

## 4-Acyloxy- and 4-Acylaminophthalonitriles and Phthalocyanines Based Thereon

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**Abstract**—Reactions of 4-hydroxy- and 4-aminophthalonitriles with substituted benzoyl chlorides gave the corresponding *N*- and *O*-benzoyl derivatives, and the latter were used to obtain copper and nickel phthalocyanine complexes. Effect of the substituents in the latter on their electronic absorption spectra was studied. The obtained complexes were found to undergo association in organic solvents.

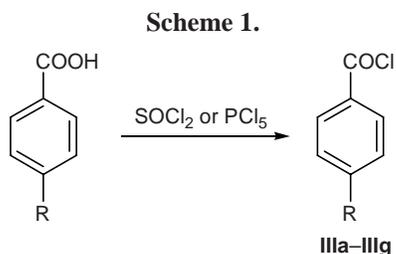
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Up to now, a large number of substituted phthalocyanines were synthesized and studied. Introduction of different substituents into the benzene rings of phthalocyanine considerably affects physicochemical properties of this unique compound. An important place among phthalocyanines is occupied by hydroxy- and amino-substituted analogs and their derivatives such as alkoxy, aryloxy, etc. [1–4]. The presence of the above substituents makes phthalocyanines soluble in organic solvents and therefore extends the scope of their practical applications. The present work was aimed at synthesizing new soluble phthalocyanines and their precursors, *O*- and *N*-benzoyl derivatives of 4-hydroxy- and 4-aminophthalonitriles, and studying substituent effects on the spectral parameters of phthalocyanine metal complexes.

In the first stage of our study we synthesized benzoyl derivatives of 4-hydroxy- and 4-aminophthalonitriles.

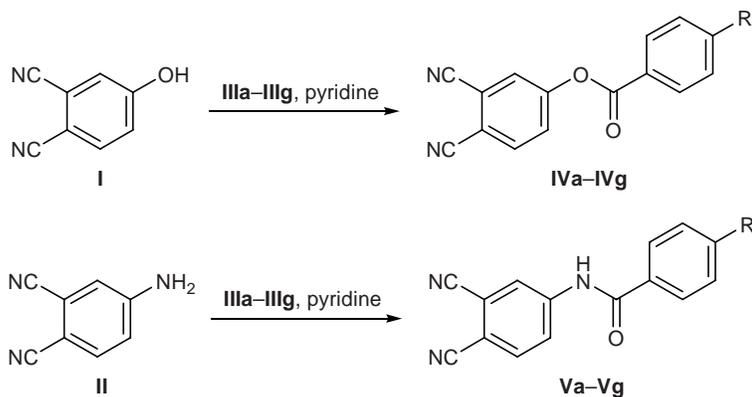
Using 4-nitrophthalimide as starting compound [5], we obtained 4-nitrophthalonitrile according to the known procedure [6]. 4-Hydroxyphthalonitrile (**I**) was synthesized by nucleophilic replacement of the nitro group in 4-nitrophthalonitrile [7], and reduction of the latter with tin(II) chloride in hydrochloric acid gave 4-aminophthalonitrile (**II**) [8]. Compounds **I** and **II** were then subjected to *O*- or *N*-acylation using substituted benzoyl chlorides **IIIa–IIIg** which were prepared in turn by treatment of the corresponding benzoic acids with excess thionyl chloride (Scheme 1) or phosphorus pentachloride (4-nitrobenzoic acid) [9].

It is known [9–11] that acylation with acid chlorides is usually carried out in the presence of a base, e.g., aqueous sodium hydroxide (Schotten–Bauman) or an organic base such as pyridine (Einhorn reaction). We used the second procedure where pyridine acted simultaneously as solvent and catalyst. Pyridine with acylating agents forms reactive species like *N*-benzoylpyridinium, and it promotes partial ionization of a hydroxy compound thus facilitating *O*-acylation. Moreover, the use of pyridine as solvent prevents the resulting esters and amides from undergoing hydrolysis; therefore, the yield of the target products increases. The reactions of nitriles **I** and **II** with benzoyl chlorides **IIIa–IIIg** afforded esters **IVa–IVg** and amides **Va–Vg**, respectively (Scheme 2). The products were separated from unreacted hydroxy and amino precursors by extraction into chloroform, followed by



R = H (**a**), C<sub>9</sub>H<sub>19</sub>O (**b**), C<sub>10</sub>H<sub>21</sub>O (**c**), C<sub>11</sub>H<sub>23</sub>COO (**d**), 4-C<sub>7</sub>H<sub>15</sub>-C<sub>6</sub>H<sub>4</sub>COO (**e**), 4-C<sub>8</sub>H<sub>17</sub>OC<sub>6</sub>H<sub>4</sub>COO (**f**), NO<sub>2</sub> (**g**).

Scheme 2.



R = H (a), C<sub>9</sub>H<sub>19</sub>O (b), C<sub>10</sub>H<sub>21</sub>O (c), C<sub>11</sub>H<sub>23</sub>COO (d), 4-C<sub>7</sub>H<sub>15</sub>C<sub>6</sub>H<sub>4</sub>COO (e), 4-C<sub>8</sub>H<sub>17</sub>OC<sub>6</sub>H<sub>4</sub>COO (f), NO<sub>2</sub> (g).

removal of the solvent and extraction into acetone. 4-Nitrobenzoic acid derivatives **IVg** and **Vg** were washed with diethyl ether to remove residual 4-nitrobenzoic acid. Compounds **IVa–IVg** and **Va–Vg** are yellowish crystalline substances or waxy materials that are readily soluble in chloroform, acetone, and benzene. They were identified on the basis of their elemental compositions and spectral data (IR, <sup>1</sup>H NMR, and mass spectra).

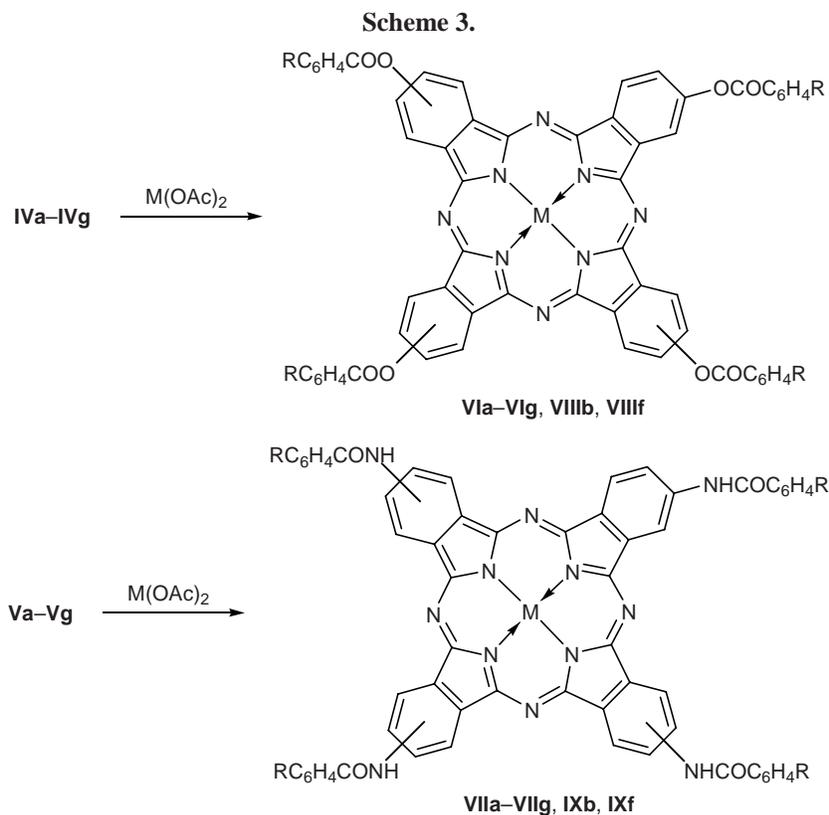
The IR spectra of phthalonitriles **IVa–IVg** and **Va–Vg** retained absorption bands due to stretching vibrations of the cyano groups (2230–2240 cm<sup>-1</sup>), whereas bands assignable to bending and stretching vibrations of hydroxy group (1310–1320 cm<sup>-1</sup>) and primary amino group (~3500, 1590–1650 cm<sup>-1</sup>) were absent. All compounds displayed an absorption band in the region 1670–1770 cm<sup>-1</sup>, which is typical of esters and amides. The IR spectra of phthalodinitriles **IV** and **Vb–Vf** contained absorption bands due to stretching (2848–2930 cm<sup>-1</sup>) and asymmetric and symmetric bending vibrations (1460–1480 and 1340–1391 cm<sup>-1</sup>) of methyl and methylene C–H bonds. The secondary amino group in compounds **Va–Vg** gave rise to absorption at 3270–3350 cm<sup>-1</sup>, and vibrations of the C<sub>Ar</sub>–O–C<sub>Alk</sub> fragments in **IVb**, **IVc**, **IVf**, **Vb**, **Vc**, and **Vf** were characterized by a frequency of 1250–1257 cm<sup>-1</sup>. Nitro-substituted phthalonitriles also displayed absorption bands in the regions 1541–1566 and 1349–1351 cm<sup>-1</sup> due to asymmetric and symmetric stretching vibrations of the nitro group [12].

In the <sup>1</sup>H NMR spectrum of dinitrile **IVb**, signals from protons in the alkoxy group appeared in the upfield region. The triplet at δ 0.88 ppm belongs to protons of the terminal methyl group, protons of the six methylene groups resonate as a broadened singlet

at δ 1.29 ppm, the β-CH<sub>2</sub> group gives rise to a multiplet at δ 1.82 ppm, and the OCH<sub>2</sub> signal is a triplet at δ 4.05 ppm. The downfield region of the spectrum contained multiplets at δ 6.92–7.80 and 7.81–8.15 ppm corresponding to aromatic protons in the nonyloxyphenyl group and three protons of the phthalonitrile fragment, respectively. Compound **Va** showed in the mass spectrum the molecular ion peak with *m/z* 247 ([*M*]<sup>+</sup>, *I*<sub>rel</sub> 100%) and ion peak with *m/z* 121 ([*M* – 126]<sup>+</sup>, *I*<sub>rel</sub> 35%, PhCONH<sub>2</sub>).

Copper phthalocyanine complexes **VIa–VIg** and **VIIa–VIIg** were synthesized by reaction of the corresponding substituted phthalonitriles **IVa–IVg** and **Va–Vg** with copper(II) acetate, and nickel complexes **VIIIb**, **VIIIf**, **IXb**, and **IXf** were obtained from nitriles **IVb**, **IVf**, **Vb**, and **Vf**, respectively, and nickel(II) acetate (Scheme 3). The reactions were carried out by heating the reactants at 170–180°C. In the syntheses of phthalocyanines **VIg**, **VIIa**, and **VIIg**, urea was added to the reaction mixture. The products were isolated by extraction into chloroform or dimethylformamide and were purified by column chromatography on aluminum oxide. Complexes **VI–IX** are blue–green (acyloxy derivatives) or green powders (acylamino derivatives) that are soluble in DMF, chloroform, and benzene. Exceptions are nitro-substituted derivatives **VIg** and **VIIg** that are soluble only in DMF. Therefore, nitro groups, regardless of their position in the molecule, reduce the solubility in organic solvents.

The isolated metal phthalocyanine complexes were characterized by elemental analyses and IR, <sup>1</sup>H NMR, and electronic absorption spectra. Their IR spectra contained absorption bands at 1612–1624, 1505–1524, 1342–1360, 1246–1288, 1170–1188, 1140–1150, 1116–1130, 1080–1092, 1048–1060, 910–950, 850–880, 770–



780, and 734–736  $\text{cm}^{-1}$ , which are typical of phthalocyanines [13]. In addition, absorption bands corresponding to the acyl fragments were present (see the IR spectra of the corresponding initial phthalonitriles, given above).

The  $^1\text{H}$  NMR spectra of copper and nickel complexes **VIc** and **VIIIb** are fairly similar. For example, the following signals are present in the spectrum of copper complex **VIc**,  $\delta$ , ppm: 0.87 t (12H,  $\text{CH}_3$ ), 1.27 s (56H,  $\text{CH}_2$ ), 1.78 m (8H,  $\beta\text{-CH}_2$ ), 4.03 t (8H,  $\text{OCH}_2$ ), 6.93 m (8H, *m*-H in  $\text{RC}_6\text{H}_4\text{CO}$ ), 7.50–7.88 m (12H,  $\text{H}_{\text{arom}}$ ), 8.10 m (8H, *o*-H in  $\text{RC}_6\text{H}_4\text{CO}$ ).

In keeping with our previous data [14], the *Q*-band in the electronic absorption spectra of acyloxy-substituted copper complexes is located at a longer wavelength than in the spectra of copper phthalocyanine; on the other hand, it is displaced by 13–15 nm toward shorter wavelengths, as compared to (tetra-4-hydroxyphthalocyaninato)copper(II). This results from reduction of the electron-donor power of the hydroxy group owing to acylation. An analogous pattern is observed for the *N*-acylated complexes. Acyloxy-substituted phthalocyanine complexes **VIa–VIg** in chloroform and DMF are characterized by relatively high intensity of

the absorption band at  $\lambda$  613–617 nm, indicating that they tend to undergo association in solution [15]. As might be expected, higher concentration of the monomeric form is observed in more polar solvents. The presence of nitro groups induces a small red shift of absorption bands in the electronic spectrum (cf. the data for complexes **VIg** and **VIa–VIb** in table). The electronic absorption spectra of *N*-acylamino-substituted copper complexes (see table) resemble those of their acyloxy analogs. Only a slight red shift of the long-wave *Q*-band may be noted for the former. The nickel complexes are characterized by a small blue shift of the absorption maxima as compared to the corresponding copper complexes (see table).

## EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi U-2001 spectrophotometer. The IR spectra were recorded in the frequency region from 400 to 4000  $\text{cm}^{-1}$  on an Avatar 360 FT-IR spectrometer from samples prepared as KBr pellets. The  $^1\text{H}$  NMR spectra were obtained on a Bruker AMD-200 instrument from solutions in  $\text{CDCl}_3$ . The mass spectra were run on a Varian Saturn 2000K mass spectrometer. The ele-

## Electronic absorption spectra of copper and nickel phthalocyanine complexes VI–IX

Compound no.	R	$\lambda_{\max}$ , nm ( $D/D_{\max}$ )	
		DMF	CHCl <sub>3</sub>
VIa	H	671 (1.00), 610 (0.63)	672 (1.00), 616 (0.75)
VIb	C <sub>9</sub> H <sub>19</sub> O	670 (1.00), 617 (0.74)	671 611, (1.00/ 1.26)
VIc	C <sub>10</sub> H <sub>21</sub> O	610, 671 (1.00/ 1.65)	672 (1.00), 613 (0.79)
VIId	C <sub>11</sub> H <sub>23</sub> COO	690 (1.00), 621 (0.45)	672 (1.00), 616 (0.51)
VIe	4-C <sub>7</sub> H <sub>15</sub> C <sub>6</sub> H <sub>4</sub> COO	671 (1.00), 618 (0.72)	672 (1.00), 614 (0.96)
VIIf	4-C <sub>8</sub> H <sub>17</sub> OC <sub>6</sub> H <sub>4</sub> COO	670 (1.00), 616 (0.85)	672 (1.00), 617 (0.93)
VIg	NO <sub>2</sub>	689 (1.00), 625 (0.69)	
VIIa	H	690 (1.00), 626 (0.41)	
VIIb	C <sub>9</sub> H <sub>19</sub> O	692 (1.00) 626 (0.86)	624
VIIc	C <sub>10</sub> H <sub>21</sub> O	692 (1.00), 638 (0.72)	625
VIIId	C <sub>11</sub> H <sub>23</sub> COO	690 (1.00), 621 (0.53)	695 (0.60), 616 (1.00)
VIIe	4-C <sub>7</sub> H <sub>15</sub> C <sub>6</sub> H <sub>4</sub> COO	700 (0.90), 643 (1.00)	696 (0.70), 615 (1.00)
VIIIf	4-C <sub>8</sub> H <sub>17</sub> OC <sub>6</sub> H <sub>4</sub> COO	690 (1.00) 627 (0.52)	692 (1.00), 644 (0.97)
VIIg	NO <sub>2</sub>	693 (1.00), 627 (0.74)	
VIIIb	C <sub>9</sub> H <sub>19</sub> O	666 (1.00), 622 (0.70)	665 (1.00), 631 (0.76)
VIIIIf	4-C <sub>8</sub> H <sub>17</sub> OC <sub>6</sub> H <sub>4</sub> COO	664 (1.00), 613 (0.97)	664 (1.00), 622 (0.82)
IXb	C <sub>9</sub> H <sub>19</sub> O	686 (1.00), 625 (0.71)	625
IXf	4-C <sub>8</sub> H <sub>17</sub> OC <sub>6</sub> H <sub>4</sub> COO	687 (1.00), 639 (0.86)	626

mental compositions were determined using a FlashEA 1112 CHNS–O analyzer.

**4-Benzoylamino- and 4-benzoyloxyphthalonitriles IVa–IVf and Va–Vf (general procedure).** A mixture of 0.01 mmol of benzoic or substituted benzoic acid and 0.14 ml (2 mmol) of thionyl chloride was heated under stirring to 40–50°C and was kept at that temperature until hydrogen chloride no longer evolved. Excess thionyl chloride was distilled off, 0.14 g (1 mmol) of dinitrile **I** or 0.14 g (1.1 mmol) of dinitrile **II** and 3 ml of pyridine were added to the residue, and the mixture was heated to 80°C and kept for 16 h at that temperature. The mixture was poured into water, and the viscous material was filtered off, dried at 50°C under reduced pressure, and dissolved in 10 ml of chloroform. The solution was filtered, the filtrate was evaporated, the residue was dissolved in 10 ml of acetone, the solution was filtered, and the filtrate was evaporated.

**3,4-Dicyanophenyl benzoate (IVa)** was obtained from 0.12 g of benzoic acid. Yield 0.21 g (84%), white powder, mp 130–132°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2234 (C≡N), 1745 (C=O). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.22–7.56 m (5H), 7.92–8.12 m (3H). Found, %: C 72.3;

H 4.8; N 11.8. C<sub>15</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>. Calculated, %: C 72.5; H 3.3; N 11.3.

**3,4-Dicyanophenyl 4-(nonyloxy)benzoate (IVb)** was obtained from 0.28 g of 4-(nonyloxy)benzoic acid. Yield 0.32 g (82%), off-white powder. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2235 (C≡N); 1735 (C=O); 2920, 2852 (C–H); 1257 (C–O–C). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.88 t (3H), 1.29 s (12H), 1.82 m (2H), 4.05 t (2H), 6.92–7.80 m (4H), 7.81–8.15 m (3H). Found, %: C 73.3; H 6.9; N 7.0. C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: C 73.8; H 6.7; N 7.2.

**3,4-Dicyanophenyl 4-(decyloxy)benzoate (IVc)** was obtained from 0.26 g of 4-(decyloxy)benzoic acid. Yield 0.33 g (83%), off-white powder. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2235 (C≡N); 1739 (C=O); 2920, 2851 (C–H); 1257 (C–O–C). Found, %: C 73.9; H 7.3; N 6.7. C<sub>25</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: C 74.2; H 7.0; N 6.9.

**3,4-Dicyanophenyl 4-(dodecanoyloxy)benzoate (IVd)** was obtained from 0.32 g of 4-(dodecanoyloxy)benzoic acid. Yield 0.39 g (87%), off-white powder. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2242 (C≡N); 1743, 1760 (C=O); 2919, 2849 (C–H). Found, %: C 72.4; H 7.1; N 6.0. C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>. Calculated, %: C 72.6; H 6.8; N 6.3.

**3,4-Dicyanophenyl 4-(4-heptylbenzoyloxy)benzoate (IVe)** was obtained from 0.34 g of 4-(4-heptylbenzoyloxy)benzoic acid. Yield 0.40 g (86%), off-white waxy material. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2235 ( $\text{C}\equiv\text{N}$ ); 1735 br ( $\text{C}=\text{O}$ ); 2924, 2853 ( $\text{C}-\text{H}$ ). Found, %: C 74.5; H 6.0; N 5.8.  $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}_4$ . Calculated, %: C 74.7; H 5.6; N 6.0.

**3,4-Dicyanophenyl 4-[4-(octyloxy)benzoyloxy]benzoate (IVf)** was obtained from 0.37 g of 4-[4-(octyloxy)benzoyloxy]benzoic acid. Yield 0.43 g (86%), off-white waxy material. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2235 ( $\text{C}\equiv\text{N}$ ); 1689, 1738 ( $\text{C}=\text{O}$ ); 2935, 2857 br ( $\text{C}-\text{H}$ ); 1259 ( $\text{C}-\text{O}-\text{C}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.87 t (3H), 1.26 s (10H), 1.85 m (2H), 4.09 t (2H), 6.88–7.12 m (4H), 7.15–7.33 m (4H), 7.88–8.33 m (3H). Found, %: C 71.0; H 7.5; N 5.3.  $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_5$ . Calculated: C 71.4; H 7.2; N 5.6.

**N-(3,4-Dicyanophenyl)benzamide (Va)** was obtained from 0.12 g of benzoic acid. Yield 0.21 g (84%), off-white powder, mp 169–171°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2214 ( $\text{C}\equiv\text{N}$ ); 1692 ( $\text{C}=\text{O}$ ); 1600, 3344 ( $\text{N}-\text{H}$ ). Found, %: C 72.7; H 4.0; N 16.7.  $\text{C}_{15}\text{H}_9\text{N}_3\text{O}$ . Calculated: C 72.9; H 3.7; N 17.0.

**N-(3,4-Dicyanophenyl)-4-(nonyloxy)benzamide (Vb)** was obtained from 0.26 g of 4-(nonyloxy)benzoic acid. Yield 0.32 g (81%), off-white powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2239 ( $\text{C}\equiv\text{N}$ ); 1769 ( $\text{C}=\text{O}$ ); 1670, 3344 ( $\text{N}-\text{H}$ ); 2921, 2852 ( $\text{C}-\text{H}$ ); 1251 ( $\text{C}-\text{O}-\text{C}$ ). Found, %: C 73.6; H 7.3; N 10.6.  $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_2$ . Calculated, %: C 74.0; H 7.0; N 10.8.

**4-Decyloxy-N-(3,4-dicyanophenyl)benzamide (Vc)** was obtained from 0.28 g of 4-(decyloxy)benzoic acid. Yield 0.32 g (80%), off-white powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2239 ( $\text{C}\equiv\text{N}$ ); 1765 ( $\text{C}=\text{O}$ ); 1670, 3344 ( $\text{N}-\text{H}$ ); 2920, 2851 ( $\text{C}-\text{H}$ ); 1253 ( $\text{C}-\text{O}-\text{C}$ ). Found, %: C 74.2; H 7.5; N 10.2.  $\text{C}_{25}\text{H}_{29}\text{N}_3\text{O}_2$ . Calculated, %: C 74.4; H 7.2; N 10.4.

**4-(3,4-Dicyanophenylcarbonyl)phenyl dodecanoate (Vd)** was obtained from 0.32 g of 4-(dodecanoyloxy)benzoic acid. Yield 0.36 g (80%), yellow powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2231 ( $\text{C}\equiv\text{N}$ ); 1755 br ( $\text{C}=\text{O}$ ); 1702, 3343 ( $\text{N}-\text{H}$ ); 2921, 2849 ( $\text{C}-\text{H}$ ). Found, %: C 72.5; H 7.7; N 9.2.  $\text{C}_{27}\text{H}_{31}\text{N}_3\text{O}_3$ . Calculated: C 72.8; H 7.0; N 9.4.

**4-(3,4-Dicyanophenylcarbonyl)phenyl 4-heptylbenzoate (Ve)** was obtained from 0.34 g of 4-(4-heptylbenzoyloxy)benzoic acid. Yield 0.40 g (86%), yellow waxy substance. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2214 ( $\text{C}\equiv\text{N}$ ); 1735 br ( $\text{C}=\text{O}$ ); 1689, 3343 ( $\text{N}-\text{H}$ ); 2924,

2853 ( $\text{C}-\text{H}$ ). Found, %: C 74.6; H 6.0; N 8.7.  $\text{C}_{29}\text{H}_{27}\text{N}_3\text{O}_3$ . Calculated, %: C 74.8; H 5.9; N 9.0.

**4-(3,4-Dicyanophenylcarbonyl)phenyl 4-(octyloxy)benzoate (Vf)** was obtained from 0.37 g of 4-[4-(octyloxy)benzoyloxy]benzoic acid. Yield 0.41 g (81%), yellow waxy substance. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2236 ( $\text{C}\equiv\text{N}$ ); 1720 br ( $\text{C}=\text{O}$ ); 1689, 3339 ( $\text{N}-\text{H}$ ); 2930, 2857 ( $\text{C}-\text{H}$ ); 1257 ( $\text{C}-\text{O}-\text{C}$ ). Found, %: C 71.3; H 8.0; N 8.5.  $\text{C}_{30}\text{H}_{37}\text{N}_3\text{O}_4$ . Calculated, %: C 71.5; H 7.4; N 8.3.

**4-(3,4-Dicyanophenyl) 4-nitrobenzoate (IVg).** A mixture of 0.19 g (1 mmol) of 4-nitrobenzoyl chloride, 0.14 g of dinitrile **I**, and 3 ml of pyridine was heated for 16 h at 80°C. The mixture was poured into water, the precipitate was filtered off, dried at 70°C under reduced pressure, washed with diethyl ether to remove *p*-nitrobenzoic acid, and extracted with chloroform, and the extract was evaporated. Yield 0.17 g (61%), white powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2242 ( $\text{C}\equiv\text{N}$ ); 1693 ( $\text{C}=\text{O}$ ); 1349, 1566 ( $\text{NO}_2$ ). Found, %: C 61.2; H 2.7; N 14.0.  $\text{C}_{15}\text{H}_7\text{N}_3\text{O}_4$ . Calculated, %: C 61.4; H 2.4; N 14.3.

**N-(3,4-Dicyanophenyl)-4-nitrobenzamide (Vg).** A mixture of 0.19 g (1 mmol) of 4-nitrobenzoyl chloride, 0.14 g of dinitrile **II**, and 3 ml of pyridine was heated for 16 h at 80°C. The mixture was poured into water, the precipitate was filtered off, dried at 70°C under reduced pressure, washed with diethyl ether to remove *p*-nitrobenzoic acid, and extracted with chloroform, and the extract was evaporated. Yield 0.18 g (64%), yellow powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2214 ( $\text{C}\equiv\text{N}$ ); 1693 ( $\text{C}=\text{O}$ ); 1693, 3350 ( $\text{N}-\text{H}$ ); 1351, 1541 ( $\text{NO}_2$ ). Found, %: C 61.4; H 3.0; N 19.0.  $\text{C}_{15}\text{H}_8\text{N}_4\text{O}_3$ . Calculated, %: C 61.7; H 2.8; N 19.2.

**Tetra[benzoyloxy(amino)]phthalocyanine copper and zinc complexes VI–IX (general procedure).** A mixture of 1 mmol of the corresponding phthalodinitrile **IV** or **V** and 0.06 g (0.3 mmol) of copper(II) acetate or 0.08 g (0.3 mmol) of nickel(II) acetate was heated for 1.5 h at 170–180°C. The mixture was extracted with chloroform, and the extract was subjected to column chromatography on aluminum oxide (Brockmann activity grade II) using chloroform–methanol (4:1 by volume) as eluent (complex **VIIa** was isolated using DMF as eluent). Compounds **VIg** and **VIIg** were purified by extraction with acetone and methanol to remove impurities.

**[2,9(10),16(17),23(24)-Tetra(benzoyloxy)phthalocyaninato]copper(II) (VIa)** was obtained from 0.25 g of compound **IVa**. Yield 0.25 g (24%), blue–green

powder. IR spectrum:  $\nu$  1745  $\text{cm}^{-1}$  (C=O). Found, %: C 67.9; H 3.5; N 10.3.  $\text{C}_{60}\text{H}_{32}\text{CuN}_8\text{O}_8$ . Calculated, %: C 68.2; H 3.1; N 10.6.

**[2,9(10),16(17),23(24)-Tetrakis[4-(nonyloxy)benzoyloxy]phthalocyaninato}copper(II) (VIb)** was obtained from 0.39 g of compound **IVb**. Yield 0.24 g (20%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1735 (C=O); 2920, 2852 (C–H); 1257 (C–O–C). Found, %: C 70.5; H 6.7; N 6.5.  $\text{C}_{96}\text{H}_{104}\text{CuN}_8\text{O}_{12}$ . Calculated, %: C 70.9; H 6.5; N 6.9.

**[2,9(10),16(17),23(24)-Tetrakis[4-(decyloxy)benzoyloxy]phthalocyaninato}copper(II) (VIc)** was obtained from 0.41 g of compound **IVc**. Yield 0.31 g (19%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1739 (C=O); 2920, 2851 (C–H); 1257 (C–O–C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.87 t (12H), 1.27 s (56H), 1.78 m (8H), 4.03 t (8H), 6.93 m (8H), 7.50–7.88 m (12H), 8.10 m (8H). Found, %: C 74.0; H 7.2; N 6.6.  $\text{C}_{100}\text{H}_{112}\text{CuN}_8\text{O}_{12}$ . Calculated, %: C 74.2; H 7.0; N 6.9.

**[2,9(10),16(17),23(24)-Tetrakis[4-(dodecanoyloxy)benzoyloxy]phthalocyaninato}copper(II) (VIId)** was obtained from 0.45 g of compound **IVd**. Yield 0.40 g (22%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1743, 1760 (C=O); 2919, 2849 (C–H). Found, %: C 70.0; H 6.2; N 6.0.  $\text{C}_{108}\text{H}_{120}\text{CuN}_8\text{O}_{16}$ . Calculated, %: C 70.1; H 6.1; N 6.5.

**[2,9(10),16(17),23(24)-Tetrakis[4-(4-heptylbenzoyloxy)benzoyloxy]phthalocyaninato}copper(II) (VIe)** was obtained from 0.47 g of compound **IVe**. Yield 0.43 g (22%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1735 br (C=O); 2924, 2853 (C–H). Found, %: C 72.0; H 5.6; N 5.5.  $\text{C}_{116}\text{H}_{104}\text{CuN}_8\text{O}_{16}$ . Calculated, %: C 72.2; H 5.3; N 5.8.

**[2,9(10),16(17),23(24)-Tetrakis{4-[4-(octyloxy)benzoyloxy]benzoyloxy}phthalocyaninato}copper(II) (VIf)** was obtained from 0.50 g of compound **IVf**. Yield 0.50 g (25%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1689, 1738 (C=O); 2922, 2851 br (C–H); 1258 (C–O–C). Found, %: C 70.6; H 5.7; N 5.2.  $\text{C}_{120}\text{H}_{112}\text{CuN}_8\text{O}_{20}$ . Calculated, %: C 70.3; H 5.5; N 5.5.

**[2,9(10),16(17),23(24)-Tetra(4-nitrobenzoyloxy)phthalocyaninato}copper(II) (VIg)** was obtained from 0.29 g of compound **IVg**. Yield 0.24 g (21%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1693 (C=O); 1349, 1566 ( $\text{NO}_2$ ). Found, %: C 60.8; H 2.7; N 9.2.  $\text{C}_{60}\text{H}_{28}\text{CuN}_8\text{O}_{16}$ . Calculated, %: C 61.0; H 2.4; N 9.5.

**[2,9(10),16(17),23(24)-Tetra(benzoylamino)phthalocyaninato}copper(II) (VIIa)** was obtained from 0.25 g of compound **Va** in the presence of 0.2 g

of urea. Yield 0.25 g (24%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1692 (C=O); 1600, 3344 (N–H). Found, %: C 68.2; H 4.0; N 15.6.  $\text{C}_{60}\text{H}_{36}\text{CuN}_{12}\text{O}_4$ . Calculated, %: C 68.5; H 3.5; N 16.0.

**[2,9(10),16(17),23(24)-Tetrakis[4-(nonyloxy)benzoylamino]phthalocyaninato}copper(II) (VIIb)** was obtained from 0.39 g of compound **Vb**. Yield 0.38 g (25%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1769 (C=O); 1670, 3344 (N–H); 2921, 2852 (C–H); 1251 (C–O–C). Found, %: C 71.0; H 7.0; N 10.1.  $\text{C}_{96}\text{H}_{108}\text{CuN}_{12}\text{O}_8$ . Calculated, %: C 71.1; H 6.7; N 10.4.

**[2,9(10),16(17),23(24)-Tetrakis[4-(decyloxy)benzoylamino]phthalocyaninato}copper(II) (VIIc)** was obtained from 0.39 g of compound **Vc**. Yield 0.33 g (20%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1765 (C=O); 1670, 3344 (N–H); 2920, 2851 (C–H); 1253 (C–O–C). Found, %: C 74.1; H 7.5; N 10.1.  $\text{C}_{100}\text{H}_{116}\text{CuN}_{12}\text{O}_8$ . Calculated, %: C 74.4; H 7.2; N 10.4.

**[2,9(10),16(17),23(24)-Tetrakis[4-(dodecanoyloxy)benzoylamino]phthalocyaninato}copper(II) (VIIId)** was obtained from 0.45 g of compound **Vd**. Yield 0.40 g (22%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1755 br (C=O); 1702, 3343 (N–H); 2921, 2849 (C–H). Found, %: C 70.0; H 7.0; N 8.8.  $\text{C}_{108}\text{H}_{124}\text{CuN}_{12}\text{O}_{12}$ . Calculated, %: C 70.3; H 6.8; N 9.1.

**[2,9(10),16(17),23(24)-Tetrakis[4-(4-heptylbenzoyloxy)benzoylamino]phthalocyaninato}copper(II) (VIIe)** was obtained from 0.47 g of compound **Ve**. Yield 0.41 g (21%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1735 br (C=O); 1689, 3343 (N–H); 2924, 2853 (C–H). Found, %: C 72.0; H 6.0; N 9.0.  $\text{C}_{116}\text{H}_{108}\text{N}_{12}\text{CuO}_{12}$ . Calculated, %: C 72.4; H 5.7; N 8.7.

**[2,9(10),16(17),23(24)-Tetrakis{4-[4-(octyloxy)benzoyloxy]benzoylamino}phthalocyaninato}copper(II) (VIIIf)** was obtained from 0.50 g of compound **Vf**. Yield 0.42 g (21%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1720 br (C=O); 1689, 3339 (N–H); 2930, 2857 (C–H); 1257 (C–O–C). Found, %: C 70.2; H 5.9; N 8.0.  $\text{C}_{120}\text{H}_{116}\text{N}_{12}\text{CuO}_{16}$ . Calculated, %: C 70.5; H 5.7; N 8.2.

**[2,9(10),16(17),23(24)-Tetra(4-nitrobenzoylamino)phthalocyaninato}copper(II) (VIIg)** was obtained from 0.29 g of compound **Vg**. Yield 0.25 g (21%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1693 (C=O); 1693, 3350 (N–H); 1351, 1541 ( $\text{NO}_2$ ). Found, %: C 61.0; H 2.9; N 14.0.  $\text{C}_{60}\text{H}_{32}\text{CuN}_{12}\text{O}_{12}$ . Calculated, %: C 61.3; H 2.7; N 14.3.

**[2,9(10),16(17),23(24)-Tetrakis[4-(nonyloxy)benzoyloxy]phthalocyaninato}nickel(II) (VIIIf)** was obtained from 0.39 g of compound **IVb**. Yield 0.32 g

(20%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1735 (C=O); 2920, 2852 (C–H); 1257 (C–O–C). Found, %: C 70.9; H 7.1; N 6.7.  $\text{C}_{96}\text{H}_{104}\text{N}_8\text{NiO}_{12}$ . Calculated, %: C 71.2; H 6.9; N 6.9.

**[2,9(10),16(17),23(24)-Tetrakis{4-[4-(octyloxy)-benzoyloxy]benzoyloxy}phthalocyaninato]nickel(II) (VIII f)** was obtained from 0.50 g of compound **IV f**. Yield 0.46 g (23%), blue–green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1689, 1738 (C=O); 2922, 2851 br (C–H); 1258 (C–O–C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.82 t (12H), 1.28 s (40H), 1.86 m (8H), 4.11 t (8H), 6.77–7.05 m (16H), 7.18–7.39 m (16H), 7.99–8.56 m (12H). Found, %: C 70.3; H 5.8; N 5.2.  $\text{C}_{120}\text{H}_{112}\text{N}_8\text{NiO}_{20}$ . Calculated, %: C 70.5; H 5.5; N 5.5.

**{2,9(10),16(17),23(24)-Tetrakis[4-(nonyloxy)benzoylamino]phthalocyaninato}nickel(II) (IX b)** was obtained from 0.39 g of compound **V b**. Yield 0.33 g (20%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1769 (C=O); 1670, 3344 (N–H); 2921, 2852 (C–H); 1251 (C–O–C). Found, %: C 71.0; H 7.1; N 10.1.  $\text{C}_{96}\text{H}_{108}\text{N}_{12}\text{NiO}_8$ . Calculated, %: C 71.3; H 6.7; N 10.4.

**[2,9(10),16(17),23(24)-Tetrakis{4-[4-(octyloxy)-benzoyloxy]benzoylamino}phthalocyaninato]nickel(II) (IX f)** was obtained from 0.50 g of compound **V f**. Yield 0.43 g (21%), green powder. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1720 br (C=O); 1689, 3339 (N–H); 2930, 2857 (C–H); 1257 (C–O–C). Found, %: C 70.3; H 6.0; N 8.0.  $\text{C}_{120}\text{H}_{116}\text{N}_{12}\text{NiO}_{16}$ . Calculated, %: C 70.6; H 5.7; N 8.2.

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