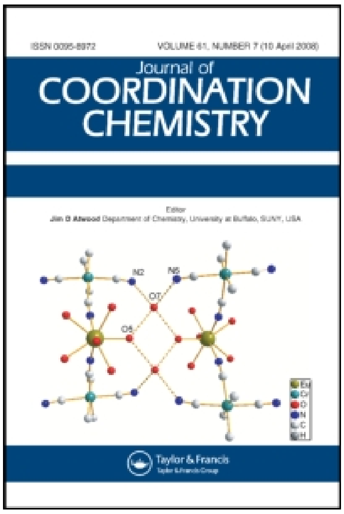

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Synthesis and characterization of new metal-free and nickel(II) phthalocyanines containing hexaazadioxa macrobicyclic moieties

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Synthesis and characterization of new metal-free and nickel(II) phthalocyanines containing hexaazadioxa macrobicyclic moieties

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Novel symmetrically tetrasubstituted metal-free and metallophthalocyanines (**5**) and (**6**) which contain four hexaazadioxamacrobicycles on peripheral positions, have been synthesized. Macrobicyclic compound **3** and has been prepared by reaction of (1,3,6,9,11,14- hexa-azatricyclo[12.2.1.1^{6,9}])octadecane (**1**) with 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**2**). Compound **4** has been synthesized by reaction of compound **3** with CuCN in dry DMF. The target symmetrical phthalocyanines were separated by column chromatography and characterized by elemental analyses, ^{1}H, ^{13}C–NMR, IR, UV–Visible and FAB mass spectroscopies.

Keywords: Phthalocyanines; Macrobicycles; Metallophthalocyanines; Mixed-donors

1. Introduction

The increasing importance and use of phthalocyanines (pcs) as advanced materials have created impetus for design variables of the central metal ion and peripheral substituents to reach the planned properties.

Phthalocyanine and metallophthalocyanines, commonly used for many years as dyes and catalysts, have recently been investigated [1, 2]. A new generation of phthalocyanine derivatives with purpose-designed substitution patterns has developed [3, 4]. Thanks to development of synthetic methodology during the last two decades, these compounds and many of their derivatives exhibit properties that are interesting for technical applications in high technology fields such as semiconductor devices, molecular electronics, electrochromic display devices, photovoltaic and solar cells, gas sensors, corrosion inhibitors, liquid crystals, non-linear optics, optical disks, electro-photography, photodynamic cancer therapy and antimycotic material [5–8]. The peripheral substitution of aromatic rings by long alkyl or alkoxy chains [9], crown ethers or azacrown moieties enhances their solubility drastically [10–12]. The rich

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coordination chemistry of phthalocyanine complexes has encouraged researchers to 'tailor' specific products with certain properties which are required for high technology applications.

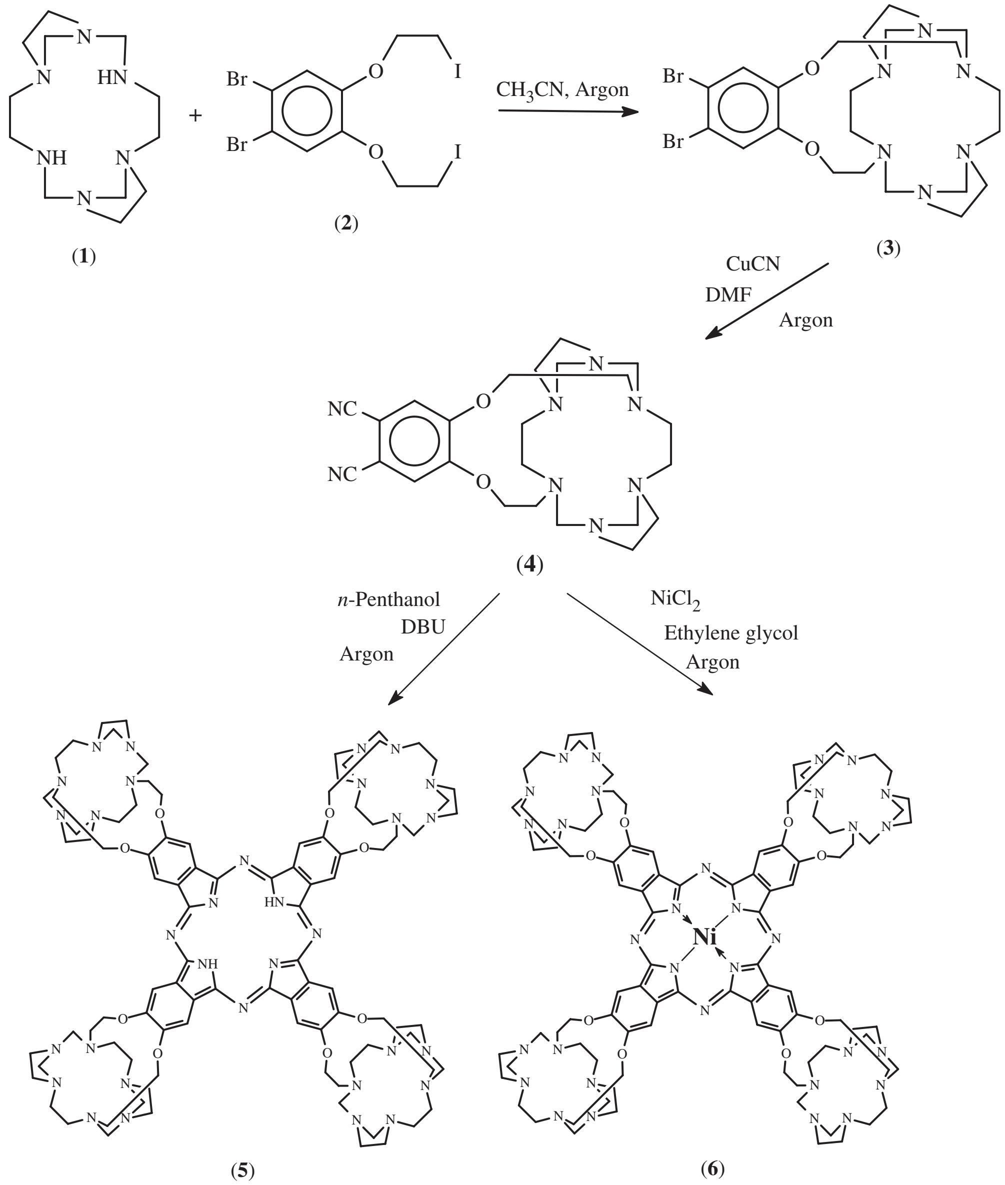
Three-dimensional polycyclic ligand systems named cryptands have recently been investigated intensively with respect to their strong selectivity towards individual alkali and alkaline earth metal cations [13, 14]. The majority of these ligands contain donor sets in which polyether donor functions predominate. However, compounds incorporating higher numbers of mixed donors such as diaza and/or dithia groups have also been synthesized [15, 16]. To enhance the coordinating properties of these macrocycles, different modifications have been made such as ring size, the nature of substituents, and the type of donor atoms [17]. recovery of valuable metal pollutants from air and water is very important. On the other hand, a generalized chelate effect, the cryptate effect, which causes high complexation stability, occurs in the formation of three-dimensional inclusion complexes than in the macrocyclic effect [18, 19].

We have previously described the synthesis of free and metal phthalocyanines which contain four 20-membered diazatetraoxa macrocycles each attached to a 15-crown-5 unit [20] and macrobicyclic moieties which contain tetrathiadiaza mixed-donor atoms [21]. In the present work, the synthesis and characterization of metal-free **5** and metallophthalocyanine (**6**) are described. These new compounds may allow new functionalized materials to be prepared, which are of importance for analytical chemistry as novel heavy metal extraction agents.

2. Results and discussion

Preparations of the target metal-free **5** and **6** are shown in scheme 1. Compound **3** was synthesized by reaction of (1,3,6,9,11,14-hexaazatricyclo[12.2.1.1.6.9]octadecane [22] **1** with 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene [23] **2** in acetonitrile containing finely ground anhydrous Na_2CO_3 as a template agent at reflux temperature in a Schlenk system under argon. The hexaazadioxa macrobicyclic compound **3** was obtained in 42.13% yield (scheme 1). Formation of **3** is evident by the characteristic changes in IR vibrations. The occurrence of a single band at 3085 and 1250–1220 cm^{-1} is attributable to the presence of Ar–H and Ar–O–C resonances, respectively, diagnostic of macrobicyclization. The disappearance of bands characteristic of N–H groups also confirms the formation of **3**. In the ^1H NMR spectra of this compound, the chemical shifts of NH protons in **1** disappear after the macrobicyclization reaction. The other resonances in the ^1H NMR and ^{13}C NMR spectra, concerning OCH_2, NCH_2 and aromatic protons and carbons, are very similar to those of the precursor compounds **1** and **2**. The mass spectra of this compound shows the base peak at $m/z = 574.4$, corresponding to the proposed formulation $[M]^+$.

Compound **4** was synthesized by treating the macrobicycle **3** with three equivalents of the CuCN according to the Rosenmund von Braun reaction [24] in a moderately high-boiling solvent such as dimethyl formamide [25] to avoid the formation of Cu(II) phthalocyanine derivative [26]. The Ar–Br groups of compound **3** were converted to a leaving group via a standard step to afford dicyano derivative **4** in an overall 65.48% yield. Comparison of the IR spectra of **3** and **4** clearly shows the conversion of the aromatic bromo substituents into the cyano form by the disappearance of the



Scheme 1. The synthesis of metal-free and metallophthalocyanines.

C–Br vibrations at 651 cm^{-1} in **3** so the sharp stretching vibrations at 2227 cm^{-1} was easily verified as C≡N absorptions. The ^{1}H NMR spectrum of **4** closely resembles that of **3** as expected. In the ^{1}H NMR of **4** in chloroform shows a singlet at $\delta = 7.66$ ppm, indicating the presence of Ar–H protons. Owing to formation chemical shifts of **4** which belong to Ar–H protons appear downfield approximately 0.33 ppm [10]. The proton-decoupled ^{13}C NMR spectrum of **4** shows C≡N as a singlet at $\delta = 113.82$ ppm, indicating substitution of the C–Br groups in **3**. Chemical shifts belonging to aromatic, crown or azacrown carbons are very close to those of **3**. In the mass spectrum of **4**, medium $[M + 1]^+$ peaks are observed for this compound $m/z = 467.3$ and at $m/z = 490.3$ together with strong $[M + Na + 1]$ peaks, and this can be attributed to the substitution reaction which occurred between C–Br with C≡N in **4**.

Condensation of four molecules of the dinitrile derivative of macrobicyclic compound **4** into the metal-free phthalocyanine (**5**) was carried out in a standard Schlenk tube with a high-boiling solvent (*n*-pentanol) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux for 24 h under argon. The target compound **5** was obtained in a 44.05% yield as a dark green solid after purification by chromatographic separation on silica gel [methanol : chloroform (1 : 9)]. Comparing the IR spectrum of metal-free **5** to that of **4**, the proposed structure is confirmed by disappearance of the C≡N vibration at 2227 cm^{-1} and the appearance of medium new absorptions at 3230 and 1645 cm^{-1} attributable to N–H and C=N groups, respectively [27, 28]. The inner core N–H protons of the metal-free phthalocyanine were also identified in the ^1H NMR spectrum. Strong shielding of the cavity protons in the phthalocyanine core of this compound was manifested by a broad resonance at $\delta = -4.32$ ppm [29, 30] at high concentration, which could be attributed to the NH resonance and identified easily with deuterium exchange. In the ^1H NMR spectrum of **5**, the signals related to aromatic and aliphatic protons of the macrobicycles and phthalocyanine skeleton are characteristic of the proposed structure. This spectrum closely resembles that of **4** as expected. A distinct difference encountered in the ^1H NMR spectra of **4** and **5**, when compared with previously obtained polymacrocycle substituted derivatives are the sharp signals, which indicate a lower tendency to aggregate even at concentration used for proton nmr measurements [31]. The proton-decoupled ^{13}C NMR spectrum of **5** gave characteristic absorbances of the given structure. This spectrum closely resembles that of the dicyano derivative compound **4**, the differences being the signals of carbon atoms of the cyano groups at $\delta = 113.82$ ppm and the phthalocyanine ring (C=N) at $\delta = 150.30$ ppm. The mass spectrum of metal-free phthalocyanine (**5**) was obtained by the LS-MS MS technique and the molecular ion peaks at $m/z = 1867.4$ $[M + 1]^+$ and at $m/z = 1890.4$ $[M + Na + 1]$ were observed.

The cyclotetramerization of macrobicyclic dicyano derivative **4** in the presence of anhydrous metal salt gave the nickel(II) phthalocyanine (**6**). The high boiling solvent for this reaction was quinoline for Ni(II) [32]. In the IR spectrum of this compound, the stretching vibrations at 2227 cm^{-1} belonging to C≡N group disappear after formation of **6**. A diagnostic feature of the cyclotetramerization reaction of **4** is the C=N stretching vibration at 1620 cm^{-1}. The significant difference is the absence of N–H vibration of the inner phthalocyanine core which is assigned to the expected result. The ^1H NMR spectrum of nickel(II) phthalocyanine (**6**) in chloroform shows a singlet at $\delta = 7.62$ ppm for aromatic protons. Aliphatic protons which belong to Ar–O–CH_2, and NCH_2 appear at $\delta = 4.22$ and 3.76, respectively, in accord with precursor compound **4** and metal-free phthalocyanine (**5**). The proton decoupled ^{13}C NMR spectrum of **6** showed a singlet nmr absorbance at $\delta = 149.25$ ppm for identical carbons that made up the phthalocyanine ring. The ^{13}C NMR characteristics of nickel(II) phthalocyanine (**6**) were quite similar to those of **4** and **5** except the disappearance of the chemical shift of C≡N. The mass spectrum of Ni(II) phthalocyanine gave the $M + 1$ and $M + Na + 1$ peaks at $m/z = 1924.04$ and 1947.04, respectively, instead of the molecular ion.

The best indications for phthalocyanine systems are given by their UV–Vis spectra in solution (figure 1). The electronic spectra of phthalocyanines (**5**) and (**6**) show

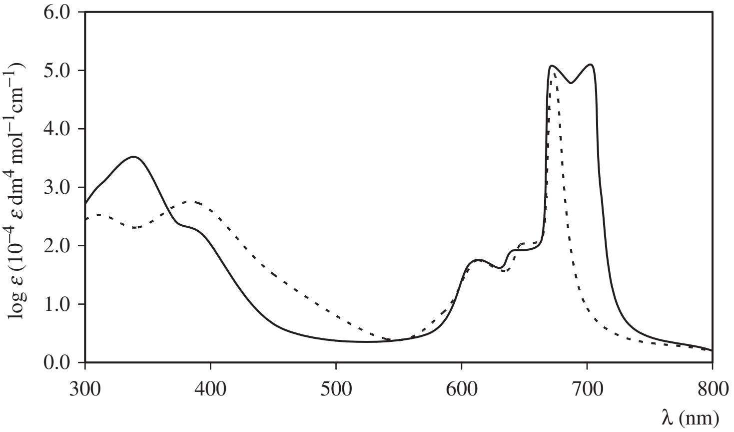


Figure 1. UV-Vis spectra of metal-free **5** and nickel(II) phthalocyanine (**6**). — (**5**), — (**6**).

the typical B and Q bands of symmetrical macrobicyclic substituted *P*c as illustrated in figure 1. In the UV–Vis spectrum of **5** in chloroform, the characteristic split Q bands were observed with absorptions at 705 and 670 nm. These intense Q bands indicate monomeric species as species with D_{2h} symmetry show two intense absorptions around 700 nm [33–35]. Such split Q band absorptions are due to the $\pi \Rightarrow \pi^*$ transition from the HOMO to the LUMO of the phthalocyanine ring related to the fully conjugated 18 Π electron system. The presence of strong absorption bands in **5** in the UV region at λ_{max} 400 and 300 nm shows superimposed bands of the phthalocyanine due to the existence of Soret band of *Pc* which have been ascribed to the deeper $\pi \Rightarrow \pi^*$ LUMO transitions [36]. However, in the Ni(II) derivative the average Q-bands are slightly shifted to the blue with respect to the parent metal-free compound [37]. The position of Q band of **6** changed due to the Ni(II) without splitting and centered around 674 nm. The single Q band in metallo derivative and splitting in its metal-free counterpart is characteristic [38]. Observed peaks, as mentioned above, indicate that the symmetry of the molecule has changed. This result is typical of metal complexes of substituted and unsubstituted *Pc* with D_{4h} symmetry [39].

3. Experimental

All reactions were carried out under argon using standard Schlenk techniques. The IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer, using KBr pellets or NaCl discs. ^{1}H and ^{13}C–NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analysis and metal content of these compounds were determined by a LECO Elemental Analyzer (CHNS O932) and Unicam 929 AA spectrophotometer. Electronic spectra were recorded on a Unicam UV–Vis spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected. (1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}])octadecane (**1**) [22] and 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**2**) [23] were synthesized according to reported procedures. Commercially available solvents were dried and purified by conventional procedure [40].

3.1. *5,6-(2′-3′-dibromobenzo)-4,7-dioxa-10,12,15,19,2 hexaazatetracyclo-[8.7.7^{12,15}.1^{19,22}] hexacosane (3)*

A two-necked round flask 500 mL containing dry acetonitrile (72 mL) and fitted with a condenser was evacuated and refilled two times with argon. Under argon, the flask was charged with (1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}])octadecane (**1**) [23] (2.009 g, 7.916 mmol), 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**2**) [24] (4.56 g, 7.916 mmol) and finely ground anhydrous Na_2CO_3 (2.09 g, 19.79 mmol) in dry acetonitrile (50 mL) and the reaction mixture was heated and stirred at 85°C for 168 h. The reaction was monitored by thin layer chromatography [chloroform : methanol (9 : 1)]. At the end of this period, the mixture was cooled to room temperature, filtered, and washed with cold dry acetonitrile. The filtrate was evaporated to dryness under reduced pressure. The product was isolated by two successive column chromatographic separations [silica gel; chloroform : petroleum ether (7 : 3) and chloroform : methanol (9 : 1)], as a pale yellow oil. Yield: 1.90 g (42.13%). Anal. Calcd for $C_{22}H_{34}O_2N_6Br_2$ (%): C, 45.99; H, 5.92; N, 14.63. Found: C, 45.20; H, 5.98; N, 15.01. (EI) MS $m/z = 574.4$ $[M]^+$. Ir (NaCl disc) ν_{max}/cm^{-1}: 3085(Ar–H), 2927–2846 (Aliph-H), 1581–1485–1459 (Ar-Skelt. vib.), 1250–1220 (Ar–O–C), 651 (C–Br). ^1H NMR ($CDCI_3$): $\delta = 7.99$ (s, 2H, Ar–H), 4.24 (t, 4H, OCH_2), 3.87 (t, 4H, NCH_2), 3.44 (s, 8H, NCH_2), 3.01 (t, 8H, NCH_2CH_2–N), 2.94 (t, 8H, CH_2–CH_2). ^{13}C NMR ($CDCI_3$): $\delta = 147.33$, 139.48, 128.73, 69.91, 69.41, 54.80, 53.05, 50.43, 46.9.

3.2. *5,6-(2′-3′-dicyanobenzo)-4,7-dioxa-1,10,12,15,19,2 hexaazatetracyclo-[8.7.7^{12,15}.1^{19,22}] hexacosane (4)*

A mixture of **3** (1.0352 g, 1.79 mmol), CuCN (0.48 g, 5.38 mmol) and dry pyridine (0.08 mL) in dry DMF (12.6 mL) were refluxed under argon for 40 h. The mixture was cooled to room temperature and then poured into aqueous ammonia (30 mL). After stirring for 2 h, the mixture was extracted with chloroform. The combined organic layers were washed with water, dried over anhydrous $MgSO_4$ and then concentrated. The residue was purified by silica gel chromatography with chloroform. The product, obtained as a pale brown oil, is soluble in chloroform, dichloromethane, and ethanol. Yield: 0.55 g (65.48%). Anal. Calcd for $C_{24}H_{34}O_2N_8$ (%): C, 61.80; H, 7.29; N, 24.03. Found: C, 61.45; H, 7.07; N, 24.32. (EI) MS $m/z = 467.3$ $[M + 1]^+$, 490.3 $[M + Na + 1]$. Ir (NaCl disc) ν_{max}/cm^{-1}: 3054 (Ar–H), 2927–2856 (Aliph-H), 2227 ($C{\equiv}N$), 1505–1461 (Ar-Skelt vib.), 1270–1216 (Ar–O–CH_2). ^1H NMR ($CDCI_3$): $\delta = 7.66$ (s, 2H, Ar–H), 4.30 (t, 4H, OCH_2), 3.58 (t, 4H, NCH_2), 3.47 (s, 8H, NCH_2), 3.10 (t, 8H, NCH_2 CH_2–N), 2.89 (t, 8H, CH_2–CH_2). ^{13}C NMR ($CDCI_3$) δ: 146.82, 129.34, 127.22, 113.82, 66.56, 53.42, 51.107, 46.52.

3.3. *Metal-free phthalocyanine (5)*

A solution of **4** (0.2041 g, 0.438 mmol) was heated in dry *n*-pentanol (2 mL) in the presence of 1.8-diazabicyclo [5.4.0] undec-7-ene [DBU] (0.064 mL, 0.428 mmol) with stirring and was refluxed for 24 h under argon. The reaction mixture was cooled to room temperature and filtered, washed successively with ethanol, ethyl acetate, diethyl ether and dried. The dark green solid was dissolved in chloroform (5 mL) and purified by silica gel chromatography with [methanol : chloroform (1 : 9)] as the eluent to give **5** as a dark green solid. This compound is soluble in chloroform, dichloromethane, and ethanol. Yield: 0.09 g (44.05%); m.p. 198–200°C. Anal. Calcd for $C_{96}H_{138}N_{32}O_8$ (%): C, 61.73; H, 7.39; N, 24.01. Found: C, 61.56; H, 7.15; N, 24.17. (FAB) MS $m/z = 1867.4$ $[M+1]^+$, 1890.4 $[M+Na+1]$. IR (KBr) ν_{max} cm^{-1}: 3230 (N–H), 3087 (Ar–H), 2925–2853 (Aliph-H), 1645 (C=N), 1270–1206 (Ar–O–CH_2). ^{1}H NMR ($CDCl_3$): $\delta = 7.82$ (s, 8H, Ar–H), 4.28 (m, 16H, OCH_2), 3.80 (m, 16H, NCH_2), 3.41 (s, 32H, NCH_2), 3.10 (m, 32H, NCH_2CH_2N), 2.99 (m, 32H, CH_2–CH_2), −4.32 (s, 2H, NH). ^{13}C NMR ($CDCI_3$): $\delta = 150.30$, 145.38, 130.20, 126.17, 70.82, 69.50, 54.42, 50.82, 44.37. UV-Vis ($CHCl_3$): λ_{max} (nm) [(10^{-5} ε (mol^{-1} cm^{-1}))]: 705 (5.04), 670 (5.02), 640 (1.91), 613 (1.75), 394 (2.18), 342 (3.50).

3.4. *Nickel(II) phthalocyanine (6)*

A mixture of **4** (0.3 g, 0.643 mmol), anhydrous $NiCl_2$ (0.051 g, 0.392 mmol) and anhydrous ethylene glycol (3 mL) was heated and stirred at 200°C for 12°h in a sealed glass tube under argon. After cooling to room temperature, the reaction mixture was treated with methanol (10 mL), stirred 2 h at room temperature and the solvent was evaporated to dryness under reduced pressure. The greenish oil was dissolved in chloroform (10 mL) and two layers were obtained. The chloroform layer was purified by column chromatography with silica gel (chloroform as the eluent). This product is soluble in chloroform, dichloromethane, DMF, THF, and pyridine. Yield: 0.105 g (34%); mp > 300°C. Found Calcd for $C_{96}H_{136}N_{32}O_8Ni$ (%): C, 59.91; H, 7.07; N, 23.29; Ni, 3.07. Found: C, 59.78; H, 7.18; N, 23.41; Ni, 3.14. (FAB) MS $m/z = 1924.04$ $[M+1]^+$, 1947.04 $[M+Na+1]$. IR (KBr) ν_{max} cm^{-1}: 3085 (Ar–H), 2924–2870 (C–H), 1620 (C=N), 1570–1465 (C=C), 1290–1214 (Ar–OCH_2). ^{1}H NMR ($CDCl_3$): $\delta = 7.62$ (m, 8H, ArH), 4.22 (m, 16H, $ArOCH_2$), 3.76 (m, 16H, NCH_2), 3.44 (s, 32H, NCH_2), 3.16 (m, 32H, NCH_2CH_2N), 2.99 (m, 32H, NCH_2CH_2). ^{13}C NMR ($CDCl_3$): $\delta = 149.25$, 146.82, 127.32, 111.28, 70.18–69.25, 52.22, 51.22, 46.38. UV-Vis ($CHCl_3$): λ_{max} (nm) [(10^{-5} ε(mol^{-1} cm^{-1}))]: 674 (4.94), 647 (2.02), 613 (1.75), 390 (2.73).

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