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## Synthesis and spectral properties of dodecaphenyl-substituted planar binuclear naphthalocyanine magnesium complex sharing a common benzene ring

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Dodecaphenyl-substituted planar binuclear naphthalocyanine magnesium complex possessing an intense absorption in the near IR region up to 1100 nm has been synthesized on the basis of novel 2,3-dicyano-6,7-diphenylnaphthalene.

Absorption in the near IR region in phthalocyanines with extended  $\pi$ -conjugation system allows one to use these compounds in photogalvanic elements,<sup>1</sup> optical electronic devices<sup>2</sup> and photooxidative catalysis.<sup>3</sup>

Previously,<sup>4,5</sup> we reported that planar binuclear phthalocyanines sharing a common benzene ring exhibit intense absorption in the near IR region and 200 nm red shift of the Q-band. Further expansion of the  $\pi$ -conjugated system in planar binuclear phthalocyanines can be in principle performed either in the aromatic or in peripheral  $\pi$ -system. However, replacement of the benzene bridge by a naphthalene results in a hypsochromic shift of the Q-band by 59 nm,<sup>6</sup> which can be explained by an increase in the HOMO–LUMO distance<sup>7</sup> in the resulting mutual  $\pi$ -system. Further expansion of aromatic bridge to a tetracene results in loss of absorption in the near IR region ( $\lambda_{max} = 690$  nm).<sup>8</sup>

Concerning the expansion of the peripheral  $\pi$ -system, until recently there is only one report of a synthesis of a planar heterodinuclear phthalo-naphthocyanine complex sharing a mutual benzene ring.<sup>9</sup> The absorption maximum of this compound is hypsochromically shifted by 38 nm with respect to the analogous binuclear phthalocyanine. However, this phenomenon was not interpreted. In our opinion, this could be related to the asymmetry in the structure of the complex in question. Note that synthesis of the planar binuclear naphthalocyanine complexes was for the first time reported recently.<sup>10,11</sup>

Extending our works on obtaining planar binuclear phthalocyanines with expanded  $\pi$ -conjugation system,<sup>4,6,10</sup> here we describe synthesis and spectral properties of a planar binuclear naphthalocyanine magnesium complex bearing twelve phenyl substituents at the periphery. Introduction of phenyl groups, we reasoned, could also increase the solubility of the target compound.

The starting 2,3-dicyano-6,7-diphenylnaphthalene **1** was synthesized by the Suzuki reaction from 6,7-dibromo-2,3-dicyanonaphthalene (Scheme 1).<sup>6,†</sup> To provide the basicity of the reaction medium, the saturated aqueous solution of K<sub>2</sub>CO<sub>3</sub> was added. 1,4-Dioxane was used as the solvent; a small admixture of acetonitrile was added to improve the solubility of 6,7-dibromo-2,3-dicyanonaphthalene. The use of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as the catalyst instead of Pd<sup>0</sup> salts widely employed in syntheses of similar compounds<sup>12–15</sup> allowed us to shorten the reaction time from 13 to 6 h. This may be due to the existence of two active sites in the catalyst molecule. We chose pyromellitonitrile as the starting compound for the synthesis of the aromatic bridge; to increase the reactivity of the



<sup>†</sup> UV-VIS spectra were recorded with a Hitachi U-4100 spectrophotometer in quartz cells ( $0.5 \times 1$ cm) using C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub> and THF as solvents. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400.13 and 100.61 MHz, respectively) using CDCl<sub>3</sub>, THF and pyridine-*d*<sub>5</sub> as solvents at 20 °C. Column chromatography was performed using neutral MN-Aluminiumoxid. Preparative TLC was performed using Merck Aluminium Oxide F<sub>254</sub> neutral flexible plates. Gel permeation chromatography was performed using Bio Beads SX-1 (Bio Rad). CHN analysis was carried out with CHNOS Elemental Analyzer Vario Micro. Mass spectra were measured on Finnigan MAT Insoc-50 (EI, 70 eV) and Vision-2000 (MALDI-TOF). IR spectra were recorded on Specord M-70 and Specord UR-20 spectrophotometers in liquid paraffin.

The Mg(OAc)<sub>2</sub>·4H<sub>2</sub>O salt was dried *in vacuo* at 100 °C for 4 h just before use.

6,7-Diphenylnaphthalene-2,3-dicarbonitrile 1. 6,7-Dibromo-2,3-dicyanonaphthalene (1.80 g, 5.36 mmol), phenylboronic acid (2.28 g, 18.70 mmol), dichlorobis(triphenylphosphine) palladium (0.038 g, 0.054 mmol), saturated aqueous solution of K<sub>2</sub>CO<sub>3</sub> (2.93 g) and 96 ml of a 1,4-dioxane-acetonitrile mixture (8:3) were placed in a two-necked flask equipped with a reflux condenser and a magnetic stirrer. The mixture was refluxed for 6 h in a stream of argon (TLC control: Al<sub>2</sub>O<sub>3</sub>, F<sub>254</sub>, C<sub>6</sub>H<sub>6</sub> as the eluent). The reaction mixture was cooled, poured into water and extracted with ethyl acetate. The organic layer was collected and evaporated; the residue was subjected to flash chromatography. The proper fraction was additionally purified by chromatography on a column with Al<sub>2</sub>O<sub>3</sub> using an ethyl acetate-hexane mixture (1:2) as the eluent. The yield of compound 1 was 1.5 g (85%), mp 230–230.3 °C,  $R_{\rm f}$  0.73 [Al<sub>2</sub>O<sub>3</sub>,  $F_{254}$ , ethyl acetate–hexane mixture (1:2) as the eluent]. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.15–7.21 (m, 4H, o-H<sub>Ph</sub>), 7.25–7.33 (m, 6H, *p*-H<sub>Ph</sub>, *m*-H<sub>Ph</sub>), 7.99 (s, 2H, 5,8-H<sub>Ar</sub>), 8.37 (s, 1,4-H<sub>Ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 110.17 (s, C<sup>2</sup>, C<sup>3</sup>), 115.97 (s, CN), 127.77 (s, *p*-C<sub>Ph</sub>), 128.29 (s, o-C<sub>ph</sub>), 129.69 (s, m-C<sub>ph</sub>), 129.94 (s, C<sup>5</sup>, C<sup>8</sup>), 132.39 (s, C<sup>6</sup>, C<sup>7</sup>), 135.66 (s, C<sup>1</sup>, C<sup>4</sup>), 139.45 (s, C<sup>9</sup>, C<sup>10</sup>), 144.44 (s, C<sub>Ph</sub> quarternary). Found (%): C, 87.27; H, 4.33; N, 8.68. Calc. for C<sub>24</sub>H<sub>14</sub>N<sub>2</sub> (%): C, 87.25; H, 4.27; N, 8.48. MS (EI), m/z: 330 (M<sup>+</sup>).



Figure 1 UV-VIS spectra of complex 3 in (1) THF and (2) chloroform.

former in statistic condensation reaction, it was converted to bis(diiminoisoindoline) derivative **2** by treatment with ammonia in the presence of sodium methoxide.<sup>7,‡</sup>

The target complex **3** was obtained by the statistic condensation method reported previously<sup>6</sup> (Scheme 2).<sup>§</sup> It was isolated by gel permeation chromatography, using THF as the eluent. The product yield amounted to 31%, which is several times higher than those

Figure 2 UV-VIS spectra of complex 4 in (1) THF and (2)  $C_6H_6$ .

reported in the literature<sup>5,7,11,16</sup> for binuclear phthalocyanine complexes. Note that only one side product, octaphenyl-substituted magnesium mononaphthalocyanine **4**, was isolated, whereas neither trinuclear phthalocyanine nor unsymmetrical substituted complexes of  $A_3B$  type<sup>5,6</sup> were found.

The absorption maximum in the UV-VIS spectra of the binuclear naphthalocyanine complex **3** is bathochromically shifted to 960 nm (Figure 1). Such a considerable bathochromic shift for this type of complex was attained for the first time.<sup>4–6</sup>

Complex **4** also shows a bathochromic shift of the Q-band (Figure 2) by more than 100 nm in comparison with monophthalocyanine complexes.

Intense  $\pi$ -stacking interactions result in aggregation effects in the UV-VIS spectra of the naphthalocyanine complexes syn-

(THF as the eluent). The solvent was evaporated, the resulting oil was washed with *n*-hexane, and the precipitate that formed was filtered off and repeatedly washed with *n*-hexane and methanol. The yield of compound **3** was 41.0 mg (31%). MS (MALDI-TOF), *m/z*: 2285 [M+Ph]<sup>++</sup>, 2209 [M]<sup>++</sup>, 2133 [M–Ph]<sup>++</sup>. UV-VIS [THF,  $\lambda_{max}/mm$  (*I*/*I*<sub>max</sub>)]: 734 (0.94), 772 (1.00), 960 (0.213). <sup>1</sup>H NMR (THF-*d*<sub>6</sub>)  $\delta$ : 7.23–7.24 (m, 60H, H<sub>Ph</sub>), 8.20 (s, 12H, 1-H<sub>NPh</sub>), 8.42 (s, 12H, 2-H<sub>NPh</sub>), 9.68 (s, 3-H<sub>Ar</sub>).

In addition, gel permeation chromatography gave 52.0 mg (32%) of complex 3,4,12,13,21,22,30,31-octaphenyl-2,3-naphthalocyanine magnesium **4**. MS (MALDI-TOF), m/z: 1345 [M]<sup>++</sup>, 1268 [M – Ph]<sup>++</sup>. UV-VIS [THF,  $\lambda_{max}$ /nm ( $I/I_{max}$ )]: 340 (0.57), 689 (0.23), 734 (0.20), 772 (1.00). <sup>1</sup>H NMR (pyridine- $d_5$ )  $\delta$ : 7.26–7.31 (m, 40H, H<sub>Ph</sub>), 8.13 (s, 8H, 1-H<sub>NPh</sub>), 8.58 (s, 8H, 2-H<sub>NPh</sub>).

Pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraimine 2. Methanol (40 ml) and sodium metal (14.0 mg, 0.60 mmol) were placed in a two-necked flask equipped with a reflux condenser and a magnetic stirrer. Once hydrogen evolution ceased, pyromellitonitrile (500 mg, 2.8 mmol) was added. Gaseous ammonia dried with KOH was passed for 4 h through the resulting solution with water cooling. The reaction progress was monitored by TLC (Al<sub>2</sub>O<sub>3</sub>, C<sub>6</sub>H<sub>6</sub> as the eluent) and by IR spectroscopy to reach the absence of vibrations of nitrile in the 2250 cm<sup>-1</sup> region.<sup>7</sup> The reaction product that formed as a brown precipitate was filtered off and washed with methanol and Et<sub>2</sub>O, yield 588 mg (99%),  $R_{\rm f}$  0 (Al<sub>2</sub>O<sub>3</sub>, F<sub>254</sub>, C<sub>6</sub>H<sub>6</sub> as the eluent). IR (liquid paraffin,  $v_{max}/cm^{-1}$ ): 3340 ( $v_{N=H}$ ), 1740 ( $v_{C=N}$ ), 1480 ( $v_{Ar(C-H)}$ ). <sup>§</sup> Bis(8<sup>2</sup>,9<sup>2</sup>,15<sup>2</sup>,16<sup>2</sup>,22<sup>2</sup>,23<sup>2</sup>-hexaphenyltrinaphthalo[h,o,v]-5,12,19,26tetraazaporphyrino)[b,e]benzene dimagnesium 3. Compounds 1 (400.0 mg, 1.21 mmol), 2 (13.0 mg, 0.06 mmol), Mg(OAc)<sub>2</sub>·4H<sub>2</sub>O (51.4 mg, 0.24 mmol), DBU (0.5 ml) and isoamyl alcohol (15 ml) were placed in a two-necked flask equipped with a reflux condenser and a magnetic stirrer. The reaction was refluxed for 12 h under argon. The reaction progress was monitored by spectrophotometry using THF as the solvent. The mixture was cooled and poured into a MeOH-H<sub>2</sub>O (1:1) mixture. The resulting blue precipitate was filtered off and washed with water and then with methanol. The target compound was isolated by gel permeation chromatography



Figure 3 Structure of complex 3 according to DFT calculations.

thesized, namely, an increase in the intensity of the Soret band with respect to the Q-band (Figure 2) and broadening of the Q-band (Figures 1 and 2).

These interactions have the most significant effect in the case of a binuclear naphthalocyanine complex, which is due to an expansion of the  $\pi$ -electron conjugation system. Absorption in the near IR region is not observed in a non-coordinating solvent (Figure 1). The use of a coordinating solvent (THF) results in partial or complete disaggregation owing to coordination to the central metal ion, as we reported previously.<sup>6</sup>

The naphthalocyanine complexes **3** and **4** were characterised by MALDI-TOF mass spectrometry. To assist the ionization of the complexes, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2propenylidene]malononitrile (DCTB) was used as the matrix. In this case the mass spectrum of complex **3**<sup>¶</sup> contained a molecular ion peak along with a peak corresponding to the interaction of matrix fragments with ions of the compound during the ionization (M<sup>+</sup> + Ph), as well as a peak corresponding to molecular ion fragmentation with abstraction of a phenyl group (M<sup>++</sup> – Ph).

For recording <sup>1</sup>H NMR spectra, polar coordinating solvents (THF and pyridine) were necessary due to the tendency of naphthalocyanine complexes, especially binuclear phthalocyanine ones, toward the aggregation phenomenon in concentrated solutions. DOSY spectroscopy<sup>17</sup> was used to confirm that the signals observed belong to the same molecule. The <sup>1</sup>H NMR spectrum of binuclear complex  $3^{\text{II}}$  is characterised by a weak downfield shift of the signals corresponding to the aromatic protons of the peripheral  $\pi$ -system (1-H<sub>Nph</sub> and 2-H<sub>Nph</sub>) with respect to the corresponding signals of the starting nitrile 1, which may be due to the effect of the naphthalocyanine macrocycle. Assignment of proton signals was based on the effect of the shielding cone of the naphthalocyanine macrocycle on the proton chemical shifts. We failed to assign the signals in the spectrum of complex 3 based on NOE observations because of the low compound concentration, which could not be increased due to aggregation. In view of this, a quantum-chemical simulation of the complex structure was performed, followed by computation of the proton chemical shifts for the resulting structure.<sup>††</sup>

 $^{\P}\,$  For MALDI-TOF (Figure 1S) and  $^{1}H\,NMR$  (Figure 2S) spectra of complex 3, see Online Supplementary Materials.

According to quantum chemical computations, complex **3** is an almost planar molecule with nearly  $C_{\rm s}$  symmetry (Figure 3). The deviation from the plane of the naphthalocyanine macrocycles does not exceed 0.1 Å for any of the atoms. Magnesium ions are coordinated in two cavities of the naphthalocyanine ligand (ion deviation from the naphthalocyanine ligand plane does not exceed 0.1 Å). Computation data confirm the conclusions made by comparing proton shielding that the signals are shifted downfield in the sequence H<sub>Ph</sub> (~7.5 ppm) < 1-H<sub>NPh</sub> (~9.1 ppm) < < 2-H<sub>NPh</sub> (~10.5 ppm) < 3-H<sub>Ar</sub> (12.1 ppm). The observed and calculated chemical shifts differ because the solvation effect and bonding of THF molecules with magnesium ions are not taken into account.<sup>18</sup>

In conclusion, 2,3-dicyano-6,7-diphenylnaphthalene has been synthesized in high yield. Starting from this compound, dodecaphenyl-substituted planar binuclear naphthalocyanine magnesium complex has been prepared. A considerable bathochromic shift of absorption up to 1100 nm has been detected for the first time for this type of complexes.

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## **Online Supplementary Materials**

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.04.019.

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<sup>&</sup>lt;sup>††</sup>*DFT calculations details.* All calculations were performed using the resources of an MVS-50K supercomputer of the Joint Supercomputer Center (JSC) (www.jscc.ru), at the DFT level of theory. Geometry optimizations were carried out using the PBE generalized gradient functional.<sup>19</sup> Geometries were optimized using the TZ2P<sup>20</sup> valence basis set and SBKJC effective core potentials for Mg, C, and N atoms.<sup>21–23</sup> Chemical shifts were calculated using the cc-pCVTZ basis set.<sup>24</sup> The shielding of TMS protons was calculated to be 31.3915 ppm for H. Vibration frequencies were used to characterize stationary point as minima. All calculations were performed using the PRIRODA program.<sup>25,26</sup>