show intense absorption at around 450 nm (the Soret band), followed by several weaker absorptions (Q bands) at higher wavelengths (690 nm). All porphyrins exhibit strong fluorescence at around 536 nm. These results are interesting with regard to the practical

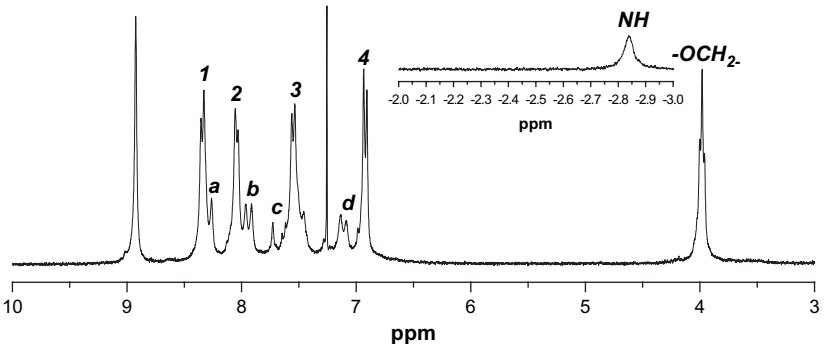



Fig. 3. $^1$H NMR spectrum of porphyrin **5b** in $CDCl_3$.

applications of these porphyrins. These fluorescent compounds have good thermal and chemical stability as compared to monomeric organic materials.

The porphyrin ring can act both as an acid and a base. Strong bases can remove the two protons on the inner nitrogen atoms of a porphyrin to form a dianion. On the other hand, the two free pyrrolic nitrogen atoms can easily be protonated by acids.

When a trace amount of acid was added to the free base porphyrin solutions, protonation of the inner nitrogen in the porphyrin rings was observed in all cases. The typical change in the absorption spectrum of porphyrin as the concentration of acid is increased is shown in Fig. 4. As the amount of *p*-toluenesulfonic acid (*p*-TSA) in the porphyrin **5c** solution was increased, the characteristic Soret bands at 444 nm were shifted to 480 nm, while the Q band at 694 nm moved to 688 nm. The simultaneous isosbestic points indicated the presence of an acid–base equilibrium process. The addition of sodium ethoxide can cause the porphyrin **5c** to undergo a deprotonation reaction (Fig. 5). This deprotonation reaction leads to a decrease in the intensity of the Q band at around 690 nm and an increase in the intensity of the Soret band at around 440 nm.

The acid–base dependence of the emission spectra of **5** in $CHCl_3$/MeOH (10/1) solution is shown in Fig. 6. In contrast to the strong fluorescence of dyes **5** in $CHCl_3$/MeOH (10/1) solution, the gradual addition of sodium ethoxide to a $CHCl_3$/MeOH (10/1) solution of **5** leads to a continuous decrease in the intensity of the fluorescence maximum (658 nm). However, a new fluorescence maximum at 713 nm was observed when acid (*p*-TSA) was added to a $CHCl_3$/MeOH (10/1) solution of **5**. The Stokes shift (SS) values for **5** in $CHCl_3$ are about 200 nm. The big difference in the SS values of **4** and **5** indicates that **5** loses more energy in the excited state (bigger SS value) than that of **4**.

The effects of pH on the porphyrin spectral changes can generally be explained by partial charge transfer from the nitrogen atom to the porphyrin π-electron system under the formation of a stabilized cation, which can be represented in different resonance structures. It is well known that porphyrins are likely to exist in solution as nonequivalent tautomers (as indicated by the 22π-electron delocalization pathways highlighted in bold for the structures) [17].

In summary, pyrazine-linked porphyrins were synthesized and their characteristics were investigated. These compounds showed specific spectral properties, owing to the extension of the π-conjugate system and protonation/deprotonation.

Table 1
Visible and fluorescence spectra of **4** and **5**

| Compound | R | M.p. (°C) | $\lambda_{max}$ [a] (nm) | $F_{max}$ [b] (nm) | SS[c] |
|---|---|---|---|---|---|
| **4a** | $-(CH_2)_2CH(CH_3)_2$ | 120–121 | 412 | 532 | 120 |
| **4b** | $-(CH_2)_9CH_3$ | 110–112 | 413 | 532 | 119 |
| **4c** | $-(CH_2)_{11}CH_3$ | 85–87 | 413 | 532 | 119 |
| **5a** | $-(CH_2)_2CH(CH_3)_2$ | >300 | 444, 694 | 658 | 214 |
| **5b** | $-(CH_2)_9CH_3$ | >300 | 444, 694 | 658 | 214 |
| **5c** | $-(CH_2)_{11}CH_3$ | >300 | 444, 694 | 658 | 214 |

[a] In $CHCl_3$.
[b] Fluorescence maximum excited at $\lambda_{max}$ values.
[c] Stokes shift ($F_{max} - \lambda_{max}$).

## 3. Experimental

### 3.1. General

All reactions were carried out under $N_2$ atmosphere unless otherwise noted. 2,3-Bis(triphenylphosphonium methyl)-5, 6-dicyanopyrazine dibromide and alkoxybenzaldehyde [15]

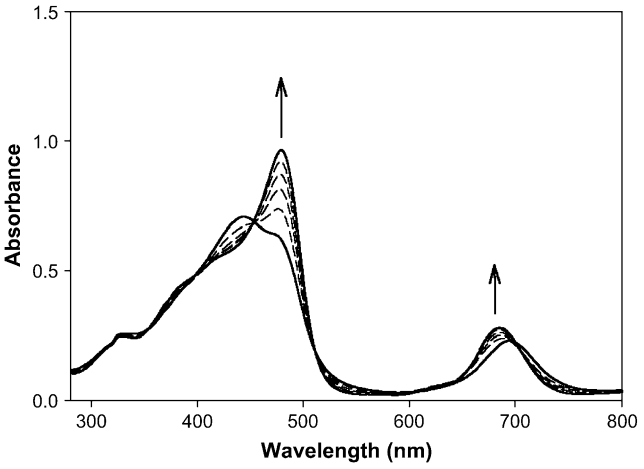



Fig. 4. Spectral change of **5c** ($2 \times 10^{-6}$ M) in chloroform/methanol (10/1) as the concentration of *p*-toluenesulfonic acid is increased.

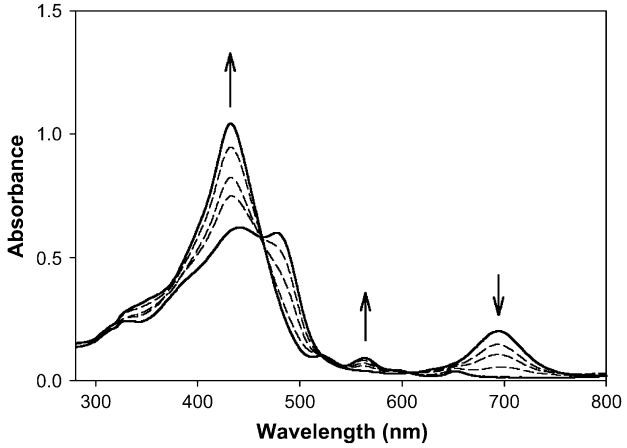



Fig. 5. Spectral change of **5c** ($2 \times 10^{-6}$ M) in chloroform/methanol (10/1) as the concentration of sodium ethoxide is increased.

were prepared by the known methods. Flash chromatography was performed with Merck-EM Type 60 (230–400 mesh) silica gel (flash). Melting points were obtained with a capillary melting point apparatus and are uncorrected. $^1$H NMR spectra were recorded on a Bruker DRX-300 FT-NMR Spectrometer using TMS as internal standard. Elemental analyses were performed on a CE, EA 1110. The visible and fluorescence spectra were measured on UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometers, respectively. MALDI-TOF-MS (matrix-assisted laser desorption ionization time-of-flight mass) spectra were obtained on a PerSeptive Biosystems Voyager-DE-Pro spectrometer with dithranol as matrix. Melting points were uncorrected.

### *3.2. Typical procedure for 2,3-dicyanopyrazine styryl dyes (**4**)*

To a suspension of 8.4 g (10 mmol) of 2,3-bis(triphenylphosphonium methyl)-5,6-dicyanopyrazine dibromide and 5 mmol of alkoxybenzaldehyde, which was prepared by the Williamson reaction of benzaldehyde with corresponding alkylbromide, in ethanol (30 ml) at room temperature was added 1.8 g (25 mmol) of sodium ethoxide (96%). The reaction mixture was refluxed for 4 h. After the reaction was complete, the reaction mixture was cooled. Terephthalaldehyde (5 mmol) was added, and then the reaction mixture was heated for reflux condition. The reaction mixture was cooled to room temperature. The precipitate was filtered. The crude product was purified by column chromatography.

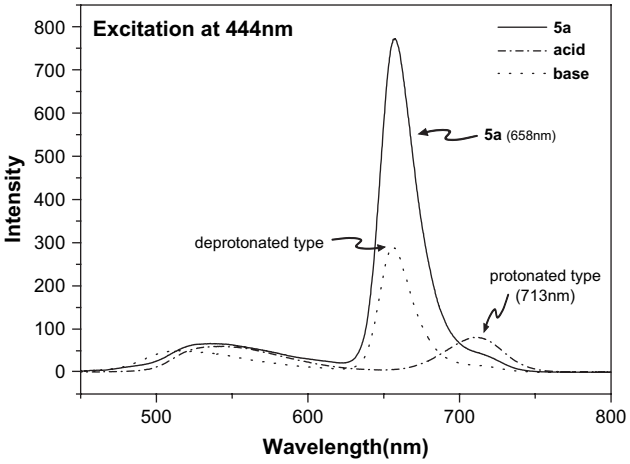



Fig. 6. The acid–base dependence of the emission spectra of **5a** in chloroform/methanol (10/1).

### *3.3. 5-{2-(4-Amyloxyphenyl)-ethenyl}-6-{2-(4-formylphenyl)-ethenyl}-2,3-dicyano-pyrazine (**4a**)*

The crude product was purified by flash chromatography (silica gel, EtOAc:hexane = 1:3) to give **4a** in 75% yield as a yellow solid. M.p. 120–121 °C; $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 10.07 (s, 1H, aldehyde), 8.14 (d, 2H, $J = 15.3$ Hz, vinyl), 7.99 (d, 2H, $J = 8.1$ Hz, phenyl), 7.85 (d, 2H, $J = 8.4$ Hz, phenyl), 7.66 (d, 2H, $J = 8.7$ Hz, phenyl), 7.56 (d, 1H, $J = 15.6$ Hz, vinyl), 7.29 (d, 1H, $J = 15.6$ Hz, vinyl), 6.99 (d, 2H, $J = 8.7$ Hz, phenyl), 4.03 (t, 2H, $J = 6.0$ Hz, Ar-O–$CH_2$), 1.87–1.81 (m, 1H, $>CH-(CH_3)_2$), 1.77–1.66 (m, 2H, methylene), 0.99 (d, 6H, $>CH-(CH_3)_2$).

Anal. Calcd. for $C_{28}H_{24}N_4O_2$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.58; H, 5.1; N, 12.27.

### *3.4. 5-{2-(4-Decyloxyphenyl)-ethenyl}-6-{2-(4-formylphenyl)-ethenyl}-2,3-dicyano-pyrazine (**4b**)*

The crude product was purified by flash chromatography (silica gel, EtOAc:hexane = 1:5) to give **4b** in 78% yield as a yellow solid. M.p. 110–112 °C; $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 10.07 (s, 1H, aldehyde), 8.09 (d, 2H, $J = 15.3$ Hz, vinyl), 7.99 (d, 2H, $J = 8.1$ Hz, phenyl), 7.85 (d, 2H, $J = 8.4$ Hz, phenyl), 7.66 (d, 2H, $J = 8.7$ Hz, phenyl), 7.56 (d, 1H, $J = 15.6$ Hz, vinyl), 7.29 (d, 1H, $J = 15.6$ Hz, vinyl), 6.99 (d, 2H, $J = 8.7$ Hz, phenyl), 4.03 (t, 2H, $J = 6.0$ Hz, Ar-O–$CH_2$), 1.84–1.77 (m, 2H, Ar-O–$CH_2CH_2$–), 1.57–1.27 (m, 14H, methylene), 0.9–0.86 (t, 3H, $CH_3$).

Anal. Calcd. for $C_{33}H_{34}N_4O_2$: C, 76.42; H, 6.61; N, 10.80. Found: C, 76.21; H, 6.54; N, 10.29.

### *3.5. 5-{2-(4-Dodecyloxyphenyl)-ethenyl}-6-{2-(4-formylphenyl)-ethenyl}-2,3-dicyano-pyrazine (**4c**)*

The crude product was purified by flash chromatography (silica gel, EtOAc:hexane = 1:4) to give **4c** in 77% yield as a yellow solid. M.p. 85–86 °C; $^1$H NMR ($CDCl_3$) $\delta$ (ppm) 10.08 (s, 1H, aldehyde), 8.14 (d, 2H, $J = 15.3$ Hz, vinyl), 7.99 (d, 2H, $J = 8.4$ Hz, phenyl), 7.85 (d, 2H, $J = 8.4$ Hz, phenyl), 7.66 (d, 2H, $J = 8.7$ Hz, phenyl), 7.56 (d, 1H, $J = 15.6$ Hz, vinyl), 7.29 (d, 1H, vinyl, $J = 15.6$ Hz, vinyl), 6.99 (d, 2H, $J = 8.7$ Hz, phenyl), 4.03 (t, 2H, $J = 6.0$ Hz, Ar-O–$CH_2$), 1.84–1.78 (m, 2H, Ar-O–$CH_2CH_2$–), 1.56–1.27 (m, 18H, methylene), 0.91–0.86 (t, 3H, $CH_3$).

Anal. Calcd. for $C_{35}H_{38}N_4O_2$: C, 76.89; H, 7.01; N, 10.25. Found. C, 76.41; H, 6.84; N, 10.12.

### 3.6. Typical procedure to synthesize **5**

A solution of compound **4** (2 mmol) and pyrrole (2 mmol) in chloroform (100 ml) was purged with nitrogen for 10 min, $BF_3$ (0.5 mmol) was added. The solution was stirred for 1 h at room temperature. Then, 2 mmol of 2,3-dichloro-4,5-dicyanoquinone (DDQ) was added and the mixture was stirred over night. The solvent was removed and the residue was triturated with chloroform. The solution was washed with 1 M aqueous sodium carbonate solution, water, brine, and dried over $Na_2SO_4$. After the solvent was removed, the crude product was purified by column chromatography.

### 3.7. 5,10,15,20-Tetra [5-{2-(4-amyloxy phenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyanopyrazino]-porphyrin (**5a**)

The crude product was purified by flash chromatography (silica gel, chloroform:triethylamine = 100:0.5) to give **5a** in 26% yield as a black solid. M.p. > 300 °C; $^1$H NMR ($CDCl_3$-$d_6$) $\delta$ (ppm) 8.91 (s, 8H), 8.39 (d, $J$ = 15 Hz, 4H, vinyl), 8.35 (d, $J$ = 7.8 Hz, 8H, phenyl), 8.10 (d, $J$ = 15 Hz, 4H, vinyl), 8.07 (d, $J$ = 8.1 Hz, 8H, phenyl), 7.66 (d, $J$ = 15 Hz, 4H, vinyl), 7.64 (d, $J$ = 6.0 Hz, 8H, phenyl), 7.32 (d, $J$ = 13.8 Hz, 4H, vinyl), 6.96 (d, $J$ = 8.7 Hz, 8H, phenyl), 4.06 (t, $J$ = 6.0 Hz, 8H, Ar-O–$CH_2$), 1.88–1.80 (m, 4H, $>CH$–$(CH_3)_2$), 1.79–1.65 (m, 8H, methylene), 0.98 (d, $J$ = 6.9 Hz, 24H, $>$CH–$(CH_3)_2$), −2.68 (s, 2H). MALDI-TOF-MS (dithranol): $m/z$ = 1984 ([$M^+$], 100), calcd. for $C_{128}H_{102}N_{20}O_4$ 1984.

Anal. Calcd. for $C_{128}H_{102}N_{20}O_4$: C, 77.48; H, 5.18; N, 14.12. Found: C, 77.12; H, 4.85; N, 13.98.

### 3.8. 5,10,15,20-Tetra [5-{2-(4-decyloxy phenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyanopyrazino]-porphyrin (**5b**)

The crude product was purified by flash chromatography (silica gel, chloroform:triethylamine = 100:0.5) to give **5b** in 18% yield as a black solid. M.p. > 300 °C; $^1$H NMR ($CDCl_3$-$d_6$) $\delta$ (ppm) 8.91 (s, 8H), 8.34 (d, $J$ = 7.5 Hz, 8H, phenyl), 8.28 (d, $J$ = 15 Hz, 4H, vinyl), 8.05 (d, $J$ = 8.4 Hz, 8H, phenyl), 7.93 (d, $J$ = 15 Hz, 4H, vinyl), 7.58 (d, $J$ = 7.8 Hz, 8H, phenyl), 7.52 (d, $J$ = 13.9 Hz, 4H, vinyl), 7.21 (d, $J$ = 14.7 Hz, 4H, vinyl), 6.94 (d, $J$ = 8.1 Hz, 8H, phenyl), 4.01 (t, $J$ = 6.0 Hz, 8H, Ar-O–$CH_2$), 1.79 (m, 8H, Ar-O–$CH_2CH_2$–), 1.57–1.27 (m, 56H, methylene), 0.86 (t, $J$ = 6.6 Hz, 12H, $CH_3$), −2.86 (s, 2H, N$H$). MALDI-TOF-MS (dithranol): $m/z$ = 2265 ([M + 1]$^+$, 100), calcd. for $C_{148}H_{142}N_{20}O_4$ 2264.

Anal. Calcd. for $C_{148}H_{142}N_{20}O_4$: C, 78.49; H, 6.32; N, 12.37. Found: C, 78.18; H, 5.99; N, 12.21.

### 3.9. 5,10,15,20-Tetra [5-{2-(4-dodecyloxy phenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyanopyrazino]-porphyrin (**5c**)

The crude product was purified by flash chromatography (silica gel, chloroform:triethylamine = 100:0.5) to give **5c** in 21% yield as a black solid. M.p. > 300 °C; $^1$H NMR ($CDCl_3$-$d_6$) $\delta$ (ppm) 8.91 (s, 8H), 8.34 (d, $J$ = 7.2 Hz, 8H, phenyl), 8.28 (d, $J$ = 15 Hz, 4H, vinyl), 8.03 (d, $J$ = 7.4 Hz, 8H, phenyl), 7.92 (d, $J$ = 15 Hz, 4H, vinyl), 7.53 (d, $J$ = 7.5 Hz, 8H, phenyl), 7.41 (d, $J$ = 13.6 Hz, 4H, vinyl), 7.08 (d, $J$ = 13.9 Hz, 4H, vinyl), 6.92 (d, $J$ = 7.6 Hz, 8H, phenyl), 4.00 (t, $J$ = 6.0 Hz, 8H, Ar-O–$CH_2$), 1.79 (m, 8H, Ar-O–$CH_2CH_2$–), 1.57–1.27 (m, 72H, methylene), 0.85 (t, $J$ = 6.3 Hz, 12H, $CH_3$), −2.86 (s, 2H, N$H$). MALDI-TOF-MS (dithranol): $m/z$ = 2377 ([$M^+$], 100), calcd. for $C_{156}H_{158}N_{20}O_4$ 2377.

Anal. Calcd. for $C_{156}H_{158}N_{20}O_4$: C, 78.82; H, 6.70; N, 11.78. Found: C, 78.58; H, 6.54; N, 11.59.

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