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New Approach to the Synthesis of Planar Binuclear Phthalocyanines of Mg, Zn and Rare Earth Elements

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Direct synthesis of planar binuclear phthalocyanine metallocomplexes sharing common annulated benzene ring providing the yields of target products up to 40%, in comparison with earlier described 5–11% yields, was developed. Generality of the elaborated method was shown by the example of synthesis of divalent (Mg, Zn) and rare-earth (Lu, Yb, Dy) metal complexes.

Keywords: Phthalocyanine, binuclear complex, planar-type, building blocks, rare earth metal complexes.

Introduction

Interest to binuclear phthalocyanines grows out of their unusual physique-chemical properties due to the structural features and the specific behavior in solutions. Extension of the π-system in this type of complexes provides effective electronic conjugation between macrocycles and consequently leads to the unique spectral properties.[1,2] Such compounds have the intensive absorption in the near IR region.[3,4] Thus, elaboration of the convenient and available approaches to this type of complexes is extremely actual.

Experimental

^{1}H NMR spectra were recorded on Bruker AM-300 (300.13 MHz). UV-vis spectra were recorded on ThermoSpectronic Helios-α in quartz cells of 0.5 cm thickness in THF. Mass-spectra were registered on Autoflex II (MALDI-TOF, matrix – 2,5-dihydroxybenzoic acid – DHB) equipment. Column chromatography was carried out on BioBeads SX-1 («BioRad»). All solvents were purified using standard procedures directly before their use. Salts $Mg(OAc)_2 \cdot H_2O$, $Zn(OAc)_2 \cdot 2H_2O$, $Lu(OAc)_3 \cdot 3H_2O$, $Yb(OAc)_3 \cdot 4H_2O$, $Dy(OAc)_3 \cdot 4H_2O$ were held in a vacuum desiccator for 4 h at 100°C. Compounds **1**,[5] **2a,b**[6,7] were prepared according to described procedures.

General procedure for planar complexes, **3a-g.** To the solution of **1** (0.48 mmol) and **2a** or **2b** (4.72 mmol) in isoamyl alcohol (30 ml) CH_3OLi (11.79 mmol) was added. The mixture was refluxed for 2 h, then corresponding acetate salt (2.83 mmol) was added and refluxing was continued for 30 min. After the reaction being completed the mixture was cooled, the solvent was evaporated at reduced pressure. The solid residue was washed with aqueous (1:1) methanol (2 × 50 ml) for removal of non-phthalocyanine impurities and then separated on BioBeads SX-1 (THF) to give complexes **3a-g**.

[1]*H NMR spectroscopic data for* **3a**. δ_H (300 MHz, THF-d_8, 25°C) ppm: 1.25 (s, 36 H, $CH_2CH_2CH_2CH_3$), 1.55-1.75 (m, 24 H, $CH_2CH_2CH_2CH_3$), 1.85-2.00 (m, 24 H, $CH_2CH_2CH_2CH_3$), 3.25-4.00 (m, 24 H, $CH_2CH_2CH_2CH_3$), 8.20 (s, 4 H, Ar), 9.38 (s, 8 H, Ar), 11.45 (s, 2 H, Ar).

[1]*H NMR spectroscopic data for* **3b**. δ_H (300 MHz, THF-d_8, 25°C) ppm: 1.20 (m, 36H, $CH_2CH_2CH_2CH_3$), 1.64-1.76 (m, 24H, $CH_2CH_2CH_2CH_3$), 1.81-2.00 (m, 24H, $CH_2CH_2CH_2CH_3$), 3.20-4.09 (m, 24H, $CH_2CH_2CH_2CH_3$), 8.25 (s, 4H, Ar), 9.34 (s, 8H, Ar), 11.50 (s, 2H, Ar).

[1]*H NMR spectroscopic data for* **3c**. δ_H (300 MHz, THF-d_8, 25°C) ppm: 1.71 (s, 54H, CH_3), 8.15-9.34 (s, 18H, Ar), 11.35 (s, 2H, Ar).

[1]*H NMR spectroscopic data for* **3d**. δ_H (300 MHz, THF-d_8, 25°C) ppm: 1.79 (s, 54H, CH_3), 8.22-9.40 (s, 18H, Ar), 11.20 (s, 2H, Ar).

[1]*H NMR spectroscopic data for* **3e**. δ_H (300 MHz, THF-d_8, 25 °C) ppm: 1.75 (s, 54 H, CH_3), 6.45-7.20 (m, 18 H, Ar), 9.45 (m, 2 H, Ar).

Results and Discussion

Classic approach to the synthesis of planar binuclear phthalocyanines is based on the mixed cyclization of initial phthalogens – phthalodinitriles or 1,3-diiminoisoindolines. This method even being modified in some way[4] leads to the target complexes in only 5-11% yields. Moreover, in the case of rare-earth elements (REE) we have found the classical method to be unsuccessful in obtaining of the target complexes even in the trace amounts. Main disadvantage of this approach, from our point of view, is a preferential progress of the side olygomerization reactions, resulting in phthalocyanine polymers[8] as the main products.

Earlier we have demonstrated the stage-by-stage macrocycle formation on the example of *clamshell*-type binuclear phthalocyanine synthesis.[9] It can be supposed that in present investigation the cyclization also proceeds consecutively, and the rate of second phthalocyanine ring formation is likely to compete with uncontrolled interaction of several unsymmetrically substituted monophthalocyanine molecules (with *o*-CN-groups or 1,3-diiminoisoindoline fragment) and phthalogens. Extent of this side process is supposed to be dependent on the nature of the central metal ion. Such argumentation has formed a basis for the develop-
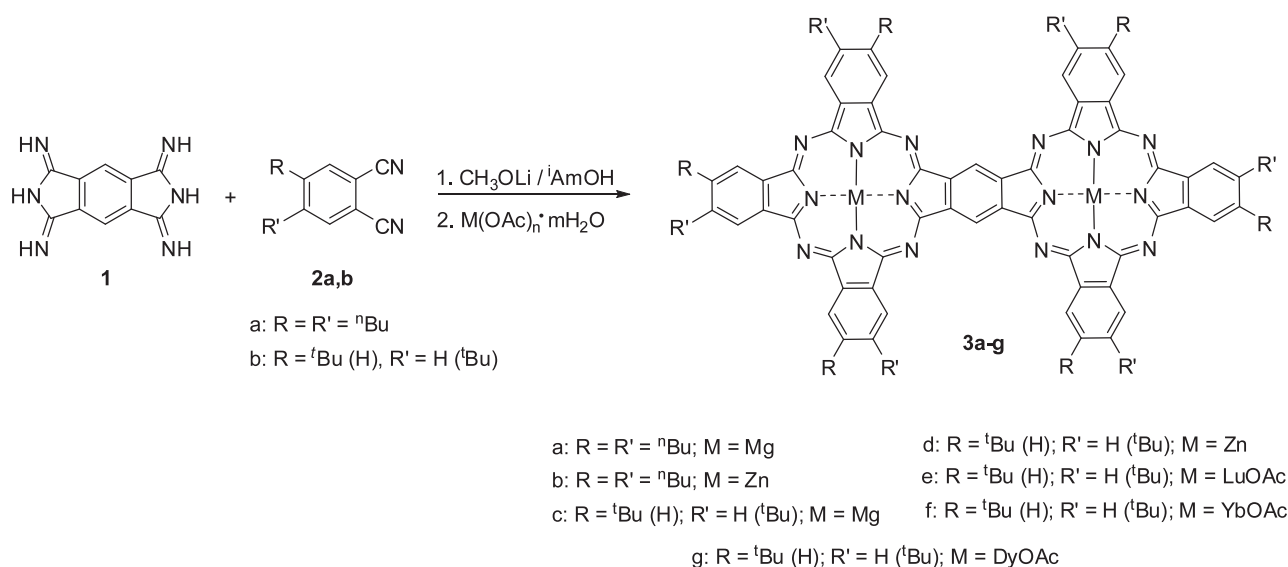
Scheme 1. Synthesis of planar binuclear phthalocyanines **3a-g**.

ment of direct synthetic method to planar binuclear phthalocyanines with common annulated benzene ring (Scheme 1).

Improvement of the macrocycle assembling efficiency was achieved using CH_3OLi as a base. Lithium cations have the least ionic radius among metals and effectively participate in the macrocycle construction forming ionic bonds with isoindolic nitrogen. Methoxide-anions as a hard nucleophilic agent attack the carbon atom of nitrile group more effectively than analogous ion generated from high-boiling alcohols upon addition of the catalytic amount of organic bases, for instance, DBU (1,8-diazabicyclo[5.4.0]undec-7ene) or during autoprotolysis (*N,N*-dimethylaminoethanol). Using the excess of CH_3OLi provides a high concentration of methoxide-anions. So it is reasonable to assume that the rate of the nucleophilic attack increases in comparison with classic method, which implies nucleophile generation in catalytic amounts.[5]

Taking these facts into account, initially we carried out a mixed cyclization of phthalogens **1** and **2a,b** in the presence of lithium methoxide. The reaction was monitored by UV-vis spectroscopy. The gradual increasing of the main absorption bands intensity – 665 and 820 nm (THF) was observed eventually. It was found that the amount of the base is the most essential factor affecting the reaction conversion. Maximum efficiency of the annulated lithium complexes formation was achieved *via* considerable increasing of CH_3OLi amount (more 20 equiv. in ratio to **1**). Following addition of Mg and Zn salts to the reaction mixtures without preliminary isolation of the lithium complexes resulted in the formation of compounds **3a-d**. After a few minutes of refluxing target complexes were obtained revealing significant bathochromic shift (14–28 nm) of earlier observed characteristic bands in their UV-vis spectra.

Isolation of the target phthalocyanine products was performed by gel-permeation chromatography on BioBeads SX-1, using THF as eluent. The yields of the compounds **3a-d** surprisingly reached 36–40%. After obtaining the binuclear phthalocyanine complexes of bivalent metals in such high yields we attempted to apply the elaborated procedure for the synthesis of analogous REE complexes, which failed to be obtained by classical approach. Indeed, Lu, Yb and Dy

complexes **3e-g** were synthesized in 21–26% yields.[10] This clearly evidences that elaborated method is general for the preparation of both bivalent and REE metal complexes. The yield decreasing from the compounds **3e-g** to complexes **3a-d** could be explained by the lower stability of the REE complexes, because their metal ions are placed outside the phthalocyanine plane due to the larger ionic radii. Detection of side binuclear ligands during isolation of planar binuclear REE complexes appears to be a good evidence of this fact. The control experiment confirms the possibility of these compounds for demetallation under the reaction conditions.

The composition of the synthesized complexes **3a-d** was confirmed by the presence of signals having characteristic isotopic pattern corresponding to molecular ion peaks in MS-MALDI-TOF. For the spectra of the REE complexes **3e-g** registered using 2,5-dihydrobenzoic acid (DHB) as a matrix signals [M^+-2OAc+2DHB] were detected instead of molecular ions ([M^+]). This result additionally confirms earlier established fact[11] of Ln–OAc bond ionic nature. In the absence of matrix the corresponding spectra could not been obtained, which is likely to be related with low stability of molecular cation-radicals ([M^+]). Mass-spectrum of complex **3a** is presented on Figure 1 as an example.
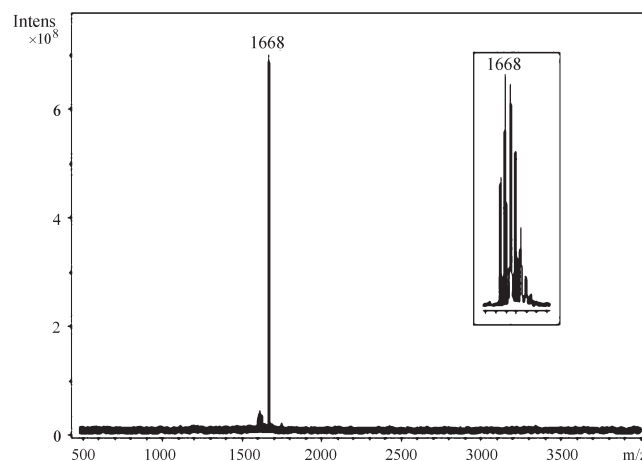

Figure 1. Mass spectrum (MALDI-TOF) of **3a** (matrix – DHB).

Table 1. UV-vis data for planar binuclear complexes **3a-g** (THF).

Compound	Q-band, λ_{max}, nm (lg ε)	M+ [m/z][a]	Yield, %
3a	363 (4.69), 724 (4.39), 848 (4.89)	1668[b]	39
3b	359 (4.85), 704 (4.62), 847 (4.92)	1751	40
3c	362 (4.76), 719 (4.51), 836 (4.99)	1332[b]	32
3d	358 (4.64), 717 (4.45), 835 (5.01)	1414	36
3e	358 (4.85), 704 (4.60), 834 (4.86)	1940[c]	26
3f	356 (4.83), 706 (4.64), 837 (4.81)	1938[c]	21
3g	353 (4.85), 707 (4.62), 837 (4.82)	1917[c]	23

[a]By MALDI-TOF mass-spectrometry. The value corresponds to the most abundant isotopic peak of the molecular ion [M+].
[b]Ion peak [M++H].
[c]Ion peak [M+-2OAc+2DHB].

For diamagnetic complexes **3a-e** ^{1}H NMR spectra were recorded wherein signals of all protons were detected. Signals of the aromatic protons in spectrum of binuclear Lu phthalocyanine **3e** were found to be shifted to a strong field on 2 ppm unlike the complexes of bivalent elements **3a-d**. Signals of the aliphatic protons have not been shifted virtually.

The planar binuclear complexes **3a-g** were characterized by UV-vis spectroscopy, their intensive absorption in the near IR region was found (Table 1) in comparison with mononuclear analogues (see Figure 2 for example).
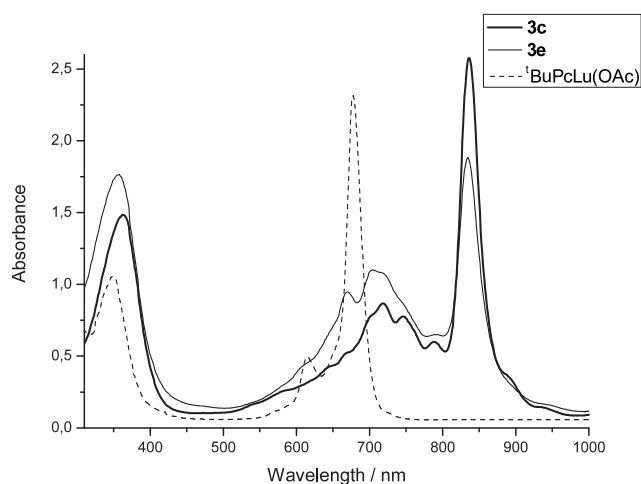

Figure 2. UV-vis spectra of complexes **3a** (bold solid line), **3e** (thin solid line) and [t]BuPcLuOAc (dashed line) in THF.

As might be seen from the Table 1, the bathochromic shift of the Q-band is observed in the case of butyl-substituted complexes **3a,b** in comparison with *tert*-butyl planar binuclear phthalocyanines **3c-g**.

The nature of lanthanide ion does not affect the character of electronic spectra of **3e-g** and the Q-band position as in the case of regular REE monophthalocyanines.[11] UV-vis spectra of binuclear complexes **3a** and **3c** are presented on Figure 2 as an example.

Conclusions

We have developed a new approach to the synthesis of annulated planar binuclear phthalocyanines in high yields. The procedure elaborated allows to produce the divalent complexes as well as REE ones being assumed to be unique building blocks for preparing the supramolecular structures owing to the mobility of axial ligands.

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