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## Synthesis and characterization of new copperphthalocyanine carrying mixed donor macrocyclic moieties

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The new phthalocyanine peripherally substituted with a twelve-membered dioxadiaz macrocycle was synthesized by cyclotetramerization of 1,2-bis(2-{4'-[(4'-methylphenyl)sulphonyl]-1',7'-dioxo-4',10'-diazacyclododecane})-4,5-dicyanobenzene (**4**) which was obtained from 1,2-bis(2-{4'-[(4'-methylphenyl)sulphonyl]-1',7'-dioxo-4',10'-diazacyclododecane})-4,5-dibromobenzene (**3**). Metallophthalocyanine was also prepared by the reaction of the dicyano-substituted macrocycle in the presence of anhydrous CuCN. The new compounds were characterized by a combination of elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR, IR, electronic and mass spectroscopies.

*Keywords:* Copper(II)phthalocyanine; N<sub>2</sub>O<sub>2</sub>; Mixed-donor macrocycle; Template effect

### 1. Introduction

Metal-free and metallophthalocyanines have been studied extensively since the beginning of the last century. These highly stable macrocyclic  $\pi$ -systems display interesting properties such as light stability and efficient light absorption in the red and visible region of the spectrum that make them potential candidates for applications in optoelectronics, photoconducting materials [1], and photosensitizers for photodynamic therapy [2]. Metallophthalocyanines have been extensively studied in the areas of gas sensors [3], liquid crystals, organic semiconductors, electrocatalysis, and field effect transistors.

Synthetic macropolycyclic polyethers containing intramolecular cavities and clefts of the appropriate size and shape are particularly interesting complexing reagents with regard to molecular recognition. They can form inclusion complexes in which the substrate contained the molecular cage [4]. Owing to their architectural and functional plasticity, macropolycyclic systems are especially attractive for designing both biomimetic and receptor molecules for inorganic and organic substrates [5].

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The unsubstituted metallophthalocyanines are colored materials but they are not generally soluble in common organic solvents. However, bulky substituents on the periphery enhance the solubility and the donor atoms of these substituents are capable of complexation [6]. In the past decade, the preparation of various peripherally substituted derivatives has generated interesting novel physical and chemical properties for many different applications in material science [7].

Macrocyclic ligands bearing mixed diazadioxo donors showing high selectivity for complexation of alkali metals, alkaline earth metals and primary alkyl ammonium cations have been of interest in molecular recognition using artificial receptor compounds [8]. Macrocyclic compounds showing lipophilicity are of special interest because of their ability to dissolve inorganic salts in nonpolar organic solvents.

We report here the synthesis and characterization of a new metallophthalocyanine containing eighth  $N_2O_2$  mixed-donor macrocyclic moieties having oxygen atoms adjacent to aromatic rings, as opposed to sulfur atoms in our previous study [9].

## 2. Experimental

### 2.1. Physical measurements

IR spectra were recorded on a Perkin Elmer 1600 FTIR Spectrophotometer, using KBr pellets or NaCl discs.  $^1H$  and  $^{13}C$ NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in  $CDCl_3$ , and chemical shifts are reported ( $\delta$ ) 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 UV2-100 spectrophotometer. Melting points were measured on an electrothermal apparatus and were corrected. 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene [10] and 4'-[(4'-methylphenyl)sulphonyl]-1,7-dioxo-4,10-diazacyclododecane [11] were synthesized according to reported procedures. Commercially available solvents were dried and purified by conventional procedures [12].

### 2.2. Preparation of 1,2-bis(2-{4'-[(4'-methylphenyl)sulphonyl]-1',7'-dioxo-4',10'-diazacyclododecane}-ethoxy)-4,5-dibromobenzene (3)

In a two necked flask, to a stirred mixture of 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene (**1**) (2.32 g, 4.1 mmol) and anhydrous  $Na_2CO_3$  (2.56 g, 24.1 mmol) in  $100\text{ cm}^3$  of dry  $CH_3CN$ , the solution of 4'-[(4'-methylphenyl)sulphonyl]-1,7-dioxo-4,10-diazacyclododecane (**2**) (2.6 g, 8.05 mmol) and anhydrous NaI (1.04 g, 6.9 mmol) in  $100\text{ cm}^3$  of dry  $CH_3CN$  was added dropwise within 1 h, at room temperature under argon. The reaction mixture was stirred for 15 days at  $68^\circ C$ , monitoring the progress with thin layer chromatography. After cooling the mixture was filtered and the solvent was removed under reduced pressure. Solid crude product was extracted in  $CHCl_3$  and evaporated to dryness. The yellowish product (**3**) was purified by using column chromatography [silica gel ( $CHCl_3:CH_3OH$ ) (8.5:1.25)]. Yield: 3.41 g (43.5%),

m.p. 140°C. Anal. Calcd for  $C_{40}H_{56}Br_2N_4O_{10}S_2$ (%): C, 49.18; H, 5.78; N, 5.74. Found: C, 49.35; H, 5.98; N, 5.51. IR (KBr pellets,  $cm^{-1}$ ): 3085 (Ar-H), 2928–2864 (C-H), 1597 (Ar-H), 1581, 1494, 1454, 1340, 1248, 1200, 1160, 1090, 1019, 651.  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.52 (d, 4H, Tos-H), 7.15 (d, 4H, Tos-H), 6.94 (s, 2H, ArH), 3.89 (m, 4H,  $CH_2-O$ ), 3.69 (s, 16H,  $CH_2-O$ ), 3.42 (s, 12H,  $NCH_2$ ), 3.13 (s, 8H,  $NCH_2$ ), 1.21 (s, 6H,  $CH_3$ ).  $^{13}C$ -NMR ( $CDCl_3$ ), ( $\delta$ : ppm): 146.59, 144.55, 132.49, 130.69, 127.79, 118.38, 117.39, 116.00, 70.26–66.63, 55.39, 53.84, 49.95, 21.61. MS ( $m/z$ ): 977  $[M + 1]^+$ .

### 2.3. Preparation of 1,2-bis(2-{4'-[4'-methylphenyl]sulphonyl}-1',7'-dioxo-4',10'-dia-zacyclododecane} ethoxy)-4,5-dicyanobenzene (4)

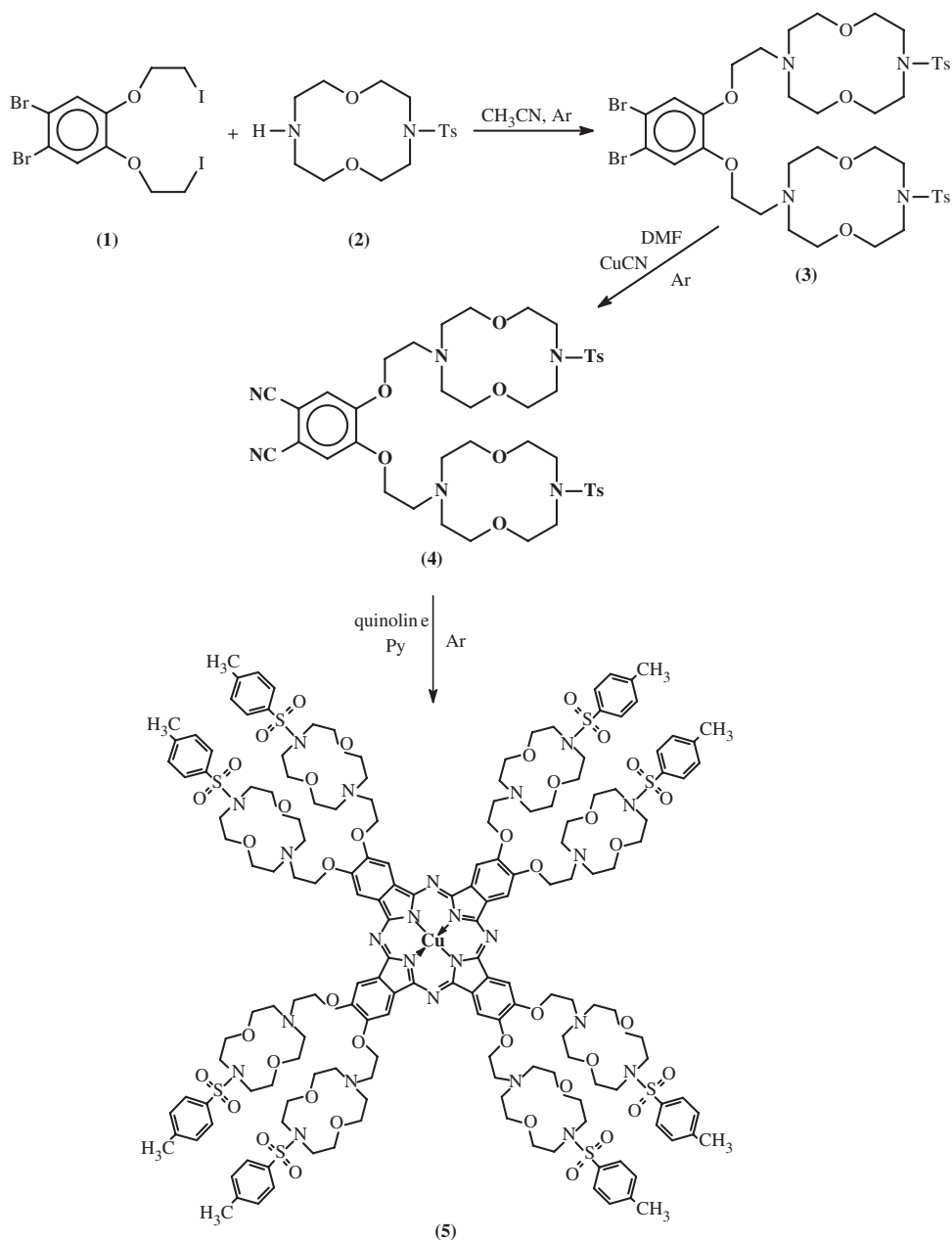
To a sealed tube, a mixture of (3) (2.14 g, 2.21 mmol), anhydrous CuCN (0.60 g, 6.7 mmol), 22 mL of dry DMF and 0.11  $cm^3$  of dry pyridine were added and refluxed for 45 h with continuous stirring, under argon. After cooling to room temperature 115  $cm^3$  of 25%  $NH_3$  was added to the mixture, which was stirred for an additional 2 h at room temperature. Then the mixture was extracted with chloroform ( $5 \times 25 cm^3$ ) and dried over anhydrous  $MgSO_4$ . Evaporation left an oily product, which was redissolved in chloroform and washed with water ( $3 \times 10 cm^3$ ). Separated organic phase was dried over anhydrous  $MgSO_4$ , filtered and then solvent was removed under reduced pressure. Dark brown solid product (4) was obtained and dried *in vacuo*. Yield: 1.17 g (61.3%), m.p. 200°C. Anal. Calcd for  $C_{42}H_{56}N_6O_{10}S_2$ (%): C, 58.05; H, 6.49; N, 9.67. Found: C, 57.93; H, 6.72; N, 9.92. IR (KBr pellets,  $cm^{-1}$ ): 3088 (Ar-H), 2925–2855 (C-H), 2221 ( $C \equiv N$ ), 1597 (Ar-H), 1504, 1460, 1336, 1288, 1159, 1122, 1090, 1019, 815.  $^1H$ NMR ( $CDCl_3$ ):  $\delta$  7.62 (d, 4H, Tos-H), 7.22 (m, 4H, Tos-H), 6.86 (s, 2H, ArH), 4.01–3.97 (m, 4H,  $CH_2-O$ ), 3.69–3.59 (m, 16H,  $CH_2-O$ ), 3.15 (m, 10H,  $NCH_2$ ), 2.86 (m, 10H,  $NCH_2$ ), 1.21 (s, 6H,  $CH_3$ ).  $^{13}C$ NMR ( $CDCl_3$ ):  $\delta$  146.37, 143.55, 129.72, 127.33, 119.61, 117.45, 69.72–68.55, 54.39, 50.65, 29.64. MS ( $m/z$ ): 866  $[M - 2]^+$ .

### 2.4. Preparation of copper(II)phthalocyanine (5)

The mixture of (4) (0.64 g, 0.74 mmol), anhydrous CuCN (0.018 g, 0.22 mmol), 1  $cm^3$  of dry quinoline and dry pyridine (0.08  $cm^3$ ) were placed into a sealed tube and heated to 210°C for 15 h under argon. After cooling to room temperature, 5  $cm^3$  of methanol was added to the mixture. Precipitate, which formed, was filtered and thoroughly washed with water and methanol. Solvent was evaporated to dryness and crude product obtained was chromatographed on a neutral alumina column using chloroform:methanol (100:1) as eluent. Dark green product (5) was obtained and dried *in vacuo*. Yield: 0.74 g (28%), m.p. > 300°C. Anal. Calcd for  $C_{168}H_{224}CuN_{24}O_{40}S_8$ (%): C, 57.00; H, 6.38; N, 9.50; Cu, 1.80. Found: C, 57.12; H, 6.17; N, 9.38; Cu, 1.85. IR (KBr pellet,  $cm^{-1}$ ): 3066 (Ar-H), 2929–2859 (C-H), 1645 ( $C \equiv N$ ), 1598 (Ar-H), 1445, 1323, 1290, 1205, 1106, 800. UV-Vis [(in  $CHCl_3$ ),  $\lambda_{max}/nm$   $10^{-5} \epsilon$  ( $mol^{-1}cm^{-1}$ ): 695 (5.12), 625 (4.86), 345 (4.70), 271 (4.90), 242 (5.02). MS ( $m/z$ ): 3538  $[M + 2]^+$ .

### 3. Results and discussion

The preparation of **(3)** and **(4)** is shown in scheme 1. Compound **3** was synthesized by reaction of 1,2-bis(2-iodoethoxy)-4,5-dibromobenzene **(1)** and 4'-[(4'-methylphenyl)sulphonyl]-1,7-dioxa-4,10-diazacyclododecane **(2)** in acetonitrile containing finely ground anhydrous  $\text{Na}_2\text{CO}_3$  as a template agent at reflux temperature in a Schlenk



Scheme 1. Preparation of Cu phthalocyanine **(5)**.

system under argon. The dibromo compound (**3**) bearing two di-azadioxa macrocyclic groups was obtained in 43.5% yield (scheme 1). The formation of macrocycle (**3**) is evident by the characteristic changes in the IR vibrations. The disappearance of characteristic N–H bands in compound (**2**) confirms the formation of **3**. In the  $^1\text{H-NMR}$  spectra of this compound, the chemical shifts of N–H protons in precursor (**2**) disappear after the macrocyclization reaction. The other resonances in the  $^1\text{H NMR}$  spectra, concerning  $\text{OCH}_2$ ,  $\text{NCH}_2$  and Ar–H appear at  $\delta=3.89$ , 3.42 and 6.94 ppm, respectively. In the proton-decoupled  $^{13}\text{C NMR}$  resonances of **3**,  $\text{OCH}_2$ ,  $\text{NCH}_2$  and Ar–C are present at  $\delta=70.26$ – $66.63$ , 55.39, 144.55 ppm, respectively. These values are very similar to those of the precursors (**1** and **2**). The mass spectrum of this compound shows the base peak at  $m/z$ : 977, corresponding to the proposed formulation  $[\text{M} + 1]^+$ .

Compound **4** was synthesized by treating macrobicycle **3** with three equivalents of the CuCN according to the Rosenmund von Braun reaction [13] in a moderately high boiling solvent such as dimethyl formamide [14] under argon to avoid the formation of Cu(II) phthalocyanine complex [15]. The Ar–Br groups of **3** were converted to a leaving group via a standard step to afford dicyano derivative **4** in an overall 61.3% 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 C–Br vibrations at  $651\text{ cm}^{-1}$  in **3**, and the sharp stretching vibration at  $2221\text{ cm}^{-1}$  was easily verified as  $\text{C}\equiv\text{N}$  absorptions. The  $^1\text{H NMR}$  spectrum of **4** closely resembles that of compound **3** as expected. The  $^1\text{H NMR}$  of **4** in chloroform shows a singlet at  $\delta=6.86$  ppm, indicating the presence of Ar–H protons. Formation of **4** causes chemical shifts of Ar–H protons to appear downfield by approximately 0.08 ppm [16]. The proton-decoupled  $^{13}\text{C NMR}$  spectrum of **4** shows  $\text{C}\equiv\text{N}$  groups as a singlet at  $\delta=117.45$  ppm. The other chemical shifts belonging to aromatic, crown or azacrown carbon resonances appear at  $\delta=69.72$ , 68.55 and 50.65 ppm, respectively, which are very close to those of compound **3**. In the mass spectrum of **4**,  $[\text{M} - 2]^+$  strong peak is observed at  $m/z=866$  confirming substitution of C–Br with  $\text{C}\equiv\text{N}$  in compound **4**.

The cyclotetramerization of macrobicyclic dicyano derivate **4** in the presence of anhydrous metal salt gave the copper(II) phthalocyanine **5**. The high boiling solvent of choice for this reaction was quinoline for Cu(II)Pc [17]. In the IR spectrum of this compound, the stretching vibrations at  $2221\text{ cm}^{-1}$  belonging to  $\text{C}\equiv\text{N}$  groups disappear after formation of **5**. A diagnostic feature of the formation of cyclotetramerization product **4**, a  $\text{C}=\text{N}$  stretching vibration, appears at  $1645\text{ cm}^{-1}$ . The Cu(II) phthalocyanine gave reproducible mass spectra with the  $[\text{M} + 2]^+$  instead of the molecular ion in **5**, at  $m/z=3538$ .

The best evidence for the phthalocyanine complex is given by UV-Vis spectra in solution (figure 1). The electronic spectra of phthalocyanine **5** show the typical B and Q bands of symmetrical macrocyclic MPc. Such Q band absorption is due to the  $\pi \rightarrow \pi^*$  transition from the HOMO to the LUMO of the phthalocyanine ring related to a fully conjugated  $18\pi$  electron system. The energy level location corresponding to those bands is illustrated in figure 1. The Cu(II)phthalocyanine (**5**) showed the expected absorption (figure 1) for the main peaks of the Q and B bands at 695 and 345 nm, respectively. This result is typical of metal complexes of substituted and unsubstituted MPc with  $\text{D}_{4h}$  symmetry [18], which is observed as a single band of high intensity in the visible region. In the UV-Vis spectrum of metal phthalocyanine in chloroform, the characteristic Q band was observed with absorption at 695 nm without splitting.

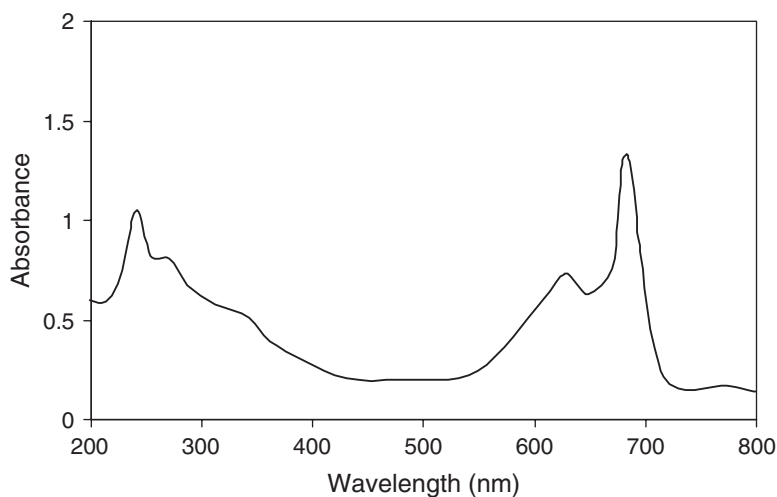


Figure 1. UV-Vis spectrum of compound (5).

#### 4. Conclusion

We synthesized compound (3) containing  $N_2O_2$ -macrocyclic moieties connected to the aromatic benzene ring with oxygen donors and ethylenic bridges by reaction of (1) and (2). The phthalonitrile derivative of 4 was obtained from the compound 3 in DMF and CuCN. Later, CuPc (5) was obtained from the reaction with 4 and CuCN in quinoline and pyridine. CuPc (5) carrying eight 12-membered diazadioxa-macrocyclic cavities containing hard oxygen atoms and medium-hard nitrogen atoms can be used as extracting reagents for alkali and alkaline earth metal ions. Furthermore, peripherally substituted phthalocyanines have interesting properties like forming liquid crystals and solubility in common organic solvents [19]. Recently it has been shown that CuPc's having electron donating and withdrawing peripheral substituents in the macrocyclic phthalocyanine ring are more reactive in oxidation reactions than unsubstituted CuPc complexes [20].

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