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Synthesis and optical properties of push–pull type tetrapyrazinoporphyrazines

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Abstract

The optical properties of push–pull type tetrapyrazinoporphyrazines based on 2,3-dicyanopyrazines were demonstrated. They have alkoxyphenyl substituent as an electron donor group at 5-position, and nitro- or sulfonyl-phenyl substituents as an electron acceptor group at 6-position of 2,3-dicyanopyrazine. The absorption and fluorescence maxima of nitro-substituted compounds were observed at 427–444 and 453–494 nm, respectively. In the case of sulfonyl-substituted compounds, the hypsochromic shift of absorption and fluorescence maxima were 59–104 and 13–79 nm, respectively.

Keywords: Pyrazine; Porphyrazine; Optical property; Push–pull; Horner–Wadsworth–Emmons (HWE) reaction

1. Introduction

As mentioned earlier the importance of dicyanopyrazine derivatives lies mainly in the chemical industry and many other fields such as food, agricultural, medicinal chemistry caused by their specific properties. A large number of publications and patents had been issued on the characteristics of dicyanopyrazine derivatives [1–4]. The specific properties of 2,3-dicyanopyrazine derivatives result from the two strong electron withdrawing cyano group on the pyrazine ring. Recently, highly functionalized 2,3-dicyanopyrazine derivatives are important in a broad range of chemistries involved in the application of dyestuff, electroluminescence material and so on [5–7]. Certain compounds can be usefully used as monomer or crosslinking materials to prepare conductive polymer [8] and as precursor to synthesize phthalocyanines.

The heterocyclic phthalocyanines have been useful compounds in chemical industry. The tetrapyrazinoporphyrazines have specific optical properties because they have symmetrical rich 18 π-electron aromatic macrocycle, which can play host to different metal ions in its central cavity. Some of their analogs have been reported for many years [9–13] because they have the potential advantage of application in optical recording media, photosensors, optical filters and copy preventing inks, etc [14–19].

We have been interested in the electron deficiency of the pyrazine ring for many years. In this study, we synthesized novel push–pull type 2,3-dicyanopyrazine derivatives, which have alkoxyphenyl substituent as an electron donor group at 5-position, and nitrophenyl (or alkoxysulfonylphenyl) substituent as an electron acceptor group at 6-position of 2,3-dicyanopyrazine. These compounds should show specific chemical, spectral properties, owing to the extension of π-conjugate system

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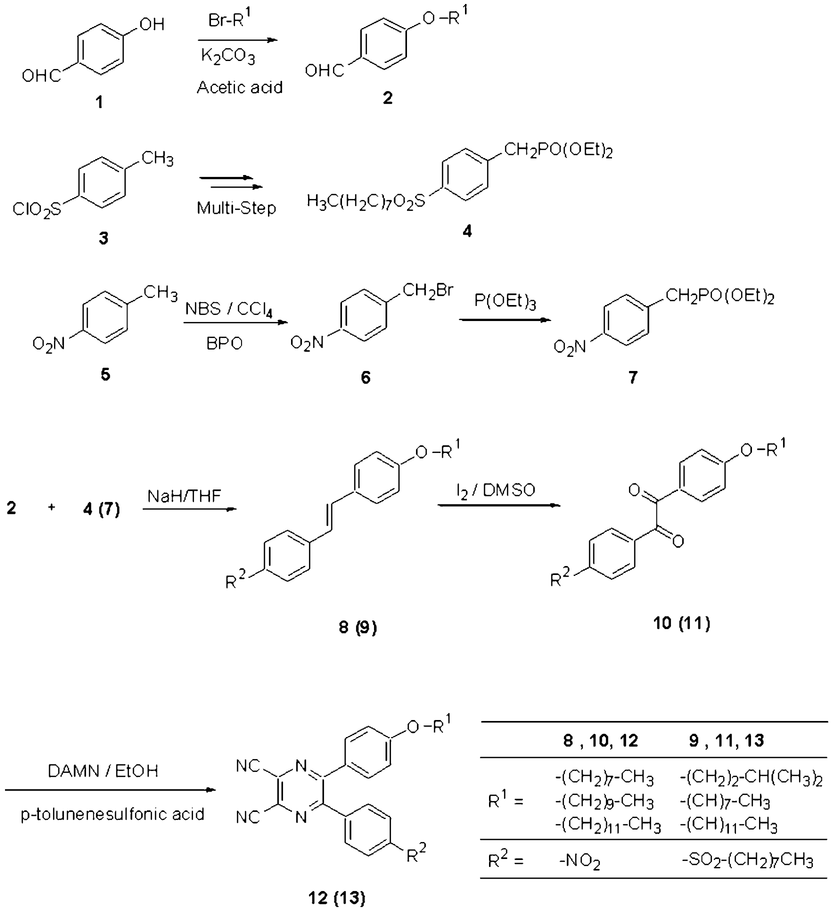
and intramolecular π–π interaction. Furthermore, the optical properties of tetrapyrazinoporphyrazines based on 2,3-dicyanopyrazines were demonstrated.

2. Results and discussion

2.1. Reaction of 2,3-dicyanopyrazine derivatives

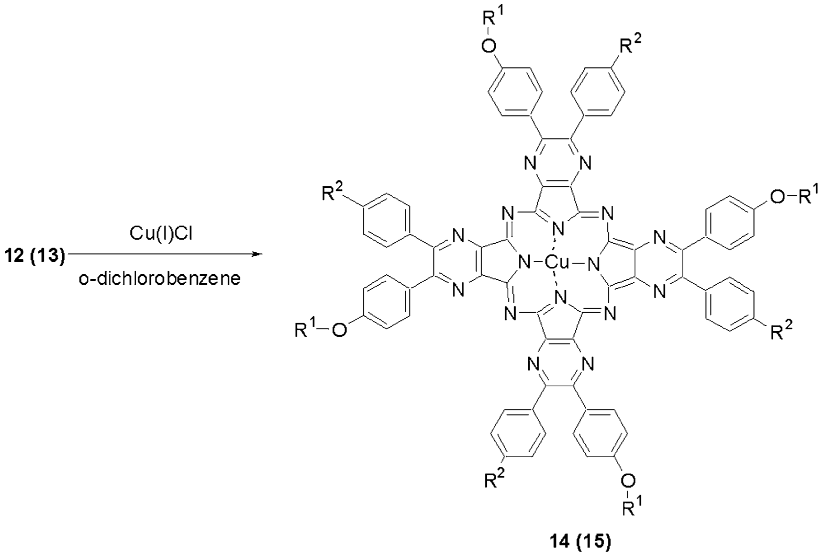
Alkoxybenzaldehydes (**2**), as an electron donor, were synthesized from 4-hydroxy benzaldehyde (**1**) by Williamson reaction with various long chain alkyl bromides in good yield (91–97%). Two different electron acceptors were also prepared by introducing sulfonyl and nitro group. 4-Octyl-sulfone benzyl phosphonate (**4**) were prepared by known method from the *p*-toluene sulfonyl chloride (**3**) via multi-steps [20]. 1-Bromomethy-4-nitrobenzene (**6**) was synthesized from *p*-nitrotoluene (**5**) by bromination in carbon tetrachloride using *N*-bromosuccinimide (NBS) in the presence of catalytic amount benzoyl peroxide (BPO) at reflux condition in 83% yield. Reaction of compound **6** with triethylphosphite gave 4-nitro benzyl phosphonate (**7**). The Horner–Wadsworth–Emmons (HWE) reaction of compounds **2** and **4** (or **7**) in tetrahydrofuran under reflux conditions gave push–pull type stilbenes, 4-(alkoxy phenyl)-4′-(nitrophenyl) stilbenes (**8**) and 4-(alkoxy phenyl)-4′-(octyloxysulfonyl) stilbenes (**9**). And then various α-diketone compounds (**10**, **11**) were prepared from corresponding compounds (**8**, **9**) in dimethylsulfoxide with iodine [21]. 2,3-Dicyanopyrazines (**12**, **13**) were synthesized by the condensation reaction of diaminomaleonitrile (DAMN) and compound **10** (or **11**) in ethanol. The reaction route is summarized in Scheme 1. The final compounds, tetrapyrazinoporphyrazines (**14**, **15**) were successfully synthesized by using excess amount of cuprous iodide and ammonium molybdate as catalyst in *o*-dichlorobenzene at refluxing condition. Their chemical structures are shown in Scheme 2. The structural assignments for resulting products were established on the basis of FT-IR, ^{1}H NMR spectral data as well as microanalyses.

From the FT-IR spectra of **8**, **10**, and **12**, the stretching vibrations of $-NO_2$ for all the products were observed as sharp and strong absorption bands appearing in 1592–1607 cm^{-1}. The observed bands at around 1146 cm^{-1} were corresponding to the sulfonyl group of compounds **9**, **11** and **13**. For the stilbene type



	8 , 10, 12	**9 , 11, 13**
R^1 =	$-(CH_2)_7-CH_3$ $-(CH_2)_9-CH_3$ $-(CH_2)_{11}-CH_3$	$-(CH_2)_2-CH(CH_3)_2$ $-(CH)_7-CH_3$ $-(CH)_{11}-CH_3$
R^2 =	$-NO_2$	$-SO_2-(CH_2)_7CH_3$

Scheme 1.



Scheme 2.

compounds **8** and **9**, we noticed the bands of ethylene at around 1630 and 1632 cm^{-1}. These bands disappeared upon **10** and **11**. The absorption band at around 1680 cm^{-1} was characteristic of the diketone. Stretching vibration of cyano group for all of **12** and **13** was observed appearing at around 2223 cm^{-1} (Fig. 1). In the case of tetrapyrazinoporphyrazines (**14**, **15**), the bands at around 2900 cm^{-1} were assigned to the methylene stretching of the alkyl group. The strong bands at around 1300 cm^{-1} were characteristic of the isoindole ring with a large contribution of the C–N stretching in the inner ring and other characteristic bands remained. Characterization of the stilbene compounds **8** and **9** were based on ^1H NMR spectral data, ethylene protons were split into a doublet, appearing in the range of 7.25–7.19 ppm (d, $J = 16.2$ Hz) and 7.02–6.97 (d, $J = 16.2$ Hz). According to the value of coupling constant of the ethylene protons, compounds **8** and **9** should exist in a *trans*-configuration. After oxidation of **8** and **9**, all of these ethylene proton peaks completely disappeared (Fig. 2). The ^1H NMR spectra of tetrapyrazinoporphyrazines (**14**, **15**) showed a broad peak at the corresponding range due to their low solubility and intermolecular interaction. The detail analyses of resulting compounds are shown in Section 3.

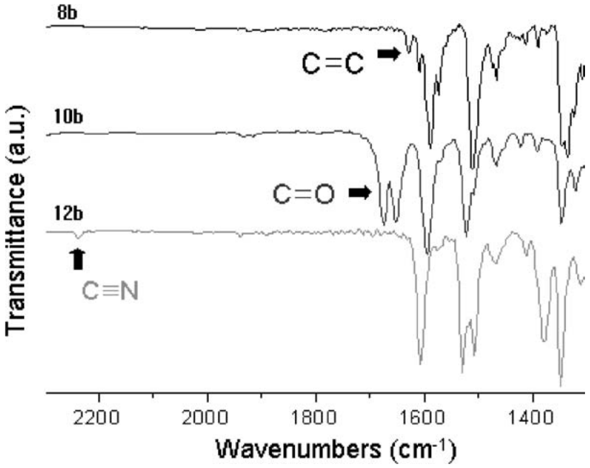


Fig. 1. FT-IR spectra of **8b**, **10b**, and **12b**.

2.2. UV–visible and fluorescence properties

Table 1 shows visible and fluorescent spectral data of stilbenes (**8**, **9**) and 2,3-dicyanopyrazines (**12**, **13**). However, the absorption peak of compounds **10** and **11** were not observed in the visible region because their π-conjugation system was broken by oxidation. The absorption and fluorescence maxima of nitro-substituted compounds (**8**, **12**) were observed at 427–444 and 453–494 nm, respectively. In the case of sulfonyl-substituted compounds (**9**, **13**), the hypsochromic shift of absorption and fluorescence maxima were 59–104 and 13–79 nm when compared with **8** and **12** because the electron withdrawing ability of nitro group was stronger than that of sulfonyl group. The hypsochromic shift value of absorption maximum was larger for stilbene than for 2,3-dicyanopyrazine compounds. It is presumably caused by the π-conjugation system. The stilbenes exhibit more planar structure compared to 2,3-dicyanopyrazines because of the steric hindrance between pyrazine moiety and close alkoxybenzen group. The absorption maximum did not change according to the length of alkoxy group.

Table 2 shows the spectral data of tetrapyrazinoporphyrazines. The absorption maxima of **14** and **15** were observed at 670 and 664 nm, respectively. The Q band of

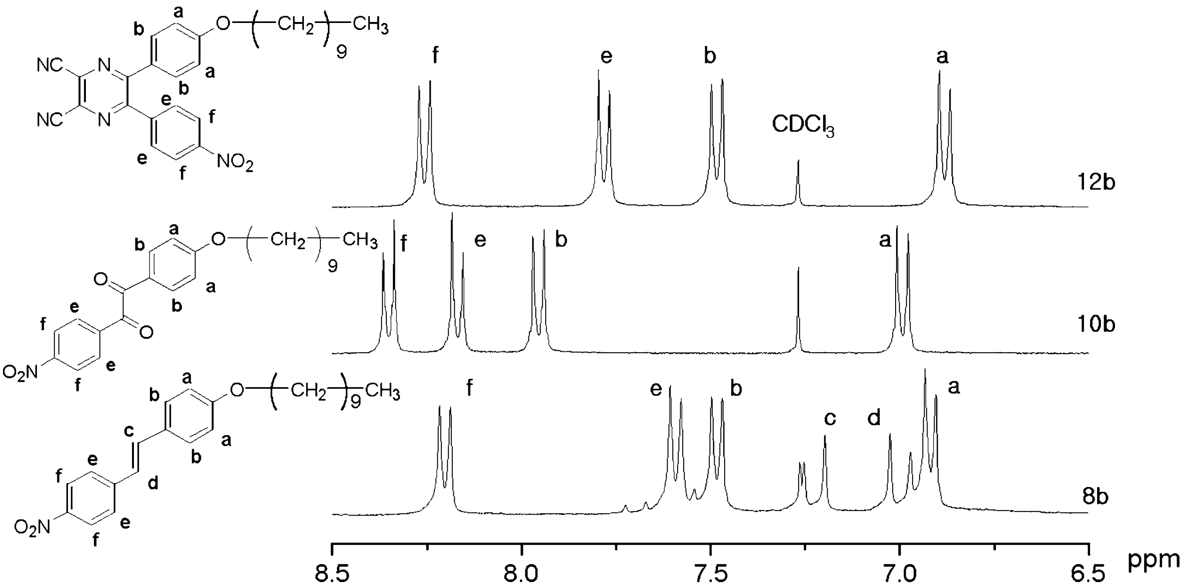


Fig. 2. 300 MHz ^{1}H spectra of **8b**, **10b**, and **12b**.

14 showed a small bathochromic shift at 6 nm as compared with **15** due to the difference of electron withdrawing ability of the nitro and sulfonyl groups. These compounds did not show detectable fluorescence. The B band (Soret band) was observed as a broad peak at around 368 nm. The Q band spectra in solution state showed the characteristic for aggregates of tetrapyrazinoporphyrazine compounds.

Fig. 3 indicated the temperature dependence of absorption spectra of **14a** and **15b** in toluene solution. The aggregate species were much more predominant at lower temperature, but monomeric species became predominant with increase of temperature. The absorption spectra of the monomeric species showed the split Q band at 670 nm. Isosbestic points were observed at around 620 and 710 nm and equilibrium mixtures of monomer and aggregates would be included in the solution. The aggregation of tetrapyrazinoporphyrazine was caused by the intermolecular hydrophobic interactions. The application of these functional dyes are under investigation. It is expected that these thermal properties can be used for optical filter, shutter etc. Applications of these new tetrapyrazinoporphyrazines for functional dye materials are under investigation.

The strange absorption curve observed in toluene should be attributed to the molecular aggregation in solution. Similar changes in molecular aggregation were also observed depending on the polarity of solvent (Fig. 4). With increase of the ratio of chloroform to toluene, the absorption at 620 nm increases and that at 670 nm decreases. The Q band spectra in toluene show the characteristic pattern of aggregates, which is replaced at lower concentration with the spectral envelope and hypsochromic shift of λ_{max} compared with

Table 1
UV–visible and fluorescent spectral data

Compd.	R^1	R^2	λ_{max} (nm)[a]	F_{max} (nm)[b]	SS (nm)[c]
8a	$-(CH_2)_7CH_3$	$-NO_2$	444	494	50
8b	$-(CH_2)_9CH_3$	$-NO_2$	444	494	50
8c	$-(CH_2)_{11}CH_3$	$-NO_2$	444	494	50
9a	$-(CH_2)_2CH(CH_3)_2$	$-SO_2(CH_2)_7CH_3$	340	415	75
9b	$-(CH_2)_7CH_3$	$-SO_2(CH_2)_7CH_3$	340	415	75
9c	$-(CH_2)_{11}CH_3$	$-SO_2(CH_2)_7CH_3$	340	415	75
12a	$-(CH_2)_7CH_3$	$-NO_2$	427	453	26
12b	$-(CH_2)_9CH_3$	$-NO_2$	427	453	26
12c	$-(CH_2)_{11}CH_3$	$-NO_2$	427	453	26
13a	$-(CH_2)_2CH(CH_3)_2$	$-SO_2(CH_2)_7CH_3$	368	440	72
13b	$-(CH_2)_7CH_3$	$-SO_2(CH_2)_7CH_3$	368	440	72
13c	$-(CH_2)_{11}CH_3$	$-SO_2(CH_2)_7CH_3$	368	440	72

[a] In chloroform.

[b] Excited at λ_{max}.

[c] Stokes' shift = $\lambda_{max} - F_{max}$.

Table 2
UV–visible spectral data of tetrapyrazinoporphyrazines

Compd.	R^1	R^2	λ_{max} (nm)[a]	F_{max} (nm)[b]
14a	$-(CH_2)_7CH_3$	$-NO_2$	368/670	–
14b	$-(CH_2)_9CH_3$	$-NO_2$	368/670	–
14c	$-(CH_2)_{11}CH_3$	$-NO_2$	368/670	–
15a	$-(CH_2)_2CH(CH_3)_2$	$-SO_2(CH_2)_7CH_3$	368/664	–
15b	$-(CH_2)_7CH_3$	$-SO_2(CH_2)_7CH_3$	368/664	–
15c	$-(CH_2)_{11}CH_3$	$-SO_2(CH_2)_7CH_3$	368/664	–

[a] In chloroform.

[b] Excited at λ_{max}.

that in chloroform. Similar results were generally observed for other derivatives.

These results indicated that the interaction between π-electrons on adjacent porphyrazine rings of **15** was weaker than that of **14** due to the bulky long chain alkyl groups.

3. Experimental

Melting points were determined using a JISICO melting point apparatus. The IR spectra were taken with a MAGNA-IR 760 spectrometer using KBr pellets. The ^{1}H NMR spectra were obtained on a VARIAN, 300 MHz UNITY INOVA. The mass spectra were recorded on a JEOL, JMS-AX505WA, HP 5890 Series II. Elemental analyses were performed on a CE, EA 1110. The visible and fluorescence spectra were measured on UNICAM 8700 and SHIMADZU RF-5301PC spectrophotometer.

3.1. General procedure of stilbenes (*8*, *9*)

The procedure by the Horner–Wadsworth–Emmons (HWE) reaction was modified as follows. To a solution of (4-nitrobenzyl)-phosphoric acid diethylester (**7**)

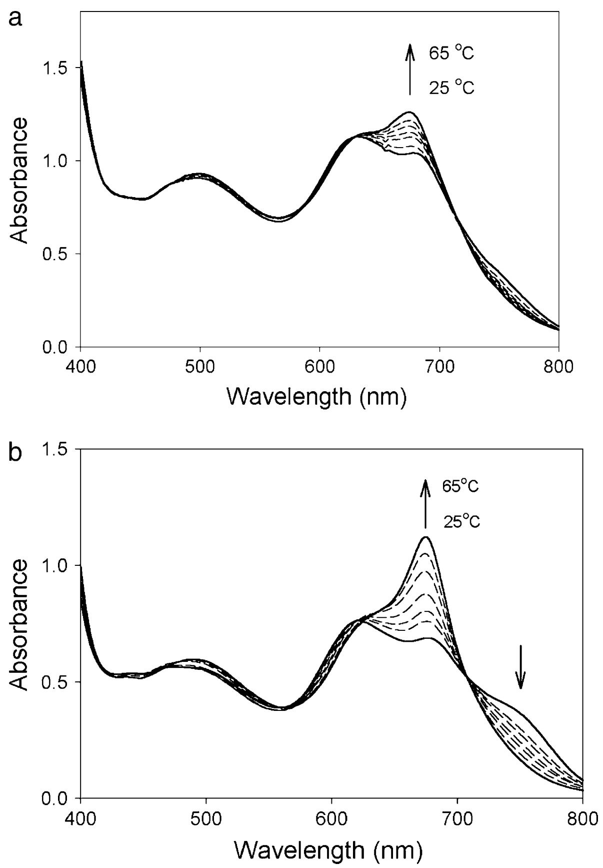


Fig. 3. Temperature dependence of the absorption spectra of 2×10^{-4} M (upper) **14a** (lower) **15b** in toluene.

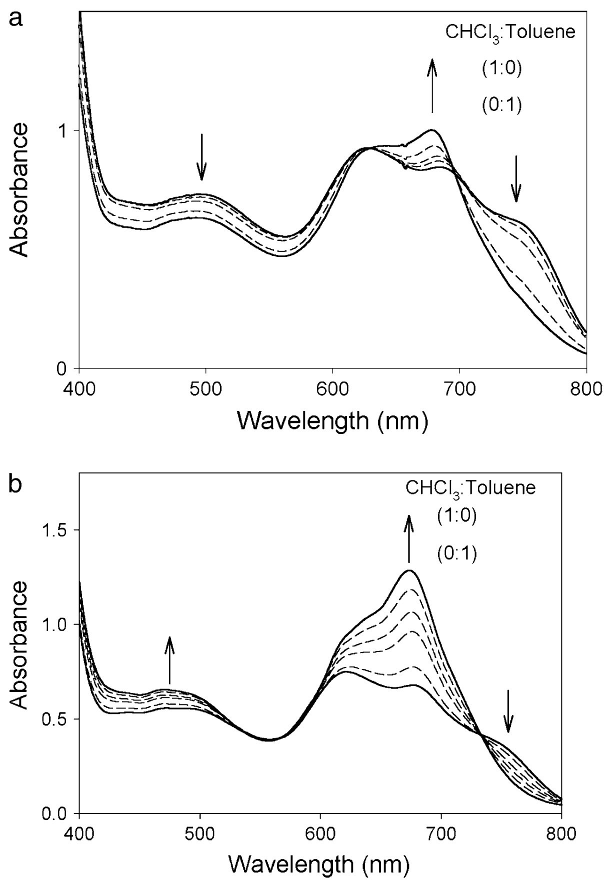


Fig. 4. Spectral changes of 2×10^{-4} M **14a** (upper) **15b** (lower) by solvent polarity.

(38.3 g, 0.14 mol) and 4-alkoxybenzaldehyde (**2**) (0.14 mol) in THF was added 60% sodium hydride (5.6 g, 0.14 mol), and then methanol was added dropwise (10 mL) slowly and the solution temperature was kept at 5–10 °C. The reaction mixture was refluxed until all of **2** disappeared by TLC. After the reaction was complete, the solvent was removed under reduced pressure. Methanol was added to the residue and the precipitate was filtered off. The crude product was recrystallized from methanol. Compound **9** was obtained by similar methods.

*3.1.1. 4-(Octyloxyphenyl)-4′-(nitrophenyl) stilbene (**8a**)*

73% yield, m.p.: 96–97 °C; ir (KBr pellet): ν (cm^{-1}) 1630 (C=C); ^{1}H NMR ($CDCl_3$-d_6): 8.21–8.18 (d, 2H, $J = 8.7$ Hz, phenyl), 7.60–7.57 (d, 2H, $J = 9$ Hz, phenyl), 7.49–7.47 (d, 2H, $J = 8.7$ Hz, phenyl), 7.25–7.19 (d, 1H, $J = 16.2$ Hz, ethylene), 7.02–6.97 (d, 1H, $J = 16.2$ Hz, ethylene), 6.93–6.90 (d, 2H, $J = 8.7$ Hz, phenyl), 4.01–3.97 (t, 2H, $O{-}CH_2CH_2$), 1.80 (m, 2H, $O{-}CH_2CH_2$), 1.46–1.30 (m, 10H, methylene), 0.91–0.87 (t, 3H, $-CH_3$).

Anal. Calcd. for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 74.58; H, 7.64; N, 3.85.

*3.1.2. 4-(Decyloxyphenyl)-4′-(nitrophenyl) stilbene (**8b**)*

68% yield, m.p.: 81–83 °C; ir (KBr pellet): ν (cm^{-1}) 1630 (C=C); ^{1}H NMR ($CDCl_3$-d_6): 8.21–8.18 (d, 2H, $J = 8.7$ Hz, phenyl), 7.60–7.57 (d, 2H, $J = 8.7$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 8.7$ Hz, phenyl), 7.25–7.19 (d, 1H, $J = 16.2$ Hz, ethylene), 7.02–6.97 (d, 1H, $J = 16.2$ Hz, ethylene), 6.93–6.90 (d, 2H, $J = 8.7$ Hz, phenyl), 4.01–3.96 (t, 2H, $O{-}CH_2CH_2$), 1.80 (m, 2H, $O{-}CH_2CH_2$), 1.46–1.28 (m, 14H, methylene), 0.91–0.86 (t, 3H, $-CH_3$).

Anal. Calcd. for $C_{24}H_{31}NO_3$: C, 75.56; H, 8.19; N, 3.67. Found: C, 75.28; H, 8.04; N, 3.58.

*3.1.3. 4-(Decyloxyphenyl)-4′-(nitrophenyl) stilbene (**8c**)*

72% yield, m.p.: 79–81 °C; ir (KBr pellet): ν (cm^{-1}) 1630 (C=C); ^{1}H NMR ($CDCl_3$-d_6): 8.21–8.18 (d, 2H, $J = 8.7$ Hz, phenyl), 7.60–7.57 (d, 2H, $J = 8.7$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 8.7$ Hz, phenyl), 7.25–7.19 (d, 1H, $J = 16.2$ Hz, ethylene), 7.02–6.97 (d, 1H, $J = 16.2$ Hz, ethylene), 6.93–6.90 (d, 2H, $J = 8.7$ Hz, phenyl), 4.01–3.96 (t, 2H, $J = 6.3$ Hz, $O{-}CH_2CH_2$), 1.80 (m, 2H, $O{-}CH_2CH_2$), 1.46–1.28 (m, 18H, methylene), 0.91–0.87 (t, 3H, $-CH_3$).

Anal. Calcd. for $C_{26}H_{35}NO_3$: C, 76.25; H, 8.61; N, 3.42. Found: C, 75.98; H, 8.50; N, 3.24.

*3.1.4. 4-(Amyloxyphenyl)-4′-(octyloxysulfonyl) stilbene (**9a**)*

68% yield, m.p.: 137–138 °C; ir (KBr pellet): ν (cm^{-1}) 1631 (C=C), 1146 ($-SO_2-$); ^{1}H NMR ($CDCl_3$-d_6): 7.87–7.84 (d, 2H, $J = 8.4$ Hz, phenyl), 7.65–7.62 (d, 2H, $J = 7.8$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 8.7$ Hz, phenyl), 7.23–7.18 (d, 1H, $J = 16.2$ Hz, ethylene), 7.02–6.96 (d, 1H, $J = 16.5$ Hz, ethylene), 6.93–6.90 (d, 2H, $J = 8.4$ Hz, phenyl), 4.02 (t, 2H, $O{-}CH_2$), 3.08 (t, 2H, $-SO_2-CH_2-$), 1.87–1.81 (m, 1H, $>CH-(CH_3)_2$), 1.77–1.66 (m, 4H, methylene), 1.35–1.23 (m, 10H, methylene), 0.99 (d, 6H, $>CH-(CH_3)_2$), 0.86 (t, 3H, $-CH_3$).

Anal. Calcd. for $C_{27}H_{38}O_3S$: C, 73.26; H, 8.65; S, 7.24; Found: C, 73.02; H, 8.50; S, 7.14.

*3.1.5. 4-(Octyloxyphenyl)-4′-(octyloxysulfonyl) stilbene (**9b**)*

72% yield, m.p.: 132–134 °C; ir (KBr pellet): ν (cm^{-1}) 1631 (C=C), 1146 ($-SO_2-$); ^{1}H NMR ($CDCl_3$-d_6): 7.87–7.84 (d, 2H, $J = 8.4$ Hz, phenyl), 7.65–7.62 (d, 2H, $J = 7.8$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 8.7$ Hz, phenyl), 7.23–7.18 (d, 1H, $J = 16.2$ Hz, ethylene), 7.01–6.96 (d, 1H, $J = 16.5$ Hz, ethylene), 6.93–6.90 (d, 2H, $J = 8.4$ Hz, phenyl), 4.01 (t, 2H, $O{-}CH_2$), 3.08 (t, 2H, $-SO_2-CH_2-$), 1.84–1.67 (m, 4H, methylene), 1.47–1.24 (m, 20H, methylene), 0.89 (m, 6H).

Anal. Calcd. for $C_{30}H_{44}O_3S$: C, 74.33; H, 9.15; S, 6.62; Found: C, 74.12; H, 9.02; S, 6.48.

*3.1.6. 4-(Dodecyloxyphenyl)-4′-(octyloxysulfonyl) stilbene (**9c**)*

64% yield, m.p.: 132–134 °C; ir (KBr pellet): ν (cm^{-1}) 1631 (C=C), 1146 ($-SO_2-$); ^{1}H NMR ($CDCl_3$-d_6, d ppm): 7.87–7.84 (d, 2H, $J = 8.4$ Hz, phenyl), 7.65–7.62 (d, 2H, $J = 7.8$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 8.7$ Hz, phenyl), 7.23–7.18 (d, 1H, $J = 16.2$ Hz, ethylene), 7.01–6.96 (d, 1H, $J = 16.5$ Hz, ethylene), 6.93–6.90 (d, 2H, $J = 8.4$ Hz, phenyl), 4.01 (t, 2H, $O{-}CH_2$), 3.08 (t, 2H, $-SO_2-CH_2-$), 1.84–1.67 (m, 4H, methylene), 1.47–1.24 (m, 28H, methylene), 0.89 (m, 6H).

Anal. Calcd. for $C_{34}H_{52}O_3S$: C, 75.51; H, 9.69; S, 5.93; Found: C, 75024; H, 9.52; S, 5.74.

*3.2. General procedure of diketones (**10**, **11**)*

A solution of **8** (0.093 mol) and iodine (18.78 g, 0.74 mol) in dimethylsulfoxide (20 ml) was heated at reflux for 5 h using Dean–Stark trap. After the reaction was complete, the resulting mixture was cooled at room temperature, and then methanol was added to the residue and the precipitate was filtered off. The crude product was recrystallized from carbon tetrachloride. Compound **11** was obtained by similar methods.

3.2.1. 1-(4′-Octyloxy phenyl)-2-(4″-nitrophenyl)-ethanedione (**10a**)

53% yield, m.p.: 92–93 °C; ir (KBr pellet): ν (cm^{-1}) 1677 (C=O); ^{1}H NMR ($CDCl_3$-d_6): 8.36–8.33 (d, 2H, $J = 8.7$ Hz, phenyl), 8.18–8.15 (d, 2H, $J = 8.7$ Hz, phenyl), 7.97–7.93 (d, 2H, $J = 9.3$ Hz, phenyl), 7.00–6.97 (d, 2H, $J = 9.0$ Hz, phenyl), 4.08–4.03 (t, 2H, O–CH_2), 1.80 (m, 2H, O–CH_2CH_2), 1.46–1.30 (m, 10H, methylene), 0.91–0.86 (t, 3H, –CH_3).

Anal. Calcd. for $C_{22}H_{25}NO_5$: C, 68.91; H, 6.57; N, 3.66. Found: C, 68.57; H, 6.40; N, 3.52.

3.2.2. 1-(4′-Decyloxy phenyl)-2-(4″-nitrophenyl)-ethanedione (**10b**)

50% yield, m.p.: 81–82 °C; ir (KBr pellet): ν (cm^{-1}) 1677 (C=O); ^{1}H NMR ($CDCl_3$-d_6): 8.36–8.33 (d, 2H, $J = 8.7$ Hz, phenyl), 8.18–8.15 (d, 2H, $J = 8.7$ Hz, phenyl), 7.97–7.94 (d, 2H, $J = 9.0$ Hz, phenyl), 7.00–6.97 (d, 2H, $J = 8.7$ Hz, phenyl), 4.08–4.03 (t, 2H, O–CH_2), 1.82 (m, 2H, O–CH_2CH_2), 1.46–1.27 (m, 14H, methylene), 0.91–0.86 (t, 3H, –CH_3).

Anal. Calcd. for $C_{24}H_{29}NO_5$: C, 70.05; H, 7.10; N, 3.41. Found: C, 69.74; H, 6.98; N, 3.37.

3.2.3. 1-(4′-Dodecyloxy phenyl)-2-(4″-nitrophenyl)-ethanedione (**10c**)

45% yield, m.p.: 80–81 °C; ir (KBr pellet): ν (cm^{-1}) 1677 (C=O); ^{1}H NMR ($CDCl_3$-d_6): 8.36–8.33 (d, 2H, $J = 8.7$ Hz, phenyl), 8.18–8.15 (d, 2H, $J = 8.7$ Hz, phenyl), 7.97–7.93 (d, 2H, $J = 9.0$ Hz, phenyl), 7.00–6.97 (d, 2H, $J = 8.7$ Hz, phenyl), 4.08–4.03 (t, 2H, O–CH_2), 1.82 (m, 2H, O–CH_2CH_2), 1.46–1.27 (m, 18H, methylene), 0.91–0.86 (t, 3H, –CH_3).

Anal. Calcd. for $C_{26}H_{33}NO_5$: C, 71.05; H, 7.57; N, 3.18. Found: C, 70.89; H, 7.38; N, 3.02.

3.2.4. 1-(4′-Amyloxy phenyl)-2-(4″-octyloxysulfonyl)-ethanedione (**11a**)

48% yield, m.p.: 83–85 °C; ir (KBr pellet): ν (cm^{-1}) 1685 (C=O), 1146 (–SO_2–); ^{1}H NMR ($CDCl_3$-d_6): 8.18–8.15 (d, 2H, $J = 7.8$ Hz, phenyl), 8.06–8.03 (d, 2H, $J = 7.8$ Hz, phenyl), 7.97–7.94 (d, 2H, $J = 8.4$ Hz, phenyl), 7.00–6.98 (d, 2H, $J = 7.8$ Hz, phenyl), 4.09 (t, 2H, O–CH_2), 3.11 (t, 2H, –SO_2–CH_2–), 1.87–1.81 (m, 1H, $>$CH–$(CH_3)_2$), 1.74–1.66 (m, 4H, methylene), 1.36–1.24 (m, 10H, methylene), 0.99 (d, 6H, $>$CH–$(CH_3)_2$), 0.86 (t, 3H, –CH_3).

Anal. Calcd. for $C_{27}H_{36}O_5S$: C, 68.61; H, 7.68; S, 6.78; Found: C, 68.47; H, 7.51; S, 6.50.

3.2.5. 1-(4′-Octyloxyphenyl)-2-(4″-octyloxysulfonyl)-ethanedione (**11b**)

52% yield, m.p.: 84–85 °C; ir (KBr pellet): ν (cm^{-1}) 1685 (C=O), 1146 (–SO_2–); ^{1}H NMR ($CDCl_3$-d_6): 8.18–8.15 (d, 2H, $J = 8.4$ Hz, phenyl), 8.06–8.03 (d, 2H, $J = 7.8$ Hz, phenyl), 7.97–7.94 (d, 2H, $J = 7.8$ Hz, phenyl), 7.00–6.98 (d, 2H, $J = 7.8$ Hz, phenyl), 4.09 (t, 2H, O–CH_2), 3.11 (t, 2H, –SO_2–CH_2–), 1.85–1.68 (m, 4H, methylene), 1.47–1.25 (m, 20H, methylene), 0.89 (m, 6H).

Anal. Calcd. for $C_{30}H_{42}O_5S$: C, 70.00; H, 8.22; S, 6.23; Found: C, 69.87; H, 8.10; S, 6.12.

3.2.6. 1-(4′-Dodecyloxyphenyl)-2-(4″-octyloxysulfonyl)-ethanedione (**11c**)

45% yield, m.p.: 80–82 °C; ir (KBr pellet): ν (cm^{-1}) 1685 (C=O), 1146 (–SO_2–); ^{1}H NMR ($CDCl_3$-d_6): 8.18–8.15 (d, 2H, $J = 7.8$ Hz, phenyl), 8.06–8.03 (d, 2H, $J = 8.4$ Hz, phenyl), 7.97–7.94 (d, 2H, $J = 8.4$ Hz, phenyl), 7.00–6.98 (d, 2H, $J = 8.4$ Hz, phenyl), 4.09 (t, 2H, O–CH_2), 3.10 (t, 2H, –SO_2–CH_2–), 1.83–1.66 (m, 4H, methylene), 1.46–1.25 (m, 28H, methylene), 0.88 (m, 6H).

Anal. Calcd. for $C_{34}H_{50}O_5S$: C, 71.54; H, 8.83; S, 5.62; Found: C, 71.34; H, 8.57; S, 5.51.

3.3. General procedure of 2,3-dicyanopyrazines (**12, 13**)

A solution of **10** (0.036 mol), DAMN (4.73 g, 0.044 mol) and *p*-toluenesulfonic acid (0.02 g) in ethanol (50 ml) was refluxed for 5 h. After the reaction was complete, the mixture was cooled at room temperature. The precipitate was filtered off and washed with methanol. The crude product was recrystallized from carbon tetrachloride. Compound **13** was obtained by similar methods.

3.3.1. 2,3-Dicyano-5-(4′-octyloxyphenyl)-6-(4″-nitrophenyl)-pyrazines (**12a**)

72% yield, m.p.: 81–83 °C; ir (KBr pellet): ν (cm^{-1}) 2232 (CN); ^{1}H NMR ($CDCl_3$-d_6): 8.27–8.24 (d, 2H, $J = 9.0$ Hz, phenyl), 7.79–7.76 (d, 2H, $J = 9.3$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 9.0$ Hz, phenyl), 6.89–6.86 (d, 2H, $J = 9.0$ Hz, phenyl), 4.01–3.97 (t, 2H, O–CH_2), 1.80 (m, 2H, O–CH_2CH_2), 1.45–1.30 (m, 10H, methylene), 0.91–0.86 (t, 3H, –CH_3).

Anal. Calcd. for $C_{26}H_{25}N_5O_3$: C, 68.56; H, 5.53; N, 15.37. Found: C, 68.34; H, 5.29; N, 15.12.

3.3.2. 2,3-Dicyano-5-(4′-decyloxyphenyl)-6-(4″-nitrophenyl)-pyrazines (**12b**)

68% yield, m.p.: 80–82 °C; ir (KBr pellet): ν (cm^{-1}) 2232 (CN); ^{1}H NMR ($CDCl_3$-d_6): 8.27–8.24 (d, 2H, $J = 8.7$ Hz, phenyl), 7.79–7.76 (d, 2H, $J = 9.0$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 8.7$ Hz, phenyl), 6.89–6.86 (d, 2H, $J = 9.0$ Hz, phenyl), 4.01–3.97 (t, 2H, O–CH_2), 1.80 (m, 2H, O–CH_2CH_2), 1.45–1.27 (m, 14H), 0.90–0.86 (t, 3H, –CH_3).

Anal. Calcd. for $C_{28}H_{29}N_5O_3$: C, 69.55; H, 6.04; N, 14.48. Found: C, 69.18; H, 5.87; N, 14.25.

3.3.3. 2,3-Dicyano-5-(4′-dodecyloxyphenyl)-6-(4″-nitrophenyl)-pyrazines (**12c**)

66% yield, m.p.: 78–80 °C; ir (KBr pellet): ν (cm^{-1}) 2232 (CN); ^{1}H NMR (CDCl$_3$-d_6): 8.26–8.23 (d, 2H, $J = 9.0$ Hz, phenyl), 7.79–7.76 (d, 2H, $J = 8.7$ Hz, phenyl), 7.49–7.46 (d, 2H, $J = 9.0$ Hz, phenyl), 6.89–6.86 (d, 2H, $J = 9.0$ Hz, phenyl), 4.01–3.97 (t, 2H, O–CH$_2$), 1.80 (m, 2H, O–CH$_2$CH$_2$), 1.45–1.27 (m, 18H, methylene), 0.90–0.86 (t, 3H, –CH$_3$).

Anal. Calcd. for $C_{30}H_{33}N_5O_3$: C, 70.43; H, 6.50; N, 13.69. Found: C, 70.10; H, 6.34; N, 13.57.

3.3.4. 2,3-Dicyano-5-(4′-amyloxyphenyl)-6-(4″-octyloxysulfonyl)-pyrazines (**13a**)

74% yield, m.p.: 98–99 °C; ir (KBr pellet): ν (cm^{-1}) 2241 (CN), 1176 (–SO$_2$–); ^{1}H NMR (CDCl$_3$-d_6): 7.95–7.92 (d, 2H, $J = 8.4$ Hz, phenyl), 7.79–7.76 (d, 2H, $J = 8.7$ Hz, phenyl), 7.48–7.45 (d, 2H, $J = 8.7$ Hz, phenyl), 6.88–6.85 (d, 2H, $J = 8.7$ Hz, phenyl), 4.02 (t, 2H, O–CH$_2$), 3.10 (t, 2H, –SO$_2$–CH$_2$–), 1.86–1.79 (m, 1H, >CH–(CH$_3$)$_2$), 1.73–1.66 (m, 4H, methylene), 1.37–1.24 (m, 10H, methylene), 0.98 (d, 6H, >CH–(CH$_3$)$_2$), 0.86 (t, 3H, –CH$_3$).

Anal. Calcd. for $C_{31}H_{36}N_4O_3S$: C, 68.35; H, 6.66; N, 10.29; O, 8.81; S, 5.89; Found: C, 68.14; H, 6.38; N, 10.10; O, 8.74; S, 5.57.

3.3.5. 2,3-Dicyano-5-(4′-octyloxyphenyl)-6-(4″-octyloxysulfonyl)-pyrazines (**13b**)

69% yield, m.p.: 87–88 °C; ir (KBr pellet): ν (cm^{-1}) 2240 (CN), 1176 (–SO$_2$–); ^{1}H NMR (CDCl$_3$-d_6): 7.95–7.92 (d, 2H, $J = 8.7$ Hz, phenyl), 7.79–7.76 (d, 2H, $J = 8.4$ Hz, phenyl), 7.48–7.45 (d, 2H, $J = 8.7$ Hz, phenyl), 6.88–6.85 (d, 2H, $J = 8.4$ Hz, phenyl), 4.05 (t, 2H, O–CH$_2$), 3.10 (t, 2H, –SO$_2$–CH$_2$–), 1.87–1.68 (m, 4H, methylene), 1.45–1.25 (m, 20H, methylene), 0.91 (m, 6H).

Anal. Calcd. for $C_{34}H_{42}N_4O_3S$: C, 69.59; H, 7.21; N, 9.55; O, 8.18; S, 5.46; Found: C, 69.35; H, 7.01; N, 9.47; O, 7.95; S, 5.38.

3.3.6. 2,3-Dicyano-5-(4′-dodecyloxyphenyl)-6-(4″-octyloxy-sulfonyl)-pyrazines (**13c**)

72% yield, m.p.: 84–86 °C; ir (KBr pellet): ν (cm^{-1}) 2246 (CN), 1168 (–SO$_2$–); ^{1}H NMR (CDCl$_3$-d_6): 7.95–7.92 (d, 2H, $J = 8.4$ Hz, phenyl), 7.79–7.76 (d, 2H, $J = 8.4$ Hz, phenyl), 7.48–7.45 (d, 2H, $J = 8.7$ Hz, phenyl), 6.88–6.85 (d, 2H, $J = 8.4$ Hz, phenyl), 4.02 (t, 2H, O–CH$_2$), 3.09 (t, 2H, –SO$_2$–CH$_2$–), 1.85–1.66 (m, 4H, methylene), 1.43–1.24 (m, 28H, methylene), 0.89 (m, 6H).

Anal. Calcd. for $C_{38}H_{50}N_4O_3S$: C, 70.99; H, 7.84; N, 8.71; O, 7.47; S, 4.99; Found: C, 70.58; H, 7.61; N, 8.49; O, 7.27; S, 4.49.

3.4. General procedure of tetrapyrazinoporphyrazines (**14, 15**)

A mixture of **12** (5.5 mmol), an equivalent amount of Cu(I)Cl, and a catalytic amount of ammonium molybdate in 10 ml *o*-dichlorobenzene was heated at 180–190 °C for 18 h. The deep greenish solution product was cooled to room temperature. The precipitate was washed with 5% HCl aqueous solution and ammonia solution. The solid product was washed with ethylacetate and acetone and methanol, repeatedly. The crude product was purified by column chromatography (chloroform/methanol: 100/1). Compound **15** was obtained by similar methods.

3.4.1. Copper tetra-2,3-[5-(octyloxy benzyl)-6-(nitro benzyl)-pyrazino]-porphyrazine (**14a**)

27% yield, m.p.: >300 °C; ir (KBr pellet): ν (cm^{-1}) 1250 (Ar–O–); ^{1}H NMR (CDCl$_3$-d_6): 8.1–7.4 (br, 24H), 6.8 (br, 8H), 4.0 (br, 8H), 1.3 (br, 60H).

Anal. Calcd. for $C_{104}H_{100}CuN_{20}O_{12}$: C, 66.25; H, 5.35; N, 14.86; Found: C, 65.79; H, 5.10; N, 14.29.

3.4.2. Copper tetra-2,3-[5-(decyloxy benzyl)-6-(nitro benzyl)-pyrazino]-porphyrazine (**14b**)

23% yield, m.p.: >300 °C; ir (KBr pellet): ν (cm^{-1}) 1250 (Ar–O–); ^{1}H NMR (CDCl$_3$-d_6, d ppm): 8.1–7.4 (br, 24H), 6.8 (br, 8H), 4.0 (br, 8H), 1.3 (br, 92H).

Anal. Calcd. for $C_{112}H_{116}CuN_{20}O_{12}$: C, 67.33; H, 5.85; N, 14.02; Found: C, 66.98; H, 5.57; N, 13.89.

3.4.3. Copper tetra-2,3-[5-(dodecyloxy benzyl)-6-(nitro benzyl)-pyrazino]-porphyrazine (**14c**)

31% yield, m.p.: >300 °C; ir (KBr pellet): ν (cm^{-1}) 1250 (Ar–O–); ^{1}H NMR (CDCl$_3$-d_6): 8.1–7.4 (br, 24H), 6.8 (br, 8H), 4.0 (br, 8H), 1.3 (br, 124H).

Anal. Calcd. for $C_{120}H_{132}CuN_{20}O_{12}$: C, 68.31; H, 6.31; N, 13.28; Found: C, 68.07; H, 6.12; N, 12.98.

3.4.4. Copper tetra-2,3-[5-(amyloxy phenyl)-6-(nitro benzyl)-pyrazino]-porphyrazine (**15a**)

34% yield, m.p.: >300 °C; ir (KBr pellet): ν (cm^{-1}) 1146 (–SO$_2$–); ^{1}H NMR (CDCl$_3$-d_6): 8.0 (br, 24H), 7.0 (br, 8H), 4.1 (br, 8H), 3.5 (br, 8H), 1.8–0.9 (br, 96H).

Anal. Calcd. for $C_{124}H_{144}CuN_{16}O_{12}S_4$: C, 66.42; H, 6.47; N, 9.99; S, 5.72; Found: C, 66.15; H, 6.31; N, 9.68; S, 5.51.

3.4.5. Copper tetra-2,3-[5-(octyloxy phenyl)-6-(nitro benzyl)-pyrazino]-porphyrazine (**15b**)

28% yield, m.p.: >300 °C; ir (KBr pellet): ν (cm^{-1}) 1146 (–SO$_2$–); ^{1}H NMR (CDCl$_3$-d_6): 8.0 (br, 24H), 7.0 (br, 8H), 4.1 (br, 8H), 3.5 (br, 8H), 1.8–0.9 (br, 144H).

Anal. Calcd. for $C_{136}H_{168}CuN_{16}O_{12}S_4$: C, 67.76; H, 7.02; N, 9.30; S, 5.32; Found: C, 67.51; H, 6.78; N, 9.12; S, 5.08.

*3.4.6. Copper tetra-2,3-[5-(dodeccyloxy phenyl)-6-(nitro benzyl)-pyrazino]-porphyrazine (**15c**)*

24% yield, m.p.: >300 °C; ir (KBr pellet): ν (cm^{-1}) 1146 (–SO_2–); ^{1}H NMR ($CDCl_3$-d_6): 8.0 (br, 24H), 7.0 (br, 8H), 4.1 (br, 8H), 3.5 (br, 8H), 1.8–0.9 (br, 208H).

Anal. Calcd. for $C_{152}H_{200}CuN_{16}O_{12}S_4$: C, 69.28; H, 7.65; N, 8.50; S, 4.87; Found: C, 68.94; H, 7.28; N, 8.37; S, 4.59.

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