

Co, Ni, Cu phthalocyanines with tetra substituted bisbenzimidazole

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Received: October 7, 2016, Accepted: January 17, 2018,

Cyclotetramerization of bulky substituted phthalonitrile derivative **3** to the Co(II)Pc, Ni(II)Pc and Cu(II)Pc derivatives [4,5,6] was accomplished in quinoline with DBU at reflux temperature. The complexes were characterized by UV-Vis, FT-IR, mass spectra and elemental analysis.

Keywords: Metal phthalocyanines, Bulky substituent, bisbenzimidazole

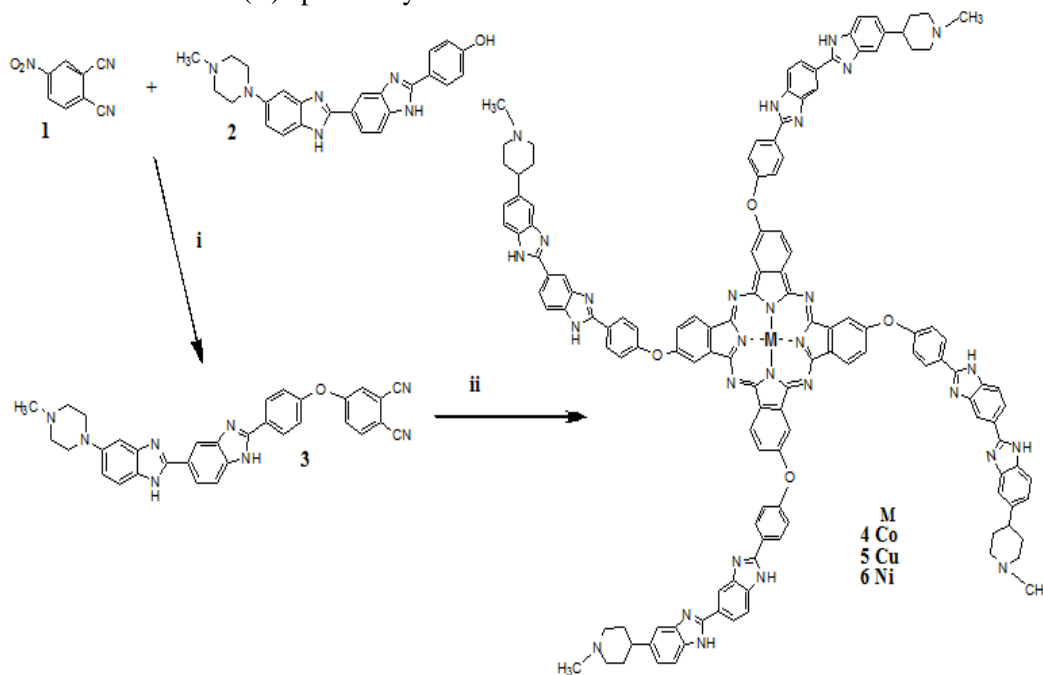
INTRODUCTION

Phthalocyanines (Pcs) were first discovered by accident in 1928 at Messrs Scottish Dyes Ltd and their geometric structure was elucidated [1,2]. They are an interesting class of compounds with increasingly diverse industrial and biomedical applications, such as photosensitization [3], non-linear optics [4], catalysis [5], etc. due to their properties and use in different fields [6,7]. Pcs can coordinate with most metals and can be substituted at the periphery and non-periphery with a variety of substituents. Axial ligands can also be bound to the central metal ion depending on the ability of the ion to coordinate. Bisbenzimidazole is an organic compound used as a fluorescent stain for DNA in molecular biology applications [8,9]. The electrochemical properties of various metal (II) phthalocyanine

(MPc) complexes have been investigated thoroughly [10-13]. These properties are important for advance applications [14-16]. In this paper, we synthesized and characterized mononuclear Co(II)Pc, Ni(II)Pc and Cu(II)Pc. The complexes were substituted with four bisbenzimidazole substituents at the peripheral (β) position, Scheme 1.

EXPERIMENTAL

Materials: Cobalt(II) acetate, nickel(II) acetate and copper(II) acetate as anhydrous metal(II) acetate salts were purchased from Merck. Quinoline was freshly used, all solvents, for example, dimethylsulfoxide (DMSO), dimethylformamide (DMF), dichloromethane(DCM) and chloroform (CHCl_3) were purchased from Merck.



Scheme 1. Synthetic route and reaction conditions for **4,5,6**. **i:** DMSO, 7 days, room temperature, **ii:** Quinoline, overnight, reflux temperature

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1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and all other reagents were obtained from suppliers and used as received. Bisbenzimidide as Hoechst 33258 was obtained from Aldrich and used without further purification. The chemical name is 2-[2-(4-hydroxyphenyl)-6-benzimidazolyl]-6-(1-methyl-4-piperazyl)benzimidazoletrihydro chloride.

Equipment: The UV-Vis absorption spectra were obtained using a Varian Cary 500 UV-Vis/NIR spectrophotometer. FT-IR data (ATR) were recorded using a Perkin-Elmer spectrum 100 FTIR spectrometer. Elemental analysis was done on a Finnigan Flash EA 1112 Series elemental analysis instrument. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam MALDI-TOF/TOF mass spectrometer. The instrument was operated in positive ion mode using an m/z range of 400 – 3000. The voltage of the ion sources was set at 19 and 16.7 kV for ion sources 1 and 2, respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV, respectively. The spectra were acquired using dithranol as the MALDI matrix, using a 354 nm Nd:YAG laser.

Synthesis: The target precursors were prepared by a nucleophilic aromatic substitution reaction between 4-nitrophthalonitrile **1** and bisbenzimidide **2**. Bisbenzimidide derivatives of metal phthalocyanines **4-6** were obtained in quinoline in the presence of DBU at the reflux temperature.

4-(4-(5-(4-Methylpiperazin-1-yl)-1H,1'H-2,5'-bibenzimidazol-2'-yl)phenoxy) phthalonitrile (3): Compound **2** (500 mg) was dissolved in dry DMSO (15 mL) and **1** (162 mg) was added in argon atmosphere. To this reaction mixture finely ground anhydrous potassium carbonate (0.650 g) was added and the same amount was added again after 24 h of stirring. After a total of 7 days of stirring, the reaction mixture was poured into water (550 mL) resulting in the formation of a dark yellow precipitate of **3**. The crude product was centrifuged several times and was further recrystallized from ethanol; finally, the pure product was dried over P₂O₅ for two weeks. Yield: 0.390 g. IR(ATR) ($\nu_{\max}/\text{cm}^{-1}$): 3078 (Ar-CH), 2232 (C \equiv N), 1591 (C=C), 1247 (C-O-C). ¹H NMR (DMSO-*d*₆): δ , ppm 13.19 (2H, br, s N-H), 8.52 (1H, s, Ar-H), 8.3 (2H, m, Ar-H), 8.1 (2H, d, J = 8.8 Hz, Ar-H), 7.9 (2H, br, s, Ar-H), 7.5 (2H, m, Ar-H), 7.4 (2H, m, Ar-H), 6.6 (2H, m, Ar-H), 3.02 (4H, m, cyclohexane-H), 2.65 (4H, m, cyclohexane-H), 1.10 (3H, br, s, CH₃). Anal. calcd. for C₃₃H₂₆N₈O: C, 71.98; H, 4.76; N, 20.35 %. Found: C, 77.18; H, 4.70; N, 15.42 %. LC-MS: m/z . calcd. 550.06, found [M]⁺: 550.61.

General procedure for 4-6: A mixture of compound **3** (0.100 g) and Co(OAc)₂(0.008 g) for **4**, Ni(OAc)₂(0.008 g) for **5** and Cu(OAc)₂(0.008 g) for **6** in 0.6 mL of quinoline with 6 drops of DBU was refluxed in a sealed tube in argon gas at 185°C for 24 h. After cooling to room temperature, the reaction mixture was treated with ethanol to precipitate the product. The residue was filtered off and then washed several times with methanol, water and finally washed with methanol, ethanol, acetonitrile and acetone for 24 h, consecutively in a Soxhlet apparatus. Finally, the dark green cobalt, nickel and copper phthalocyanines were dried over P₂O₅ for 10 days. All of these compounds are soluble in DMSO and have mp > 350°C.

Cobalt phthalocyanine (4): Yield 0.030 g. UV-vis (DMSO): λ_{\max}/nm 680, 343. IR (ATR): ($\mu_{\max}/\text{cm}^{-1}$) 3050 (Ar-CH), 1564 (C=C), 1259 (C-O-C). Anal. calcd. for C₁₃₂H₁₀₄N₃₂O₄Co: C, 70.11; H, 4.64; N, 19.82. Found: C, 70.49; H, 4.65; N, 20.05%. MALDI-TOF-MS: m/z calcd. 2261.38, found 2273.4 [M+Li+5H]⁺.

Nickel phthalocyanine (5): Yield 0.035 g. UV-vis (DMSO): λ_{\max}/nm 682, 341. IR (ATR): ($\mu_{\max}/\text{cm}^{-1}$) 3050 (Ar-CH), 1564 (C=C), 1256 (C-O-C). Anal. calcd. for C₁₃₂H₁₀₄N₃₂O₄Ni: C, 70.12; H, 4.64; N, 19.82. Found: C, 69.49; H, 3.50; N, 19.81%. MALDI-TOF-MS: m/z calcd. 2261.14, found 2272.4 [M+Li+4H]⁺.

Copper phthalocyanine (6): Yield 0.025 g. UV-vis (DMSO): λ_{\max}/nm 684, 334. IR (ATR): ($\mu_{\max}/\text{cm}^{-1}$) 3050 (Ar-CH), 1564 (C=C), 1255 (C-O-C). Anal. calcd. for C₁₃₂H₁₀₄N₃₂O₄Cu: C, 69.97; H, 4.63; N, 19.78. Found: C, 70.49; H, 4.50; N, 18.85%. MALDI-TOF-MS: m/z calcd. 2266.0, found 2269.9 [M+4H]⁺.

RESULTS AND DISCUSSION

4-Nitrophthalonitrile **1** was synthesized as reported in [17]. Bisbenzimidide **2** was obtained from commercial suppliers. The synthesis of phthalodinitrile **3** was based on the reaction of compound **3** with an excess of compound **2**. The reactions were carried out in dry DMSO in the presence of K₂CO₃ as a base, at room temperature, and good yields were obtained. The 4-nitrophthalonitrile **1** reacted with commercial bisbenzimidide **2** to obtain compound **3** in a reasonable good yield. MPcs **4**, **5** and **6** were prepared by cyclotetramerization of phthalonitrile **3** in the presence of anhydrous Co(OAc)₂, Ni(OAc)₂, and Cu(OAc)₂, respectively, by using quinoline with DBU at the reflux temperature, Scheme 1. Column chromatography on silica gel using CHCl₃ as mobile

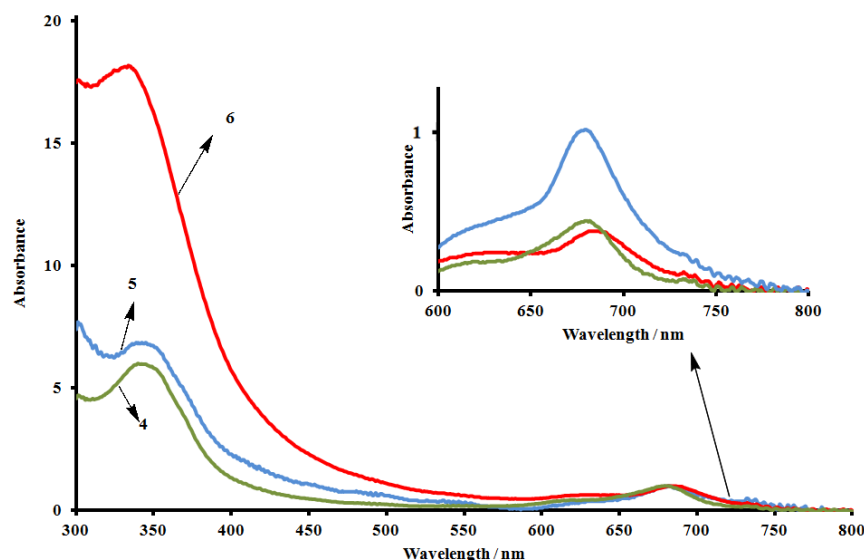


Fig. 1. Absorption spectra of **4-6** in DMSO

phase was used to purify complexes **4-6**. The structure and purity of the CoPc, NiPc and CuPc derivatives were confirmed by UV-Vis, IR, mass spectral data and elemental analyses.

The IR spectra of **4-6** clearly indicated the absence of OH groups of **2**. CN vibrational peaks were observed at 2232 cm^{-1} for compound **3**. A diagnostic feature of the formation of **4-6** from the phthalodinitrile derivative **3** was the disappearance of the sharp CN vibration of the latter. The IR spectra were very similar for compounds **3-6** and showed Ar-O-Ar peaks at 1247 , 1259 , 1256 , 1255 cm^{-1} , respectively.

Elemental analysis results were also consistent with the theoretical values of the proposed structures for **3-6**.

The purified Pcs were further characterized by mass spectra. The expected mass values corresponded to the found values for all complexes. Both protonated ion peaks for complexes **4-6** and a Li adducted ion peak were found, except for complex **6** which has a molecular ion peak. The ion peaks of complexes **4-6** were observed at 2273.4 , 2272.4 and 2269.9 amu , respectively. These results confirm that the complexes have been synthesized successfully.

The UV-Vis spectra of **4-6** in DMSO are shown in Fig. 1. The Pcs show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300-400 nm (B-band) and the other in the visible region at 600-750 nm (Q-band) and are characteristic of Q-band transition of M(II)Pcs with D_{4h} [18] Aggregation behavior of Pc is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and it is dependent on concentration, nature of solvent and substituents,

metal ions and temperature [19]. Aggregation in M(II)Pcs is typified by the broadened or split Q-band, the high energy band being due to the aggregate and the low energy band due to the monomer [18]. The UV-Vis spectra of the metal phthalocyanines resemble those of other Pcs. The broad Q-band with the vibration band at almost 620 nm for **4-6** has been reported to indicate aggregation of phthalocyanine complexes in general [18]. In Fig. 1, complexes **4-6** show Q-band absorptions of the monomers at 681, 679, 683 nm, respectively, in DMSO. Red shifting of the spectra observed in Q-bands of **4, 5** and **6** is due to the electron density enhancement caused by the central metal [20]. The complexes **4-6** show B-bands at 343, 341 and 334 nm in DMSO, respectively. Typical of Pcs, the intensity of the B-bands is high relative to the Q-band; this may be due to aggregation. The bulky substituents of the Pc molecules considerably affect the degree of conjugation between the rings and substituent. It can be seen from the electronic absorption spectra of complexes **4-6** that the Q-band is broad.

CONCLUSION
We described the synthesis and characterization of novel Co(II), Ni(II) and Cu(II) phthalocyanine derivatives which contain a bisbenzimidate unit on each benzo group substituent at peripheral position. The effect of bisbenzimidate as a bulky substituent to the Pc molecule was observed.

Acknowledgments: This work was supported by the Research Fund of the Yildiz Technical University (Project No: 27-01-02-07).

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ФТАЛОЦИАНИНИ НА Co, Ni И Cu С ТЕТРАЗАМЕСТЕН БИСБЕНЗИМИД

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Постъпила на 7 октомври, 2016 г.; приета на 17 януари, 2018 г.

(Резюме)

Проведена е циклотетрамеризация на обемистия заместен фталонитрил 3 с производните Co(II)Pc, Ni(II)Pc and Cu(II)Pc [4,5,6] в хиолин с 1,8-диазабицикло[5.4.0]ундек-7-ен при температура на кипене. Комплексите са охарактеризирани чрез елементен анализ, UV-Vis, FT-IR и масови спектри.