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[e014]

Synthesis of some 5,9,14,18,23,27,32,36-octabutoxynaphthalocyanine metal complexes in modified microwave oven.

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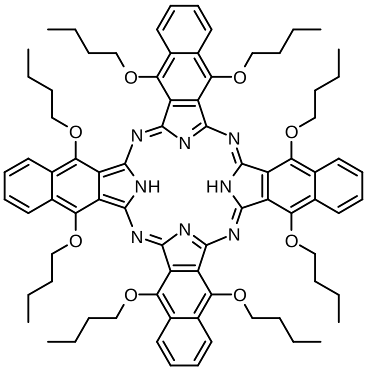
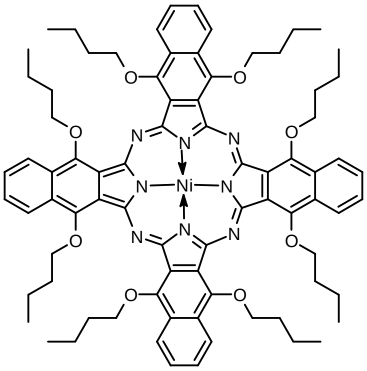
Abstract: The improved synthesis of metal (copper, nickel, zinc) 5,9,14,18,23,27,32,36-octabutoxynaphthalocyanines using modified microwave oven described. The comparison with conventional synthesis was made.

5,9,14,18,23,27,32,36-Octabutoxynaphthalocyanine (**I**) and its metal complexes were synthesized for first time in 1988 [1].

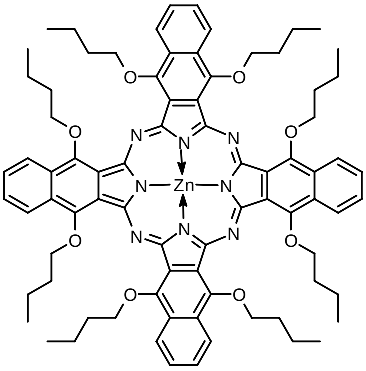


I

Metal complexes of **I** were investigated and patented for medicinal and technical uses due to its near infrared absorption, very good solubility in non-polar solvents and high oxidation and thermal stability. In medicine, nickel 5,9,14,18,23,27,32,36-octabutoxynaphthalocyanine (**II**) [2] and zinc 5,9,14,18,23,27,32,36-octabutoxynaphthalocyanine (**III**) [3] were investigated for photodynamic therapy of cancer. Also, **II** patented for therapy of cardiovascular diseases [4]. In electrophotography, **III** [5] and copper 5,9,14,18,23,27,32,36-octabutoxynaphthalocyanine (**IV**) [6] were patented as toner components. Also, **IV** was patented for use as colorant in printer ribbons [7]. Solar control laminates of solar cells on base **II** [8] and **IV** [9] also were patented. Absorbance in IR-region and thermal stability of title compounds allowed patent IR-cutting filters on base **III** [10] and **IV** [11] for use in space and aviation equipment. Application of **IV** Langmuir-Blodget films in gas sensors was studied [12].



II



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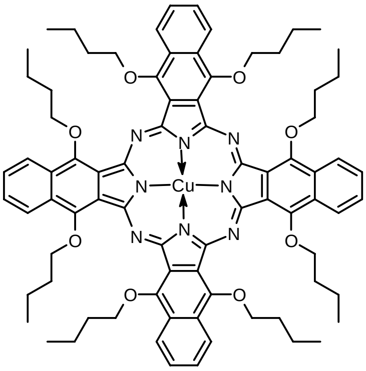
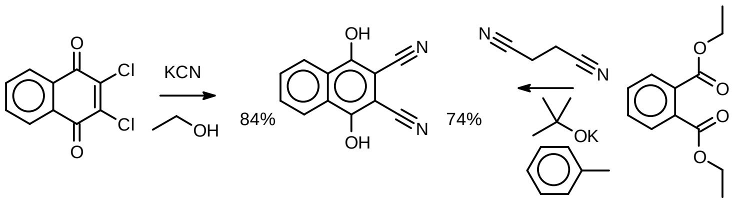


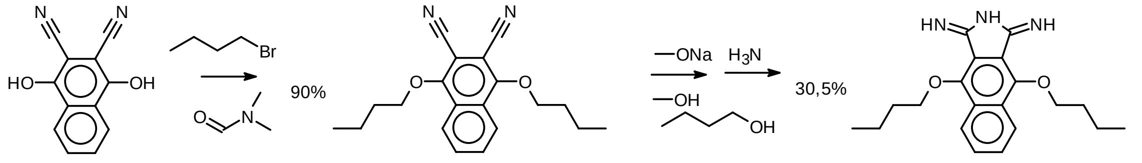
IV

The key compound for **I** and its metal complexes synthesis is 1,4-dihydroxy-2,3-naphthalenedicarbonitrile (**V**). There are several synthetic ways to **V**, from which we have used as historically first synthesis starting from 2,3-dichloro-1,4-naphthoquinone (**VI**) and alkali metal cyanide [13] as less dangerous Claisen condensation of phthalates (**VII**) with succinic dinitrile (**VIII**) [14].



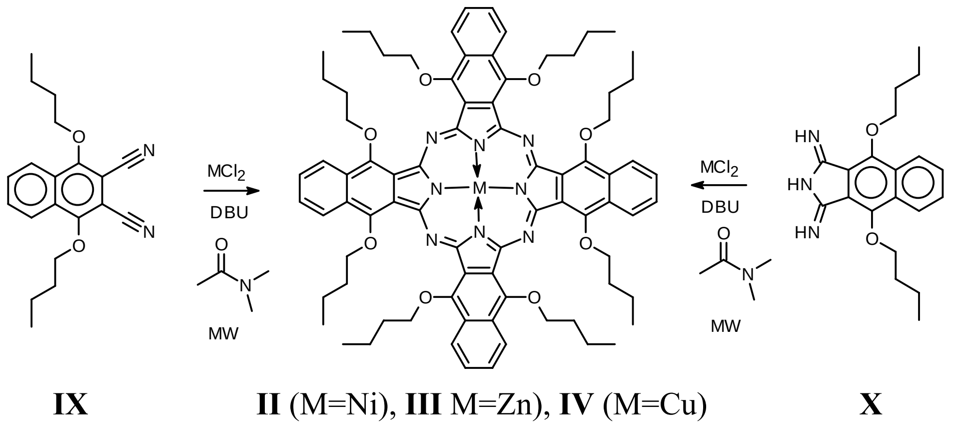
VI V VIII VII

Alkylation of **V** with butyl halide gives 1,4-dibutoxy-2,3-naphthalenedicarbonitrile (**IX**) [15], which can to be starting compound for template synthesis of **I** metal complexes. More reactive starting compound 4,9-dibutoxy-1,3-diimino-1H-benz[f]isoindole (**X**) forms under action of dry ammonia gas on **IX** but the yield of **X** (30.5%) is low [16].



V **IX** **X**

Template synthesis of metal complexes **II**, **III**, and **IV** under microwave irradiation was carried out in the modified microwave oven described earlier [17]. The yields of desired compounds after 15-20min irradiation, workup with chloroform – water and chromatographic purification were 70-95%. The yields in runs started from **X** are in all cases higher, that starting from **IX**.



IX **II** (M=Ni), **III** M=Zn), **IV** (M=Cu) **X**

Compound **II** was also synthesized by methods [18] with yield 43% and [15] with total yield 65% (starting from **IX**) employing conventional heating. So, MW heating has significant advantage over conventional heating.

Metal complexes **II**, **III**, and **IV** have strong absorption band in near IR region: 844nm (**II**), 847nm (**III**), and 851nm (**IV**). Mass-spectra (70eV) only fragments of butyl substituent (m/z 57) shoves clearly, but peaks of fragments with higher m/z have very low intensity (majority traces), and no molecular ion is present. ^{1}H NMR (recorded only for **II**) shoves butoxy substituent and two deteriorated aromatic quartets. ^{13}C NMR (recorded only for **II**) shoves also two groups of signals – four aliphatic and six aromatic carbons. The purity of **II** according to NMR spectra is 98.9%.

Experimental

General method for synthesis of [5,9,14,18,23,27,32,36-octabutoxy-37H,39H-tetranaphto[2,3-b:2',3'-g:2",3"-l:2'",3'"-q]porphyrazinato(2-)-κN^{37},κN^{38},κN^{39},κN^{40}] metal. Compounds, 0.100mmol (0.322g **X** or 0.339g **XI**), 0.026mmol of MCl_2 (0.034g $NiCl_2$, or 0.036g $ZnCl_2$, or 0.035g $CuCl_2$), 0.002mmol (0.003g) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 2ml of N,N-dimetylacetamide were placed to the round-bottom 250ml flask. The flask was mounted on kern of rotatory evaporator mechanism in modified microwave oven [17] and irradiated with stirring by rotating flask during 15-20min. After end of reaction 20 ml of water and 40 ml of chloroform were added and the mixture was poured to a separation funnel. Water layer was additionally extracted with three portions 40ml of chloroform. Combined chloroform extracts were dried over sodium sulphate, filtered and solvent was evaporated at rotatory evaporator. The residue was dissolved in benzene and chromatographed on silica gel column (hexane – benzene), collecting first brown colored fraction with R_f 0.5 (hexane : benzene 2 : 1 v/v) on "Armsorb KSKG" ("Akunk", Yerevan, Armenia) silica gel on aluminium foil plates. Solvent was evaporated at rotatory evaporator yielding desired **II** [17], or **III** [18], or **IV** [19].

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19. **II**, UV-VIS: (nm, toluene) 746, 844. ^{1}H NMR (δ, ppm, CDCl$_3$) 1.026 (triplet, 24H, -CH$_3$), 1.652 (sextet, 16H, $\text{-OCH}_2\text{CH}_2\text{C}\underline{\text{H}}_2\text{CH}_3$), 2.207 (quintet, 16H, $\text{-OCH}_2\text{C}\underline{\text{H}}_2\text{CH}_2\text{CH}_3$), 5.037 (triplet, 16H, -OCH$_2$-), 7.849 (deteriorated quartet, 16H, β-aromatic H), 8.934 (deteriorated quartet, 16H α-aromatic H). ^{13}C NMR (δ, ppm, CDCl$_3$) 14.22, 19.60, 32.76, 76.36, 124.33, 126.80, 128.21, 129.02, 130.26, 148.81. MS: m/z(%) 671(0.2), 652(0.2), 638(tr.), 545(tr.), 520(tr.), 502(tr.), 483(tr.), 353(tr.), 266(tr.), 248(tr.), 235(tr.), 223(tr.), 210(tr.), 171(tr.),

159(tr.), 136(tr.), 118(tr.), 112(tr.), 105(0.3), 104(0.2), 103(0.2), 101(tr.), 99(tr.), 91(tr.), 85(tr.), 84(tr.), 83(tr.), 77(0.3), 76(tr.), 74(tr.), 73(tr.), 72(0.9), 71(0.9), 70(0.4), 69(0.4), 68(tr.), 67(tr.), 59(tr.), 58(5.3), 57(86.4), 56(27.6), 55(11.1), 53(1.5), 52(tr.), 51(1.4), 50(1.7), 49(tr.), 45(1.5), 44(5.3), 43(27.6), 42(14.8), **41(100.0)**, 39(18.1), 38(2.9), 37(1.5), 36(tr.), 33(1.6). Elemental analysis: found C 71.25, H 6.60, N 8.30; calculated C 71.26, H 6.58, N 8.31 required for $C_{80}H_{88}N_8NiO_8$.

20. **III**, UV-VIS: (nm, toluene) 749, 847. MS: m/z(%) 671(0.2), 652(tr.), 639(tr.), 545(tr.), 520(tr.), 501(tr.), 483(tr.), 352(tr.), 266(tr.), 249(tr.), 235(tr.), 221(tr.), 210(tr.), 170(tr.), 159(tr.), 135(tr.), 118(tr.), 105(0.2), 104(0.2), 103(0.3), 101(tr.), 99(tr.), 92(tr.), 85(tr.), 84(tr.), 82(tr.), 77(0.4), 76(0.2), 75(tr.), 74(tr.), 72(0.7), 71(0.7), 70(0.5), 69(0.5), 68(tr.), 67(tr.), 59(0.2), 58(5.5), 57(85.3), 56(28.2), 55(10.7), 53(1.3), 52(tr.), 51(1.1), 50(1.9), 49(tr.), 45(1.7), 44(5.1), 43(28.5), 42(15.3), **41(100.0)**, 39(18.5), 38(3.1), 37(1.9), 36(tr.), 33(1.5). Elemental analysis: found C 70.88, H 6.56, N 8.24; calculated C 70.91, H 6.55, N 8.27 required for $C_{80}H_{88}N_8O_8Zn$.

21. **IV**, UV-VIS: (nm, toluene) 752, 851. MS: m/z(%) 671(tr.), 652(0.3), 638(tr.), 544(tr.), 520(tr.), 502(tr.), 481(tr.), 353(tr.), 266(tr.), 249(tr.), 235(tr.), 223(tr.), 211(tr.), 171(tr.), 160(tr.), 136(tr.), 111(tr.), 105(0.4), 104(0.5), 103(0.1), 100(tr.), 92(tr.), 85(tr.), 84(0.1), 83(tr.), 77(0.4), 76(tr.), 75(tr.), 74(tr.), 72(0.7), 71(0.7), 70(0.5), 69(0.5), 68(tr.), 67(tr.), 58(5.5), 57(85.2), 56(26.9), 55(13.0), 53(1.8), 51(1.2), 50(1.2), 49(tr.), 45(1.6), 44(6.0), 43(26.8), 42(15.1), **41(100.0)**, 39(17.6), 38(2.5), 37(1.3), 33(1.5). Elemental analysis: found C71.00, H 6.57, N 8.27; calculated C 71.01, H 6.55, N 8.28 required for $C_{80}H_{88}CuN_8O_8$.