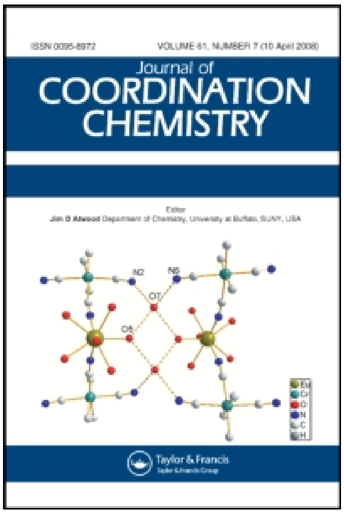

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Direct electrochemical synthesis of substituted phthalocyanines: the advantages and problems <i>versus</i> classic phthalocyanine preparation

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Direct electrochemical synthesis of substituted phthalocyanines: the advantages and problems *versus* classic phthalocyanine preparation

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Direct electrochemical procedure was applied for tetramerization of a series of substituted phthalodinitriles (4-nitrophthalodinitrile, 3-phenylthiophthalodinitrile, etc.) at relatively low temperatures (25–125°C) in ethanol and *N*,*N*-dimethylethanolamine. In case of use of sacrificial metal (Cu, Ni and Zn) anodes, the corresponding metal complexes were obtained. Products were characterized by UV- and IR-spectroscopy and elemental analysis data. Peculiarities of the electrochemical synthesis of substituted phthalocyanines are discussed.

Keywords: Substituted phthalocyanines; Electrosynthesis; UV-spectra

1. Introduction

Direct electrochemical synthesis is a technique rapidly developed during the last 30 years [1–4]. In phthalocyanine (Pc) chemistry, this method was applied for obtaining a non-substituted phthalocyanine and some of its complexes using sacrificial metal anodes or dissolved metal salts as metal ion precursors and phthalodinitrile in protic solvents [5, 6]; a detailed mechanism for phthalodinitrile tetramerization was proposed. Among other phthalocyanines, PcLi. having free-radical properties was electrochemically obtained and characterized [7]. Further, formation of phthalocyanine and its metal complexes from phthalodinitrile, 1,3-diiminoisoindoline, urea and phthalic anhydride or phthalimide was studied in a series of non-aqueous protic and aprotic solvents [8]; a comparative investigation of classic and electrochemical techniques showed that electrosynthesis with use of 1,3-diiminoisoindoline is possible in aprotic solvents, different than phthalodinitrile where only protic solvents can be used [5, 6, 8]. Electrosynthesis with use of urea and phthalic anhydride does not lead to satisfactory yields of products [8]. An advantage of the electrochemical procedure for phthalocyanine synthesis is considerably lower temperature (0–100°C) in comparison with traditional methods (generally at 170–250°C [9, 10], although sometimes at 100°C [13]).

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Substitution of H-atoms in benzene rings of the Pc molecule allows changing physical and chemical properties of these compounds, such as solubility, electronic absorption spectra, acid-base, redox and catalytic properties [11–13]. In particular, introduction of strong electron-acceptor groups, such as nitro, can expand the properties of these pigments. Classic synthesis of substituted phthalocyanines from phthalodinitriles (or other precursors) and metal salts are usually carried out at >160–170°C in high-boiling organic solvents or without solvent [9–13]. In this work, we report an electrochemical process for substituted metal-free phthalocyanines and some metal complexes at considerably lower temperature (25–130°C) in comparison with traditional techniques.

2. Experimental

2.1. *Materials and equipment*

4-*t*-butylphthalodinitrile, 4-phenylthiophthalodinitrile, 3-phenylthiophthalodinitrile, 3-phenoxyphthalodinitrile, 4-hydroxyphthalodinitrile, 4-α-naphthoxyphthalodinitrile, 3-α-naphthoxyphthalodinitrile, 3-nitrophthalodinitrile, 4-nitrophthalodinitrile, 3-β-naphthoxyphthalodinitrile, 4-β-naphthoxyphthalodinitrile, tetracyanodiphenyl ether (4,4′-oxodiphthalodinitrile), 4-aminophthalodinitrile, and tetrachlorophthalodinitrile were supplied by NIOPIK (Moscow, Russia). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and absolute ethanol were purchased from Aldrich and used as supplied. Metals were used in distinct forms: copper wire, nickel and vanadium sheets, zinc or bismuth cores (they were washed with diluted HCl before use). *N*,*N*-Dimethylethanolamine was distilled at reduced pressure before use. LiCl was dried in a conventional oven at 130°C before use as supporting electrolyte. An undivided electrochemical cell (50 cm^3) with graphite electrodes, connected with a power supply (Photodyne), thermometer and magnetic stirring was used for electrochemical preparation of phthalocyanines. Electronic absorption and IR spectra were recorded with Perkin-Elmer equipment. Elemental analysis data were obtained using a Perkin-Elmer CHONS analyzer.

2.2. *Preparation and purification of phthalocyanines*

Generally, 0.5–0.8 g of a substituted phthalodinitrile and 0.03 g of LiCl were put into a 50 mL flask containing 20–30 mL of a solvent (EtOH or *N*,*N*-dimethylethanolamine) and stirred for a few minutes until complete dissolution. Then, 2–3 drops of DBU were added. To obtain a metal-free phthalocyanine, graphite/graphite electrodes were used; in case of metal complexes, corresponding metal anode was used. The applied current was 20–40 mA, initial voltage 20–40 V, and electrolysis time 1.5–2.5 h (with continuous stirring). The temperature varied in the range 25–78°C (in EtOH) and 25–130°C (in DMEA). Finishing the electrolysis, the solution was cooled to room temperature and remained in the cell for 24 h. Then, the brown-blue or green solid was filtered, washed in a Soxhlet extractor and recrystallized by standard techniques described in table 1. The final violet or green crystals correspond to metal-free phthalocyanines or their metal complexes. UV-spectral data of all synthesized complexes are presented

Table 1. Experimental data on the electrochemical synthesis of substituted phthalocyanines.

			Initial phthalodinitrile								
				Weight		Synthesis conditions		Yield			
Final product	Metal	Mol. weight	Mol. weight	*g*	mmol	Solvent	*T* (°C)	*g*	mmol	%	Purification applied/ Observations
	4-Nitrophthalodinitrile										
4-$(NO_2)_4$-PcM	HH	694.4	173.1	0.992	5.74	Ethanol	78 (Reaction begins at r.t.)	0.013	0.019	1.3	Reprecipitation from DMF by 18% HCl, washing with DMF + 18% HCl (1:1), then 18% HCl (4 times) and water. There is no product insoluble in DMF.
	Cu	755.9		1.598	9.24	Ethanol	78 (Reaction begins at r.t.)	0.29	0.384	16.6	Washing with DMF + 18% HCl and water.
	Ni	751.1		1.161	6.71	Ethanol	78 (Reaction begins at r.t.)	0.104	0.138	8.2	Reprecipitation from DMF by adding some drops of pyridine and conc. HCl, washing with DMF + 18% HCl (1:1), 18% HCl and water.
	Bi (free Pc obtained)			1.7305	10.00	Ethanol	78 (Reaction begins at r.t.)	0.131	0.187	7.5	**Tetrakis(4-nitro-Pc)H_2 is obtained.** Reprecipitation from DMF by 18% HCl (3 times), washing with 18% HCl and water.
	Zn	757.8		1.1340	6.55	Ethanol	78 (Reaction begins at r.t.)	0.162	0.214	13.1	Reprecipitation from DMF by 18% HCl, washing with 18% HCl (3 times) and water.
	Ta (O) (free Pc obtained)			0.41	2.37	Ethanol	78 (Reaction begins at r.t.)	0.042	0.06	10.2	**Tetrakis(4-nitro-Pc)H_2 is obtained.** Reprecipitation from DMF by 18% HCl (3 times), washing with 18% HCl and water.

(*continued*)

Table 1. Continued.

			Initial phthalodinitrile								
				Weight		Synthesis conditions		Yield			
Final product	Metal	Mol. weight	Mol. weight	*g*	mmol	Solvent	*T* (°C)	*g*	mmol	%	Purification applied/ Observations
	3-*Phenylthiophthalodinitrile*										
3-$(PhS)_4$-PcM	HH	947.2	236.3	0.224	0.948	DMEA	132	0.009	0.009	4.0	Precipitation with conc. HCl, filtration and washing with acetone.
	HH	947.2		0.550	2.327	DMEA	132	0.051 with impurities	0.05	9.2	Precipitation with conc. HCl, filtration and washing with DMF + 18% HCl (3 times) and water.
	Cu	1008.7		0.950	4.02	DMEA	132	0.16	0.159	15.8	Precipitation with conc. HCl, filtration and washing with 18% HCl, hot water (3 times), DMF + 18% HCl (4 times), acetone + water (2 times).
	Ni	1005.9		0.444	4.02	DMEA	132, 1.5 h	0.045 (sol. in $CHCl_3$) + 0.058 insoluble. Total 0.103	0.102	15.8	Precipitation with conc. HCl, filtration and washing with DMF + water and then acetone. Mixture of metal-free and nickel Pc.

	Tetracyanodiphenyl ether (4,4′-oxodiphthalodinitrile)										
4-[4′,5′-$(CN)_2$-PhO$]_4$-PcM	HH	1082.8	270.2			Ethanol	75	Traces	Soluble only in H_2SO_4.		
	HH	1082.8	270.2	0.539	1.99	DMEA	110–130	0.130	0.120	24.1	Precipitation with 18% HCl, filtration and washing with water and ethanol. Reprecipitation from DMF by 18% HCl, washing with DMF + 18% HCl and water.
	Cu	1144.4	270.2	0.950	3.52	DMEA	128	0.64	0.130	14.8	Washing with conc. HCl, water, ethanol, acetone. Soluble only in H_2SO_4.
	Ni	1139.5	270.2	0.444	1.64	DMEA	132	0.02	0.010	2.5 (Calcd for PcH_2)	**Mixture of PcH_2 and PcNi is obtained.** Reprecipitation from conc. HCl by NH_3, washing with water. Soluble only in H_2SO_4.
	Bi (free Pc obtained)		270.2	0.514	1.90	DMEA	132	0.159	0,147	30.9 (Calcd for PcH_2)	**PcH_2 is obtained.** Reprecipitation with 18% HCl, washing with water and acetone.
	Zn	1146.2		0.484	1.79	DMEA	132	0.052	0.045	10.1	Washing with ethanol, acetone, DMF + 18% HCl, water, acetone. Reprecipitation from DMF by 18% HCl, washing with DMF + 18% HCl and water.
4-(α-NfO$)_4$-PcM	*4-α-naphthoxyphthalodinitrile*										
	HH					Ethanol	75	Traces			
3-(β-NfO$)_4$-PcM	*3-β-naphthoxyphthalodinitrile*										
	HH					Ethanol + toluene	75	Traces in spectra (in benzene and $CHCl_3$).			Precipitation with conc. HCl, filtration, washing with DMF + 18% HCl and water.

in table 2 and UV-spectra for three copper complexes are shown in figures 1–3. Elemental analysis data of the complexes after final purification are presented in table 3.

3. Results and discussion

It is possible to obtain, in some cases, phthalocyanines or their metal complexes by direct electrochemical procedure at temperatures below 100°C. Thus, using 4-nitrophthalodinitrile as a precursor, a metal-free tetrakis(4-nitro)phthalocyanine and its Cu, Ni and Zn complexes were products. With vanadium as a sacrificial electrode, no phthalocyanine was detected in EtOH or DMEA. Visually Pc formation began on the cathode surface, but rapidly finished (in 2–4 min.) when a definite concentration of vanadyl ions was accumulated in a solution. In the electrosynthesis conditions, vanadyl ions most inhibit macrocycle formation; meanwhile in classic syntheses vanadium complexes are obtained without problems [9, 10].

Using (4-nitro)phthalodinitrile, it is possible to carry out the electrosynthesis at room temperature in an undivided cell. Compared to standard non-substituted phthalodinitrile, whose electrochemical synthesis is possible in solution at room temperature in a divided cell [6], in a *solid phase* of phthalonitrile close to a high-surface cathode in an undivided cell at 0–25°C [14] and >55°C in solution in an undivided cell [8], the presence of NO_2 in the 4 position makes one CN of the ligand more accessible for nucleophilic attack by DBU with further cyclotetramerization. In fact, 4-nitrophthalodinitrile is one of the best substituted phthalocyanine precursors, allowing phthalocyanines with relatively high yields [12]. Yields in the electrochemical method are smaller in comparison with standard non-substituted phthalocyanine [8], probably due to formation of by-products. Possibility to obtain substituted phthalocyanines at considerably lower temperature in comparison with classic techniques seems attractive for further research in phthalocyanines.

Only three substituted phthalonitriles – 4-nitrophthalodinitrile, 3-phenylthiophthalodinitrile and tetracyanodiphenyl ether (4,4′-oxodiphthalodinitrile) – produce electrochemically corresponding metal-free phthalocyanines and their complexes with satisfactory yields (8–31%) (table 1), typical also for classic syntheses of substituted phthalocyanines (10–55%) [9–13, 15]. In some cases, using a sacrificial metal anode, formation of a metal-free phthalocyanine or its mixture with a metal phthalocyaninate is observed by UV-spectroscopy (for example, in the systems Bi or Ta – 4-nitrophthalodinitrile, Bi or Ni-tetracyanodiphenyl ether). 4-α- and 3-β-naphthoxyphthalodinitriles form products electrochemically only as traces, as observed, for instance, in UV-spectra of 4-(α-NfO)$_4$-PcHH (figure 4). Using other phthalodinitriles, it was impossible to obtain phthalocyanines *via* direct electrochemical synthesis, although they are formed by traditional techniques [11–13].

Electronic absorption spectra of the electrochemically synthesized metal-free and metal phthalocyaninates (table 2, figures 1–3) and tetra-(4-nitro)Pc and tetra-(4-PhS)Pc complexes, obtained by traditional techniques [12, 13], are almost identical. In case of tetra-(4-nitro)PcCu (figure 1), typical for nitrophthalocyanines, small splitting of the Q-band for two bands with the same intensities with splitting magnitude of 15–20 nm is observed. IR-spectral data are typical for substituted phthalocyanines.

Table 2. Electronic absorption and IR spectra of the formed phthalocyanines.

Compound	Solvent/Observations	Absorption bands λ_{max} (nm)	IR spectral data ν (cm^{-1})
4-$(NO_2)_4$-PcHH	α-Cl-naphthalene	720, 684, 652, 624, 350	740 (s), 1025, 1085, 1345 (v.s.), 1530 (s, benzene rings C–C), 1700 (s, w), 3300–3000 (w, C–H)
	H_2SO_4	783, 743, 705, 664, 307	
4-$(NO_2)_4$-PcCu	α-Cl-naphthalene	703, 694, 627, 351	750 (s), 790 (s), 1110 (s), 1170 (s), 1365 (v.s.), 1550 (s), 1680
	H_2SO_4	764, 740, 667, ~410, 305	
4-$(NO_2)_4$-PcNi	α-Cl-naphthalene	692, 622, 344	750 (s), 780, 1110, 1180, 1340 (v.s), 1550 (s)
	H_2SO_4	759, 676, ~400, 308	
4-$(NO_2)_4$-PcZn	α-Cl-naphthalene	704, 698, 631, 344	750 (s), 785 (s), 1120 (s), 1355 (v.s.), 1530 (s), 1640
	H_2SO_4	764, 684, ~410, 308	
3-$(PhS)_4$-PcHH	$CHCl_3$	738, 709, 676, 643, ~450, 334	700, 740 (v.s.), 800, 890, 1030 (v.s.), 1090, 1120, 1229, 1322 (s), 1490 (s, C–C of pyrrol rings), 1580 (benzene rings C–C)
3-$(PhS)_4$-PcCu	$CHCl_3$	720, ~685, 647, 442, 333	690, 740 (v.s.), 798, 902, 1010, 1110 (s), 1140, 1230 (s), 1310 (s), 1460 (s), 1570 (s, benzene rings C–C)
	Trichlorobenzene	724, ~687, 489, 439, 340	
4-[4′,5′-$(CN)_2$-PhO]$_4$PcHH	α-Cl-naphthalene	704, 670, 644, 609, 345	740 (s), 840, 960, 1020 (s, C–O), 1110 (s), 1220 (v.s.), 1300, 1360, 1480 (v.s.), 1600 (s), 1710 (s), 2250, 1780
	H_2SO_4	870, 812, 770, ~425, 306	
	DMF + MeONa	675, 609, 340	
4-[4′,5′-$(CN)_2$-PhO]$_4$PcCu	H_2SO_4	818, 728, ~504, 429, 305	760, 835, 960, 1050 (C–O), 1090 (s), 1225 (v.s.), 1402, 1459 (s, C–C of pyrrol rings), 1590 (s), 1660, 1720, 1801, 2235 (benzene rings C–C), 3400–3300 (wide, C–H)
4-[4′,5′-$(CN)_2$-PhO]$_4$PcZn	α-Cl-naphthalene	684, 619, 344	
	H_2SO_4	812, 734, 429, 309	
4-(α-NfO)$_4$-PcHH	CH_2Cl_2	702, 667, 640, 607, ~400, 336	
3-(β-NfO)$_4$-PcHH	$CHCl_3$	722, 690, 660, 625, ~410, 331	495, 755 (s), 1040 (s), 1250 (s), 1340 (s), 1450 (s), 1655 (s)

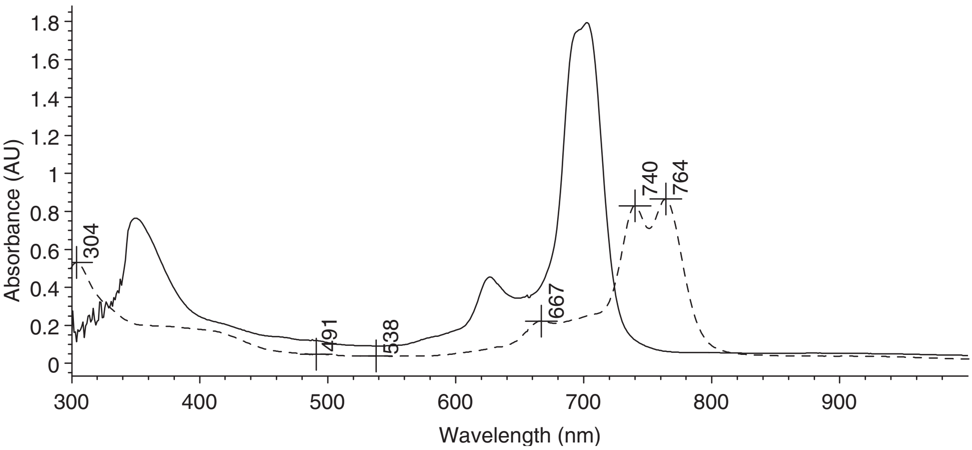

Figure 1. Electronic absorption spectra of copper tetrakis-(4-nitro)-phthalocyaninate: continuous line – in α-chloronaphthalene, dotted line – in H_2SO_4.

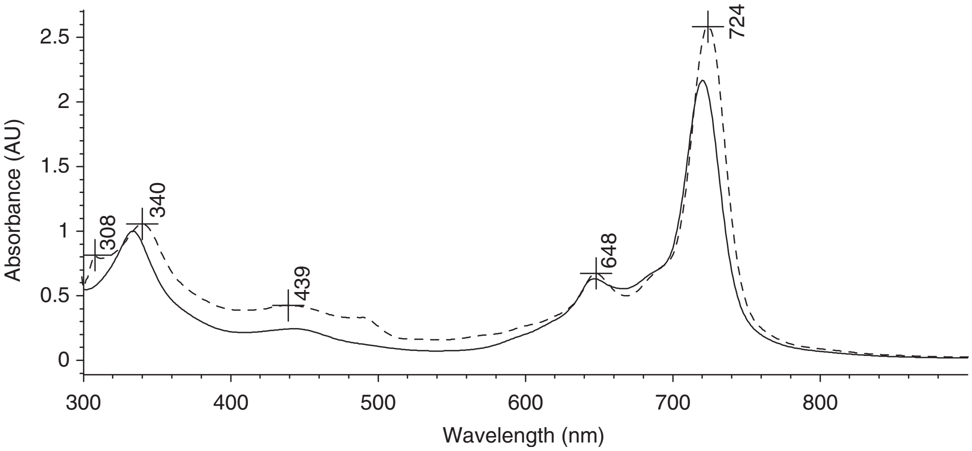

Figure 2. Electronic absorption spectra of copper tetrakis-(3-phenylthio)-phthalocyaninate: continuous line – in chloroform, dotted line – in trichlorobenzene.

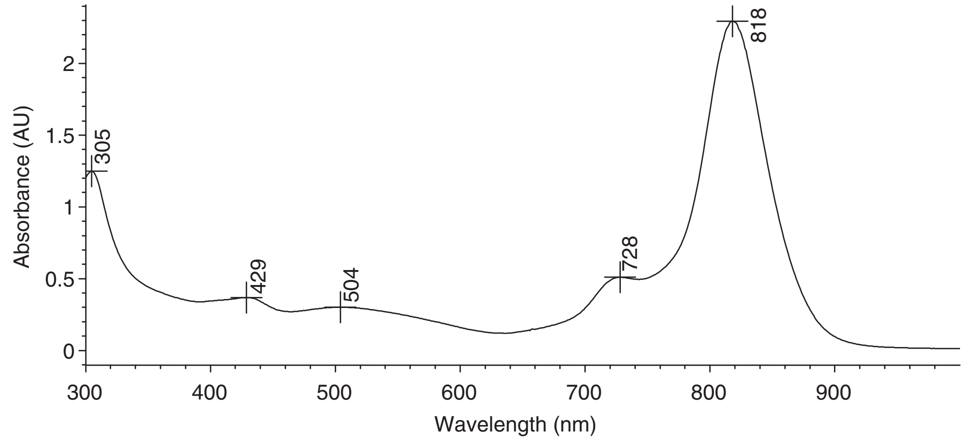

Figure 3. Electronic absorption spectra of $4\text{-}[4',5'\text{-}(CN)_2\text{-}PhO]_4PcCu$ in H_2SO_4.

Table 3. Elemental analysis data of the phthalocyanines.

	Found/Calculated, wt. (%)		
Compound	C	H	N
3-(PhS)$_4$-PcHH $C_{56}H_{34}N_8S_4$	70.88/71.01	3.77/3.59	12.02/11.83
3-(PhS)$_4$-PcCu $C_{56}H_{32}CuN_8S_4$	66.40/66.62	3.01/3.17	11.04/11.10
3-(PhS)$_4$-PcNi $C_{56}H_{32}NiN_8S_4$	66.57/66.80	3.32/3.18	11.28/11.13
4-(NO$_2$)$_4$-PcHH $C_{32}H_{14}N_{12}O_8$	54.84/55.34	2.33/2.01	24.15/24.10
4-(NO$_2$)$_4$-PcCu $C_{32}H_{12}CuN_{12}O_8$	50.52/50.84	2.32/1.59	22.33/22.23
4-(NO$_2$)$_4$-PcNi $C_{32}H_{12}NiN_{12}O_8$	50.59/51.15	2.07/1.60	22.26/22.37
4-(NO$_2$)$_4$-PcZn $C_{32}H_{12}ZnN_{12}O_8$	50.63/50.67	1.95/1.58	21.97/22.17
4-[4′,5′-(CN)$_2$-PhO]$_4$PcHH $C_{64}H_{26}N_{16}O_4$	70.61/70.92	2.57/2.40	20.37/20.69
4-[4′,5′-(CN)$_2$-PhO]$_4$PcCu $C_{64}H_{24}CuN_{16}O_4$	66.87/67.08	2.31/2.09	19.34/19.56
4-[4′,5′-(CN)$_2$-PhO]$_4$PcZn $C_{64}H_{24}ZnN_{16}O_4$	66.72/67.00	2.28/2.09	19.39/19.54

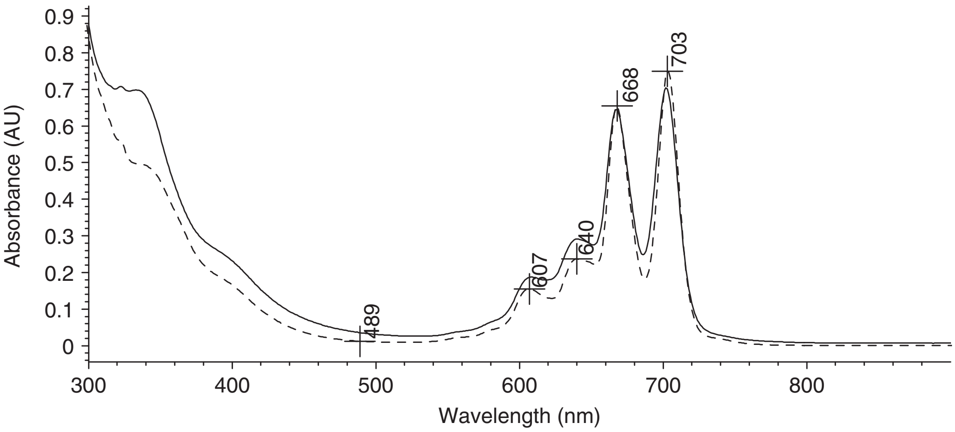

Figure 4. Electronic absorption spectra of 4-(α-NfO)$_4$-PcHH: continuous line – in methylene chloride, dotted line – in benzene.

All complexes are practically insoluble in usual organic solvents; copper complexes are slightly more soluble in comparison with nickel complexes of the same phthalocyanine.

4. Conclusions

Substituted metal-free phthalocyanines and their metal complexes were obtained by direct electrosynthesis at 25–130°C in alcohol media using 3-phenylthiophthalodinitrile, 4-α-naphthoxyphthalodinitrile, 4-nitrophthalodinitrile, 3-β-naphthoxyphthalodinitrile, and tetracyanodiphenyl ether (4,4′-oxodiphthalodinitrile) as precursors. Compositions and properties of the formed products correspond to those synthesized by classic techniques at considerably higher temperature (>160°C). Some metals (Bi, Ta) did not produce phthalocyaninates. Inhibition of 4-nitrophthalodinitrile tetramerization by vanadyl cations prevented use of V as a sacrificial anode. It is possible to carry out low-temperature (20–130°C) electrosynthesis of substituted phthalocyanines, although with slightly lower yields (8–31%); possibility of electrochemical synthesis depends on electron-donor (acceptor) properties of substituents and positions in benzene rings.

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