Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2009, **19**, 24–26

Mendeleev Communications

Preparation of nanosized sandwich-type structures based on planar binuclear phthalocyanines

Victor E. Pushkarev,[a] Alexander Yu. Tolbin,[a,b] Anastasiya V. Ryabova[c] and Larisa G. Tomilova*[a,b]

[a] *Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 524 9508; e-mail: pushkarev@org.chem.msu.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 0290; e-mail: tom@org.chem.msu.ru*
[c] *A. M. Prokhorov Institute of General Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 503 8764; e-mail: Nastya.Ryabova@gmail.com*

DOI: 10.1016/j.mencom.2009.01.010

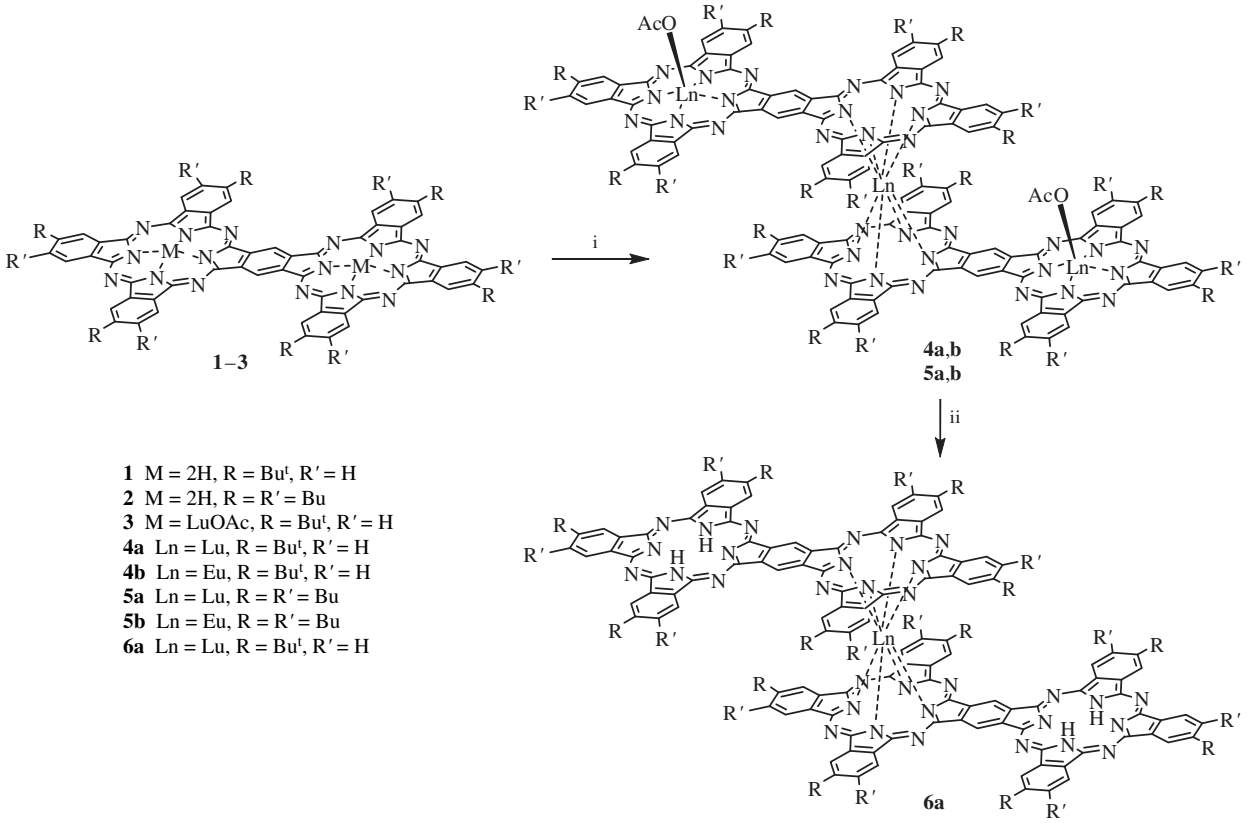
The specific features of sandwich-type complexes formation from hexa-*tert*-butyl and dodeca-*n*-butyl-substituted binuclear phthalocyanines and europium and lutetium acetates are described.

Binuclear phthalocyanines sharing a common benzene ring have a wide range of characteristic properties due to their expanded π-electron system.[1–3] On the other hand, sandwich-type phthalocyanines of rare-earth elements (REE) also show unique characteristics due to the specific overlapping of ligand π-orbitals.[4–6] Thus, preparation of sandwich-type complexes based on annelated phthalocyanine ligands opens new prospects for their practical application, as nanosized materials among other uses. Recently,[1,7] we reported optimal methods developed for synthesising binuclear phthalocyanines with a common benzene ring, as well as new REE complexes based on them. The purpose of this study was to synthesize sandwich-type structures using ligands of this type as building blocks.

The main feature of annelated binuclear phthalocyanines is that their ligands contain two complexing sites, which may result in the formation of a mixture of products with different planarity, and hence in an extremely low process selectivity. Therefore, studies of this process require varying the types of starting compounds, their ratios and synthetic conditions.

In this work, sandwich-type phthalocyanines were obtained from ligands **1** and **2**, as well as from lutetium complex **3**, using a modified technique (Scheme 1) based on the synthetic procedure reported previously for classic homo- and heteroleptic phthalocyanine REE complexes.[6,8]

Initially, we studied the reaction of compounds **1**, **2** with europium and lutetium acetates (mole ratio of 2:3) to give double-



1 M = 2H, R = Bu^t, R′ = H
2 M = 2H, R = R′ = Bu
3 M = LuOAc, R = Bu^t, R′ = H
4a Ln = Lu, R = Bu^t, R′ = H
4b Ln = Eu, R = Bu^t, R′ = H
5a Ln = Lu, R = R′ = Bu
5b Ln = Eu, R = R′ = Bu
6a Ln = Lu, R = Bu^t, R′ = H

Scheme 1 *Reagents and conditions*: i, $Ln(OAc)_3 \cdot nH_2O$ (for **1**, **2**), cat. MeOLi, TCB–*n*-hexadecanol (50:1), reflux, 1h; ii, H_2SO_4, then H_2O (ice).

decker phthalocyanines **4**, **5**.† The progress of the reactions and the composition of the products were monitored by UV-VIS spectroscopy and MALDI-TOF mass spectrometry. In fact, the main absorption maxima of the starting ligands disappeared in UV-VIS spectra, whereas new bands appeared whose shape matched those of reduced forms of bisphthalocyanines. In addition to the peaks of the main products, the mass spectra of the reaction mixtures were found to contain low-intensity signals corresponding to triple- and quadruple-decker derivatives of compounds **4** and **5**. For example, the MALDI-TOF spectra of the reaction mixtures in the synthesis of complex **4a** showed peaks of $[M – 2OAc + 2DHB]^+$ ions with masses of 4857 and 6315 corresponding to its triple- and quadruple-decker derivatives. The resulting phthalocyanine complexes were treated by gel-permeation chromatography on Bio-Beads S-X1 cross-linked polymer using THF as the eluent. The first fractions contained a mixture of sandwich-type oligomers, as follows from the considerable broadening of the Q band in their UV-VIS spectra and from the absence of signals in the MALDI-TOF spectra in the mass range from 1000 to 30000. After that, a mixture of lower-molecular oligomeric products was eluted, which contained, among others, triple- and quadruple-decker derivatives. The last fraction contained target products **4** or **5**. Unfortunately, the use of **3** as the starting compound did not allow us to increase the yields of products **4** and **5** due to a considerable increase in the content of oligomeric products, which appears quite logical. This observation, along with the data obtained above, provide indirect evidence of their sandwich-type structure, since oligomerisation in the systems in question are only possible through complexing involving REE ions and becomes more likely for **3**-type compounds in comparison with the corresponding ligands.

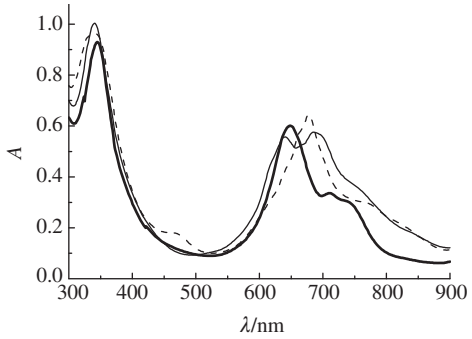


Figure 1 UV-VIS specta of **4a** reduced form (bold line) and **6a** reduced (solid line) and neutral form (dashed line) in THF.

† *Synthetic procedure*. A mixture of compound **1** or **2** (0.052 mmol) and $Ln(OAc)_3 \cdot nH_2O$ (Ln = Lu, Eu) (0.078 mmol) was refluxed for 1 h under argon in TCB (1 ml) with *n*-hexadecanol (30 mg) in the presence of a catalytic amount of MeOLi until the original phthalocyanine ligand disappeared completely. The progress of the reaction was monitored by TLC (SiO_2, THF as the eluent) and by UV-VIS spectroscopy. After the synthesis was completed, MeOH (80%, 30 ml) was added to the reaction mixture. The precipitate was filtered off, washed with MeOH (3×10 ml) and dried in a vacuum desiccator (100 °C). The resulting powder was dissolved in THF and chromatographed using a 40×2.5 cm column (Bio-Beads S X1, THF as the eluent); the last green fraction was collected. Compounds **4** and **5** were characterised by UV-VIS spectroscopy (Table 1, Figure 1) and MALDI-TOF mass spectrometry. The structure of complex **5b** was also confirmed by ^{1}H NMR spectroscopy. Similarly, in the absence of REE salts, complexes **4** and **5** were obtained from compound **3** in yields below 30%.

4a: yield 55%. MS (MALDI-TOF), *m*/*z*: 3399 $[M – 2OAc + 2DHB]^+$.

4b: yield 50%. MS (MALDI-TOF), *m*/*z*: 3022 $[M – 2OAc]^+$.

5a: yield 64%. MS (MALDI-TOF), *m*/*z*: 4071 $[M – 2OAc + 2DHB]^+$.

5b: yield 53%. ^{1}H NMR ($[^2H_8]$THF, 1 vol.% $N_2H_4 \cdot H_2O$) δ: 1.50 (m, 36H, Me), 2.19–2.44 (m, 24H, γ-CH_2), 2.63–2.86 (m, 24H, β-CH_2), 3.91–4.37 (m, 24H, α-CH_2), 6.81–8.12 (m, 12H, Ar), 10.99 (br. s, 2H, Ar). MS (MALDI-TOF), *m*/*z*: 3694 $[M – 2OAc]^+$.

Table 1 UV-VIS data for compounds **1**–**6**.

Compound	λ_{max}/nm (THF)	
	Reduced form[a]	Neutral form
1[1]	—	343, 662 (sh.), 687, 835
2	—	346, 668, 698, 840 (sh.)
3[7]	—	358, 670, 704, 834
4a	343, 647	328, 347, 464, 680
4b	347, 658	330, 349, 484, 688
5a	345, 649	331, 351, 465, 683
5b	349, 665	332, 353, 482, 688
6a	341, 640, 686	327, 342, 460, 678

[a] $N_2H_4 \cdot H_2O$ was used as the reducing agent.

Note that no complexes with a metal:ligand ratio of 1:2 were found in the products of the above reaction, even if the appropriate ratio of the starting compounds was used. This fact can be explained by the lower orbital symmetry of structures of this kind in comparison with phthalocyanines **4**, **5**, and hence a decrease in their thermodynamic stability. On the other hand, by re-precipitation of complex **4a** from sulfuric acid (Scheme 1) we succeeded for the first time in isolation and spectral characterisation of bisphthalocyanine **6a** (Figure 1) incorporating two fragments of the free ligand.

The structures of target bisphthalocyanines **4**–**6** were confirmed using MALDI-TOF mass spectrometry. For lutetium complexes **4a** and **5a**, the mass spectra obtained using 2,5-dihydroxybenzoic acid (DHB) as the matrix show peaks of $[M – 2OAc + 2DHB]^+$ instead of molecular ion peaks ($[M]^+$), whereas signals of $[M – 2OAc]^+$ predominate for europium compounds **4b** and **5b**. This result is evidence of the high mobility of acetate counterions, which in turn is a good justification of why multiple-decker products are formed in the reactions of interest. The mass spectrum of complex **6a** shows a molecular ion peak $[M]^+$ only (Figure 2). An ^{1}H NMR was also recorded for paramagnetic europium complex **5b** following its quantitative convesion to the reduced form by treatment with hydrazine hydrate, as we previously did for classical sandwich-type REE complexes;[6,8] the spectrum contained all types of protons. The spectrum of compound **5b** manifests a downfield shift of the signals, which is typical of europium complexes in comparison with complexes of diamagnetic lanthanides;[7,8] it is most pronounced for aromatic protons.

The UV-VIS spectra of the resulting compounds show regularities similar to those in the spectra of classical bisphthalocyanines (see Table 1, Figure 1). In fact, changing from lutetium to europium or from ligand **1** to ligand **2** results in a bathochromic shift of the main absorption bands. Moreover, the UV-VIS spectra of compounds **4**–**6** show absorption in the range of 750–800 nm, which is evidence that the π-conjugation typical of annelated binuclear phthalocyanines remains in their molecules.

Furthermore, we discovered the tendency of the resulting complexes to form nanosized particles, which was found to be

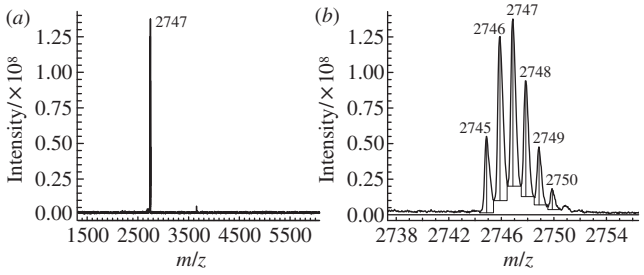


Figure 2 (*a*) MALDI-TOF mass spectrum and (*b*) molecular ion peak of compound **6a**.

characteristic of lutetium complexes **4a** and **5a**.‡ In fact, data obtained for solutions of complexes **4a** and **5a** in THF using a dynamic light scattering spectrometer (Photocor Complex®, Russia) show that the mean diameter of nanosized particles is about 60 nm.

Hence, it can be assumed that formation of nanoparticles is based on aggregation phenomena related to the presence of two coordination-unsaturated lutetium ions in the molecules of bisphthalocyanines in question. This hypothesis is indirectly confirmed by the absence of nanoparticles in solutions of europium complexes **4b** and **5b**; europium is characterised by formation of weaker bonds with extra-ligands, and hence aggregation processes in complexes **4b** and **5b** are less pronounced. A more detailed study of the formation conditions for nanosized particles based on phthalocyanines of this type will be published elsewhere.

Thus, we were the first to demonstrate that it is possible to obtain nanosized sandwich-type structures based on π-conjugated phthalocyanines with a common benzene ring and to study spectral features of this new class of compounds.

This study was supported by the Russian Foundation for Basic Research (grant no. 05-03-33202) and the Programme for Fundamental Studies of the Presidium of the Russian Academy of Sciences ‘Development of Methods for Synthesising Chemical Compounds and Creating New Materials’.

‡ *Preparation of nanoparticles*. The THF solutions of complexes **4a** and **5a** with 5×10^{-5} mol dm^{-3} concentration were held overnight at room temperature. Dynamic light scattering experiment was subsequently carried out to determine an average particle size.

References

1 A. Yu. Tolbin, V. E. Pushkarev, L. G. Tomilova and N. S. Zefirov, *Izv. Akad. Nauk, Ser. Khim*., 2006, 1112 (*Russ. Chem. Bull., Int. Ed*., 2006, **55**, 1155).
2 S. G. Makarov, C. Litwinski, E. A. Ermilov, O. N. Suvorova, B. Röder and D. Wöhrle, *Chem. Eur. J*., 2006, **12**, 1468.
3 S. G. Makarov, A. V. Piskunov, O. N. Suvorova, G. Schnurpfeil, G. A. Domrachev and D. Wöhrle, *Chem. Eur. J*., 2007, **13**, 3227.
4 N. Ishikawa, T. Okubo and Y. Kaizu, *Inorg. Chem*., 1999, **38**, 3173.
5 I. V. Zhukov, V. E. Pushkarev, L. G. Tomilova and N. S. Zefirov, *Izv. Akad. Nauk, Ser. Khim*., 2005, 184 (*Russ. Chem. Bull., Int. Ed*., 2005, **54**, 189).
6 V. E. Pushkarev, E. V. Shulishov, Yu. V. Tomilov and L. G. Tomilova, *Tetrahedron Lett*., 2007, **48**, 5269.
7 A. Yu. Tolbin, V. E. Pushkarev and L. G. Tomilova, *Mendeleev Commun*., 2008, **18**, 94.
8 V. E. Pushkarev, M. O. Breusova, E. V. Shulishov and Yu. V. Tomilov, *Izv. Akad. Nauk, Ser. Khim*., 2005, 2024 (*Russ. Chem. Bull., Int. Ed*., 2005, **54**, 2087).

Received: 9th July 2008; Com. 08/3174