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Characterization and optical properties of tetrapyrazinoporphyrazines with phenylene dendron group

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Abstract

The treatment of the ethynyl compound **3** with one equivalent of 3,4-bis-(4-methoxyphenyl)-2,5-diphenyl-cyclopenta-2,4-dienone in degassed *p*-xylene afforded the corresponding 2,3-dicyanopyrazine derivatives containing a phenylene dendron group (**4**). The absorption spectra of the tetrapyrazinoporphyrazinato copper complexes (**5**) with long alkyl groups dramatically changed due to molecular aggregation depending on the polarity of the solvent. The variation in their aggregation behaviors depending on the polarity of the solvent was well correlated with their chemical structures.

Keywords: Dendrimers; Porphyrazine; Absorption spectra; Aggregation

1. Introduction

Owing to their potential applications as photosensitizers in solar energy conversion [1] and photodynamic therapy [2] applications, phthalocyanines and their metal complexes have recently received considerable attention. Their properties were found to be influenced by the nature of the peripheral substituents and the central metal ion. In the case of phthalocyanine macrocycles having long alkyl chains, segregation occurred between the rigid aromatic moieties and the flexible alkyl chains, leading to the formation of a columnar mesophase. One of the intrinsic problems of using phthalocyanine macrocycles is their strong proclivity for stacking which leads them to form aggregated species in solution [3]. It has been found that such stacking can lead to efficient nonradioactive energy relaxation, thereby reducing their triplet-state population and, consequently, significantly decreasing their photosensitizing efficacy [4].

On the other hand, dendrimers are macromolecules with highly branched and regular structural units [5]. A dendritic shell could create a distinct microenvironment for the incorporated core and enable it to have unique photochemical, photophysical, electrochemical, and catalytic properties. Polyphenylene dendrons, which are characterized by their shape-persistent structure and out-of-plane twisted phenyl components, have been successfully attached to various functional groups [6,7]. We were recently able to develop convenient methods of synthesizing a new type of porphyrazine containing both flexible (linear) and more rigid (dendritic) groups. In this paper, we report a general method for the synthesis of 2,3-dicyanopyrazines and their conversion to copper porphyrazines equipped with polyphenylene dendrons, which shows that the polyphenylene dendrimers increase the solubility of porphyrazine in common organic solvents. The variation in their aggregation behaviors depending on the polarity of the solvent was well correlated with their chemical structures.

2. Results and discussion

2.1. Synthesis of 5-(4-ethynylphenyl)-6-(4-alkoxyphenyl)-pyrazine-2,3-dicarbonitrile derivatives and tetrapyrazinoporphyrazines

1,2-Bis-(4-methoxyphenyl)-ethane-1,2-dione (**1**) was prepared by a method described in a previous report [8]. The

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condensation reaction of compound **1** with one equivalent of 1,3-diphenylacetone in the presence of potassium hydroxide under reflux conditions gave 3,4-bis-(4-methoxyphenyl)-2,5-diphenyl-cyclopenta-2,4-dienone (**2**) in a yield of 85% after recrystallization from methanol (Scheme 1).

The preparation of 5-(4-ethynylphenyl)-6-(4-alkoxyphenyl)-pyrazine-2,3-dicarbonitrile (**3**) has been described in literature [9]. The linear long alkyl ether moiety was chosen to improve the solubility of the resulting porphyrazines in common organic solvents. The treatment of compound **3** with one equivalent of compound **2** in degassed *p*-xylene afforded the corresponding 2,3-dicyanopyrazine derivatives (**4**). The ^{1}H NMR spectrum of compound **4c** indicated that the $-CH_3$ protons appeared as a triplet at 0.88 ppm and that the two $-OCH_3$ signals appeared as singlets at 3.64 and 3.67 ppm, respectively.

The tetrapyrazinoporphyrazinato copper complexes (**5**) were prepared by reacting compound **4** with one equivalent of cuprous chloride in *o*-dichlorobenzene in the presence of hexaammonium heptamolybdate tetrahydrate as a catalyst, and were obtained in a yield of 20–23% after purification by silica-gel column chromatography (Scheme 2). The synthesized tetrapyrazinoporphyrazinato copper complexes (**5**) were characterized by UV–vis spectroscopy, MALDI-TOF-MS (matrix-assisted laser desorption ionization time-of-flight mass) spectroscopy, elemental analysis and ^{1}H NMR spectroscopy. Fig. 1 shows the spectrum of compound **5c** in $CDCl_3$ at 25 °C, which provides structural information. In the aliphatic region, a broad singlet resonance corresponding to the *O*-methylene protons (O-CH_2) is observed at 4.02 ppm. The proton resonances in the aromatic region of compound **5c** are observed in the form of a broad peak in the corresponding range, due to the intermolecular interaction, as shown in Fig. 1. The reaction pathways are summarized in Scheme 2.

2.2. Optical properties (absorption and emission spectra)

The absorption and fluorescence maxima of the dicyanopyrazine compounds **4** were observed at 398 nm and 433 nm, respectively. The Stokes shift, which indicates the energy loss in the excited state, was 35 nm. Compounds having a smaller Stokes shift are able to convert their absorption energy to fluorescence more efficiently.

The Q-band spectra caused by the first π–π* transition of the tetrapyrazinoporphyrazinato copper complex (**5**) equipped with polyphenylene dendrons in chloroform showed the characteristic pattern for a monomeric species, and the fluorescence maxima excited at the B-band maxima (384 nm) were observed at around 492 nm.

Fig. 2 shows the effect of solvent polarity on the absorption spectra of the porphyrazine **5c** when carbon tetrachloride was added to the chloroform solution. As the ratio of carbon tetrachloride to chloroform was increased, the absorptions at 640–670 nm and 590–610 nm decreased. The Q-band spectra in CCl_4 show the characteristic pattern of dimeric and/or polymeric species, which are replaced at lower concentration with the spectral envelope. Isosbestic points were observed at around 410 nm, 565 nm, 640 nm and 682 nm, and equilibrium mixtures of monomers and aggregate were included in the solution.

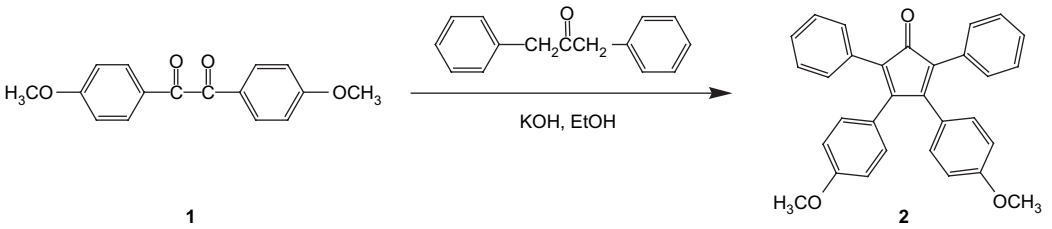
Fig. 3 shows the temperature dependence of the absorption spectra of the porphyrazine **5c** in dimethylsulfoxide (DMSO) solution. The aggregate species were much more predominant at lower temperature, whereas the monomeric species became more predominant as the temperature was increased. The temperature dependencies of the absorption spectra of these porphyrazines allow them to be used as an optical shutter when embedded in window glasses. The potential applications of these new porphyrazines as functional π-electron materials are currently under investigation. Similar changes in molecular aggregation were also observed depending on the concentration of the porphyrazines (**5**). As the concentration of the porphyrazine (**5c**) in DMSO was increased (from 6.7×10^{-6} mol/l to 6.7×10^{-5} mol/l), the absorption at 664 nm decreased (Fig. 4).

In summary, we have synthesized a new type of tetrapyrazinoporphyrazinato copper complex equipped with polyphenylene dendrons from 2,3-dicyanopyrazines. Tetrapyrazinoporphyrazinato copper complexes (**5**) with long alkyl groups dramatically changed its absorption spectra by molecular aggregation depending on the polarity of solvent. Molecular aggregations and their functionality as nonlinear optical (NLO) materials will be reported elsewhere.

3. Experimental

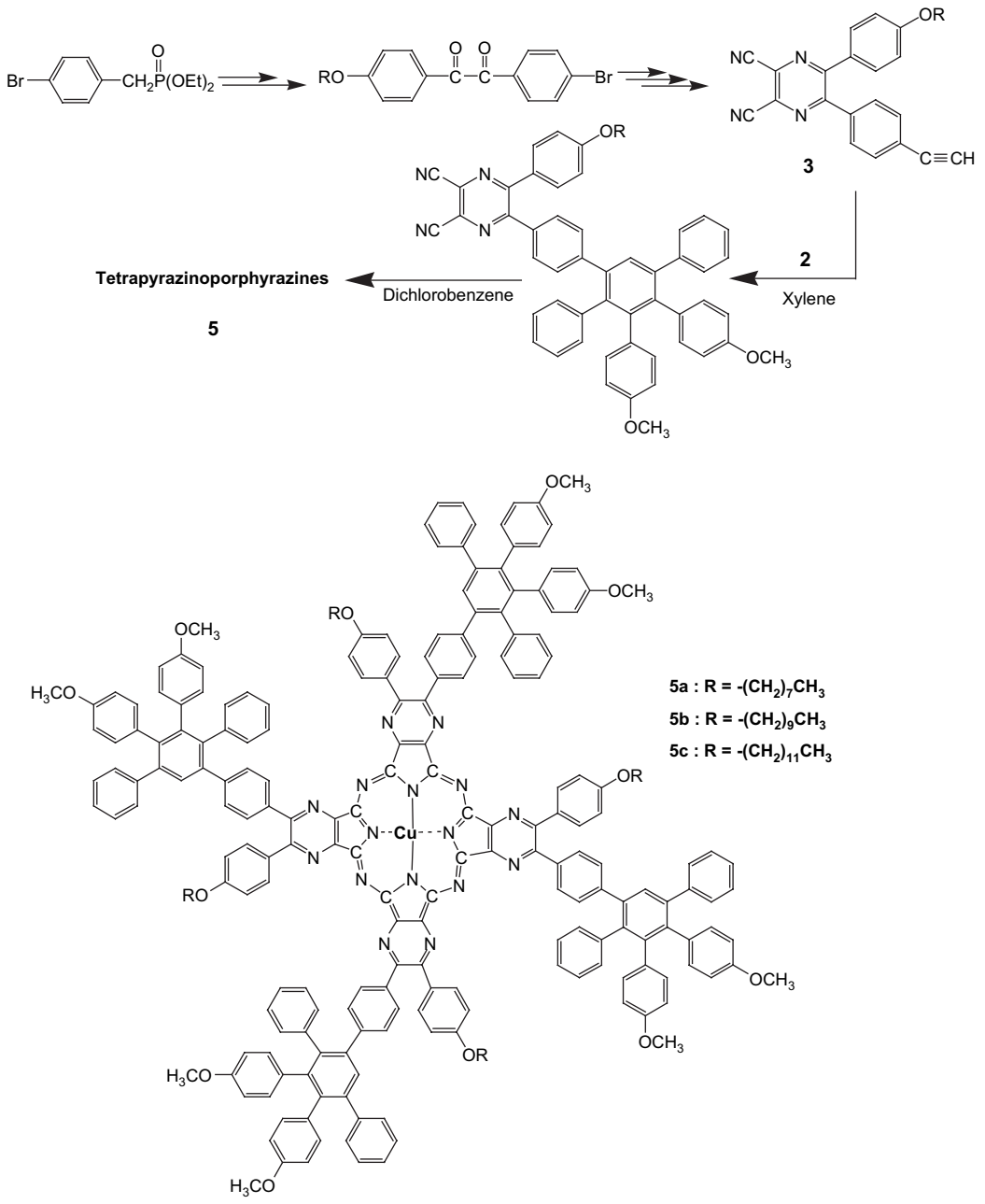
3.1. General

All reactions were carried out under N_2 atmosphere unless otherwise noted. 1,2-Bis-(4-methoxyphenyl)-ethane-1,2-dione [8] and 5-(4-ethynylphenyl)-6-(4-alkoxyphenyl)-pyrazine-2,3-dicarbonitrile [9] were prepared by the known methods.



1 2

Scheme 1.



Scheme 2.

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 spectrophotometer. 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. 3,4-Bis-(4-methoxyphenyl)-2,5-diphenyl-cyclopenta-2,4-dienone (**2**)*

A solution of 10 mmol of compound **1** and 10.5 mmol of 1,3-diphenylacetone in 25 ml of ethanol was heated at reflux and 300 mg of KOH in 2 ml of hot ethanol was carefully added in two portions. The solution turned dark red and the product, being less soluble than the starting material, precipitated. The reaction mixture was refluxed for 6 h. After the reaction was complete, the product was filtered, washed with distilled water followed by ethanol. The crude product was recrystallized from methanol.

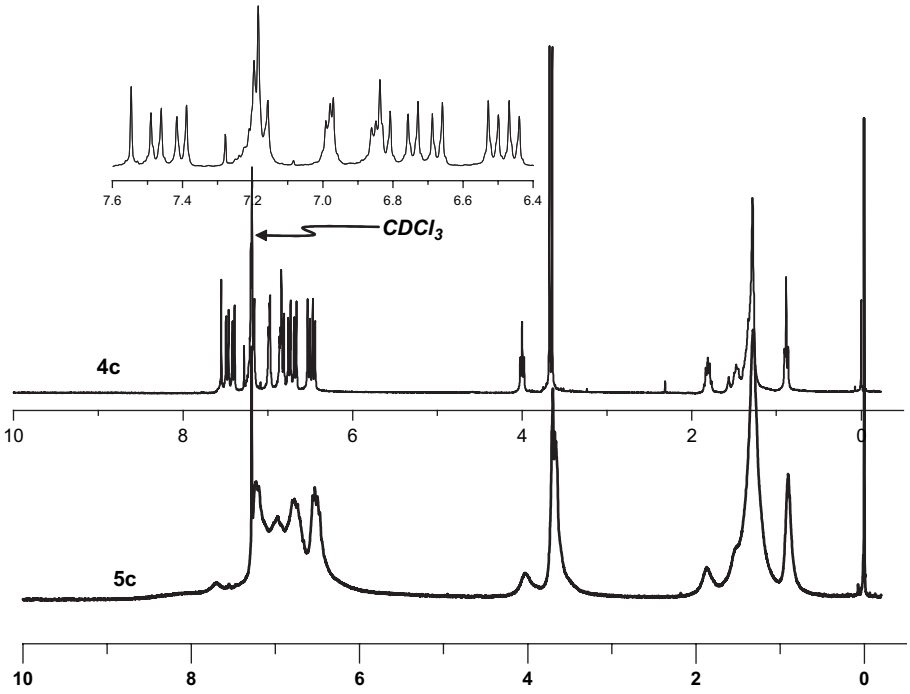


Fig. 1. ^{1}H NMR (300 MHz) spectra of compounds **4c** and **5c**.

Yield 85%, m.p. 220–221 °C; ^{1}H NMR (DMSO-d_6) δ (ppm) 3.72 (s, 6H, OCH_3), 6.79 (d, 4H, $J = 9.0$, ArH), 6.82 (d, 4H, $J = 9.0$, ArH), 7.14 (d, 4H, $J = 6.0$, ArH), 7.16 (m, 6H, $J = 6.0$, ArH).

Anal. Calcd. for $C_{31}H_{24}O_3$: C, 83.76; H, 5.44. Found: C, 83.80; H, 5.37.

*3.3. Typical procedure to synthesize compound **4** with 3,4-bis-(4-methoxyphenyl)-2,5-diphenyl-cyclopenta-2,4-dienone (**2**) and 5-(4-ethynylphenyl)-6-(4-dodecyloxyphenyl)-pyrazine-2,3-dicarbonitrile (**3**)*

The mixture of compounds **2** (4.7 mmol), **3** (4.7 mmol) and *p*-xylene (12 ml) was degassed and refluxed under argon atmosphere for 20 h. After the reaction was completed, the mixture was added to cold ethanol and the precipitate was filtered off. The crude product was purified by column chromatography in silica gel, eluting with hexane:ethylacetate (4:1).

*3.3.1. Compound **4a***

Yield 68% , m.p. 96–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.9$, CH_3), 1.28–1.55 (m, 10H, CH_2), 1.88 (m, 2H, CH_2), 3.63 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.99 (t, 2H, $J = 6.9$, OCH_2), 6.42 (d, 2H, $J = 8.9$, ArH), 6.45 (d,

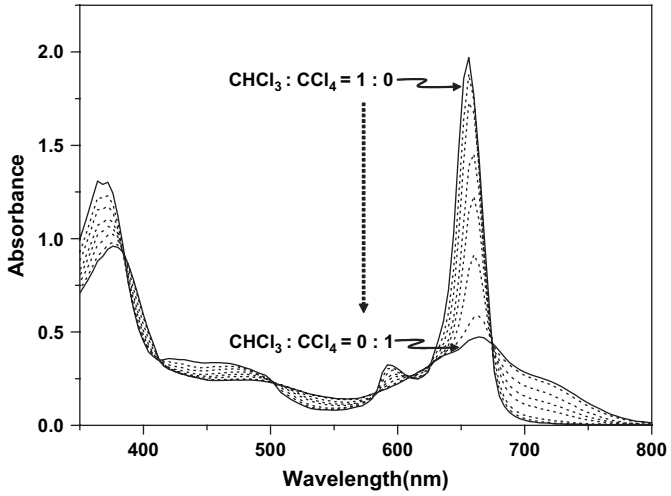


Fig. 2. The effects of carbon tetrachloride on the absorption spectra of compound **5c** in chloroform.

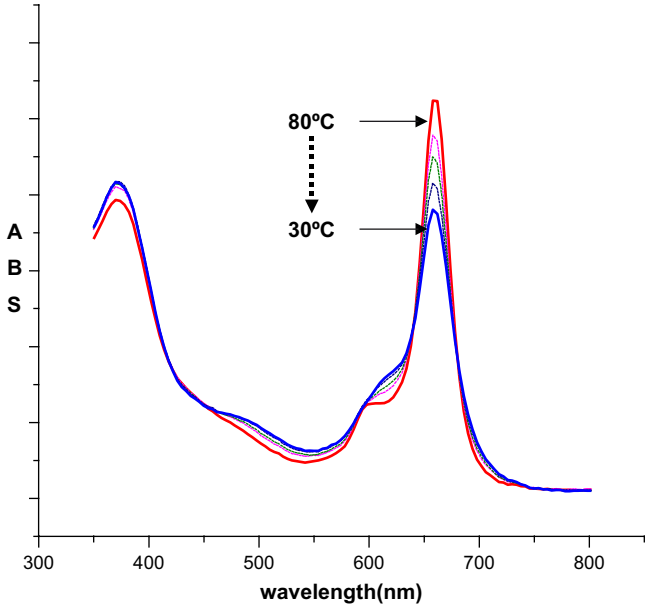


Fig. 3. Temperature dependence of the absorption spectra of compound **5c** in DMSO.

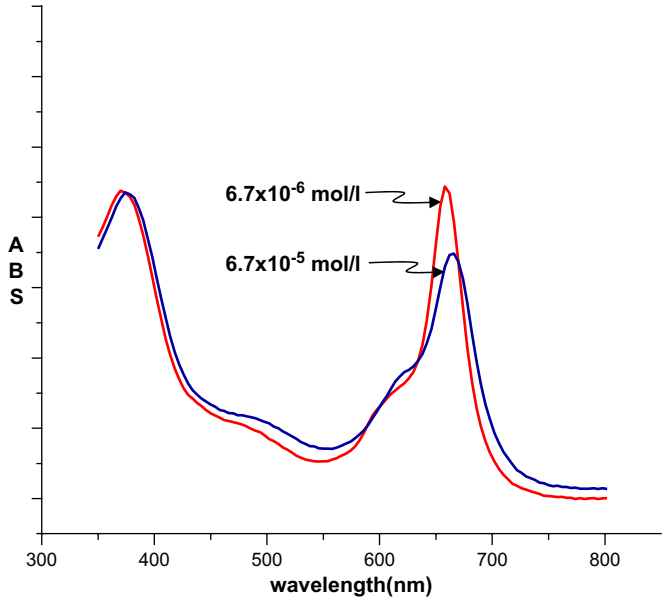


Fig. 4. Concentration dependence on the absorption spectra of compound **5c** (6.7×10^{-6} mol/l − 1 cm cell and 6.7×10^{-5} mol/l − 0.1 cm cell) in DMSO.

2H, $J = 8.9$, ArH), 6.51 (d, 2H, $J = 8.6$, ArH), 6.64 (d, 2H, $J = 8.6$, ArH), 6.79–6.82 (m, 4H, ArH), 6.96 (m, 2H, ArH), 7.14–7.18 (m, 8H, ArH), 7.39 (d, 2H, $J = 8.3$, ArH), 7.47 (d, 2H, $J = 8.9$, ArH), 7.52 (s, 1H, ArH).

Calcd. for $C_{58}H_{50}N_4O_3$: C, 81.85; H, 5.92; N, 6.58. Found: C, 82.03; H, 5.93; N, 6.41.

3.3.2. Compound **4b**

Yield 72%, m.p. 83–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.9$, CH_3), 1.28–1.33 (br s, 14H, CH_2), 1.88 (m, 2H, CH_2), 3.63 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.99 (t, 2H, $J = 6.9$, OCH_2), 6.44 (d, 2H, $J = 8.9$, ArH), 6.50 (d, 2H, $J = 8.9$, ArH), 6.66 (d, 2H, $J = 8.6$, ArH), 6.73 (d, 2H, $J = 8.6$, ArH), 6.79–6.82 (m, 4H, ArH), 6.96 (m, 2H, ArH), 7.14–7.18 (m, 8H, ArH), 7.38 (d, 2H, $J = 8.3$, ArH), 7.46 (d, 2H, $J = 8.9$, ArH), 7.53 (s, 1H, ArH).

Calcd. for $C_{60}H_{54}N_4O_3$: C, 81.98; H, 6.19; N, 6.37. Found: C, 82.15; H, 6.02; N, 6.28.

3.3.3. Compound **4c**

Yield 71%, m.p. 82–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.9$, CH_3), 1.28–1.55 (m, 18H, CH_2), 1.88 (m, 2H, CH_2), 3.63 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.99 (t, 2H, $J = 6.9$, OCH_2), 6.42 (d, 2H, $J = 8.9$, ArH), 6.45 (d, 2H, $J = 8.9$, ArH), 6.48 (d, 2H, $J = 8.6$, ArH), 6.51 (d, 2H, $J = 8.6$, ArH), 6.79–6.82 (m, 4H, ArH), 6.96 (m, 2H, ArH), 7.14–7.18 (m, 8H, ArH), 7.39 (d, 2H, $J = 8.3$, ArH), 7.47 (d, 2H, $J = 8.9$, ArH), 7.52 (s, 1H, ArH).

Calcd. for $C_{62}H_{58}N_4O_3$: C, 82.09; H, 6.44; N, 6.18. Found: C, 82.01; H, 6.51; N, 6.11.

3.4. Typical procedure to synthesize tetrapyrazinoporphyrazinato copper complexes (**5**)

The mixture of compound **4** (1 mmol) and CuCl (1 mmol) was refluxed in 1,2-dichlorobenzene (5 ml) in the presence of hexaammonium heptamolybdate tetrahydrate as catalyst. After refluxing for 8 h, the solvent was removed partially *in vacuo*. The crude product was purified by column chromatography in silica gel, eluting with chloroform.

3.4.1. Compound **5a**

Yield 22%, m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (br s, 12H, CH_3), 1.31–1.46 (br s, 40H, CH_2), 1.87 (br s, 8H, CH_2), 3.70 (br m, 24H, OCH_3), 3.99 (br s, 8H, OCH_2), 6.47–7.23 (br m, 108H, ArH).

Calcd. for $C_{232}H_{200}N_{16}O_{12}Cu$: C, 80.35; H, 5.81; N, 6.46. Found: C, 81.01; H, 6.04; N, 6.33. MALDI-TOF-mass-spectrum: *m/z*: 3468.37 (100%, M^+, calcd. 3467.72).

3.4.2. Compound **5b**

Yield 20%, m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (br s, 12H, CH_3), 1.31–1.46 (br s, 56H, CH_2), 1.87 (br s, 8H, CH_2), 3.70 (br m, 24H, OCH_3), 3.99 (br s, 8H, OCH_2), 6.47–7.23 (br m, 108H, ArH).

Calcd. for $C_{240}H_{216}N_{16}O_{12}Cu$: C, 80.52; H, 6.08; N, 6.26. Found: C, 81.01; H, 6.20; N, 6.13. MALDI-TOF-mass-spectrum: *m/z*: 3580.47 (100%, M^+, calcd. 3579.95).

3.4.3. Compound **5c**

Yield 23%, m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (br s, 12H, CH_3), 1.31–1.46 (br s, 72H, CH_2), 1.87 (br s, 8H, CH_2), 3.70 (br m, 24H, OCH_3), 3.99 (br s, 8H, OCH_2), 6.47–7.23 (br m, 108H, ArH).

Calcd. for $C_{248}H_{232}N_{16}O_{12}Cu$: C, 80.68; H, 6.33; N, 6.07. Found: C, 81.43; H, 6.42; N, 6.18. MALDI-TOF-mass-spectrum: *m/z*: 3693.55 (100%, M^+, calcd. 3692.14).

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