Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2013, **23**, 137–139

Mendeleev
Communications

Synthesis of a stable J-type dimer based on the 2-hydroxy-9(10),16(17),23(24)-tri(*tert*-butyl)phthalocyanine zinc complex

Alexander Yu. Tolbin,[a] **Victor E. Pushkarev,**[a,b] **Irina O. Balashova**[a] **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: tolbin@inbox.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*

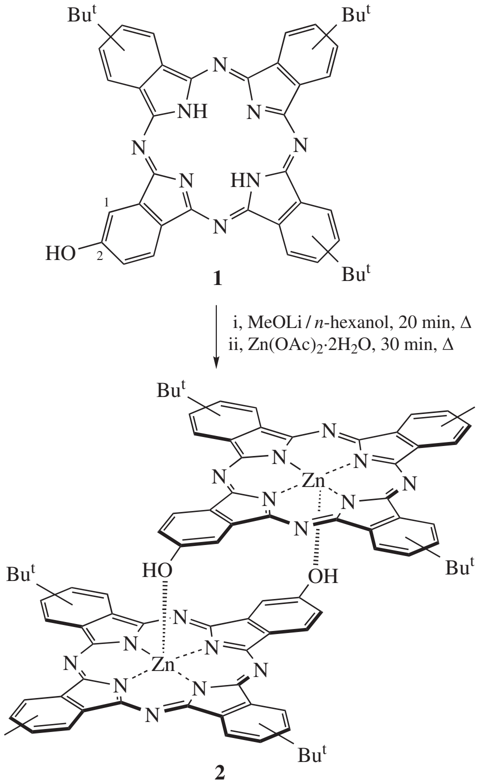
DOI: 10.1016/j.mencom.2013.05.005

Interaction of 2-hydroxy-9(10),16(17),23(24)-tri(*tert*-butyl)phthalocyanine with zinc acetate in the presence of lithium methoxide affords a stable J-type dimer. Its formation was simulated by density functional theory (DFT).

Supramolecular ensembles based on macroheterocyclic compounds are of considerable current interest. The presence of functional groups, in particular, donor atoms as the constituents of macrocomplex compounds, and acceptor sites as central metal ions makes it possible to access a wide variety of dimeric structures.[1–4] The dimerization of cyanine dyes with the formation of specifically ordered H- and J-type aggregates is well known.[5,6] The performance of quantum-chemical calculations to simulate dimeric structures and the development of target-oriented methods for the synthesis of particular compounds are practically important because the dimerization of π-conjugated macrocyclic compounds affects their physicochemical properties, in particular, spectroscopic and optical properties. Structures of this type were also prepared based on phthalocyanine; however, they were unstable in solutions.[7,8]

We were the first to obtain the stable dimer based on a functionally substituted phthalocyanine zinc complex, to study its spectroscopic properties, and to perform the DFT calculations including TDDFT to simulate the electronic absorption spectra of possible isomers.

In an attempt of preparing a traditional zinc complex with 2-hydroxy-9(10),16(17),23(24)-tri(*tert*-butyl)phthalocyanine by the interaction of the corresponding ligand with zinc acetate, we synthesized here its J-type dimer (Scheme 1).[†]



1

2
J-type dimer

Scheme 1

The synthesis was performed in *n*-hexanol with the successive addition of lithium methoxide and zinc acetate. The electronic spectrum of the resulting compound exhibited a red-shifted band, which suggested the occurrence of specific solvatochromic and electronic effects and corresponded to the formation of J-type associates.[9–11] We detected this absorption band regardless of solvent and concentration. As an example, Figure 1 compares the electronic absorption spectra of monomeric and dimeric complexes.

The MALDI-TOF mass spectrum contains only one peak with *m*/*z* 1522, which corresponds to a dimeric product (Figure 2).

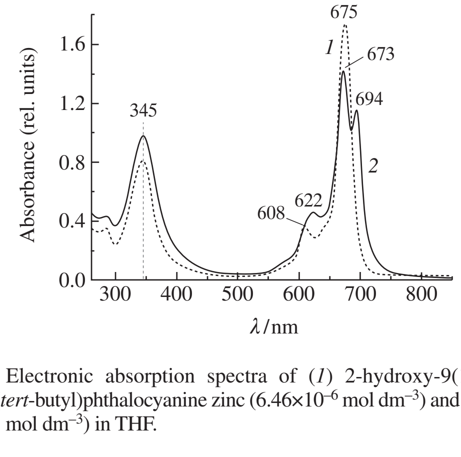


Figure 1 Electronic absorption spectra of (*1*) 2-hydroxy-9(10),16(17),23(24)-tri(*tert*-butyl)phthalocyanine zinc (6.46×10^{-6} mol dm^{-3}) and (*2*) dimer **2** (1.07×10^{-5} mol dm^{-3}) in THF.

[†] *Synthetic procedure*. To a solution of compound **1** (300 mg, 0.429 mmol) in *n*-hexanol (5 ml), MeOLi (82 g, 2.158 mmol) was added, and the mixture was refluxed for 20 min. Then, $Zn(OAc)_2 \cdot 2H_2O$ (188 mg, 0.858 mmol) was added, and the mixture was refluxed for another 30 min. After that, the solvent was evaporated and the crude product was treated with aqueous methanol (2×50 ml) followed by chromatographic purification on Bio-Beads SX-1 (eluent: THF). The column gave two fractions, the first one being the target dimer (yield, 82%), while the second mainly contained a monomeric by-product. ^{1}H NMR (400 MHz, THF-d_8) δ: 1.52 (s, 54 H, Bu^t), 1.53–2.48 (br. m, 16 H, Ar), 7.02–10.00 (br. m, 8 H, Ar). UV-VIS (THF, λ_{max}/nm): 345, 673, 694. MS (MALDI-TOF), *m*/*z* (%): 1522 $[M]^{+\bullet}$ (100).

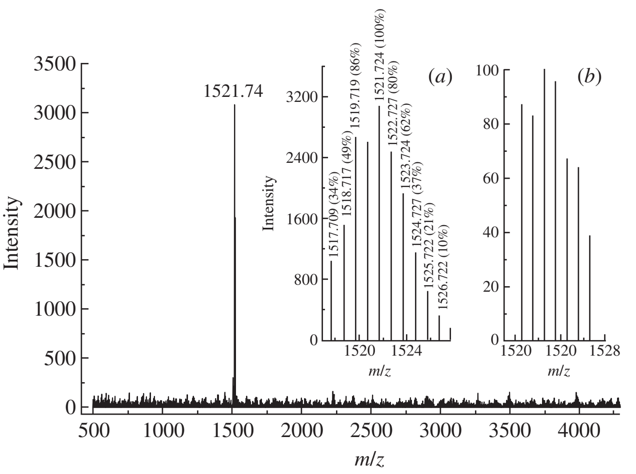


Figure 2 MALDI-TOF mass spectrum of dimer **2** and the isotope splitting of the molecular ion: (*a*) theoretical and (*b*) experimental ($[M-H]^+$).

The main special feature of the ^{1}H NMR spectrum of compound **2**, as compared with that of the corresponding monomer (Figure 3), is the presence of a large set of signals at 7.0–10.2 ppm for aromatic protons and 1.7–2.3 ppm for the aliphatic protons of *tert*-butyl groups. A similar pattern was observed previously in the spectra of double-decker complexes based on analogous A_3B type ligands,[12,13] and it is indicative of the limited mutual rotation of macrocycles in dimer **2** because of the π–π interaction. Moreover, signals in the spectrum of **2** appear in a wider range, as compared with analogous sandwich complexes of lutetium, which is consistent with a hypothesis on a mutual shift of macrocycles in the test dimer. Note that the temperature dependence of spectra over a range of 20–60 °C was not significant, which testifies the thermal stability of compound **2** in solution.

Dimer **2** is highly stable. We failed to decompose it by refluxing in high-boiling *o*-dichlorobenzene and 1,2,4-trichlorobenzene or under the treatment with concentrated sulfuric acid. Dimeric product **2** remained undecomposed for a long time (to a month) in solvents (benzene, THF, DMSO, DMF and methanol) at spectral concentrations (~10 μmol dm^{-3}). In the experiments, we evaluated its stability based on the retention of a bathochromic band (~700 nm) in the absorption spectra.

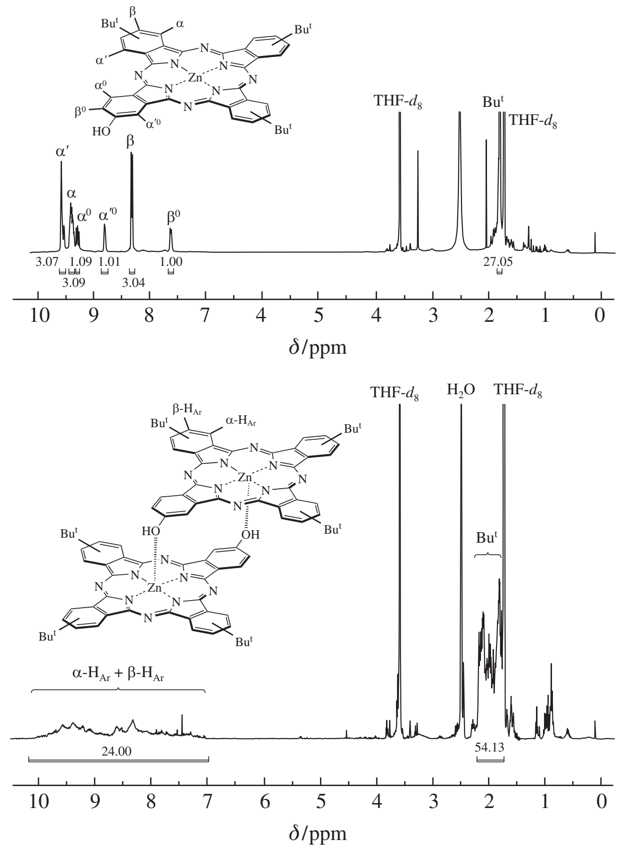


Figure 3 ^{1}H NMR spectra of the monomeric and dimeric complexes in THF-d_8 (~0.32 mmol dm^{-3}).

The formation of dimeric complexes with a number of other substituted ligands was not previously observed under either analogous or modified conditions. Thus, only monomeric complexes were formed from alkyl- and alkoxy-substituted phthalocyanines with a normal branched chain, in particular, from 2-hydroxy-9,10,16,17,23,24-hexabutylphthalocyanine.[12] It is believed that rigid and bulky *tert*-butyl groups exert a steric effect in the process of the mutual orientation of ionized macrocycles on the formation of a dimer. Using quantum-chemical calculations (DFT method), we found that the structure of the resulting dimer is stabilized by the coordination of the oxygen atoms of neighbouring macrocycles to zinc ions. The distance between the dimer macrocycles is about 2.8 Å, which is consistent with the calculated averaged sphere diameter of *tert*-butyl groups [Figure 4(*a*)]. However, the calculation data suggest the occur-

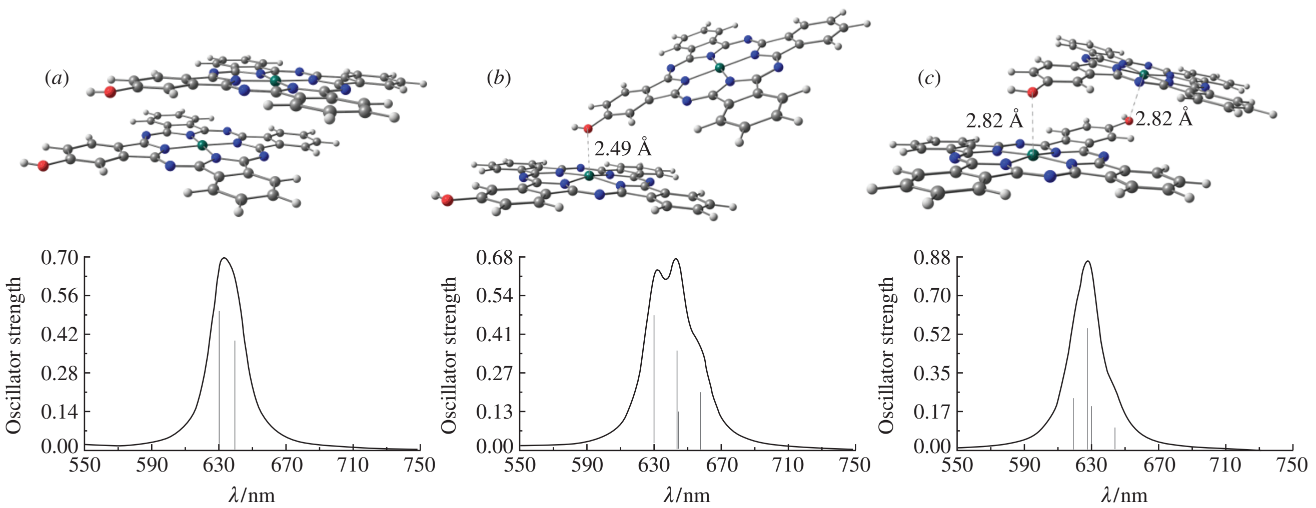


Figure 4 DFT-optimized structures and the TDDFT spectra of dimers with the parallel and angular arrangements of macrocycles (PBE/3z): (*a*) mirror, (*b*) angled, and (*c*) closed. Peripheral substituents are omitted for shortening the calculation time. The half-width of Lorentzian line shape was set to 8 nm.

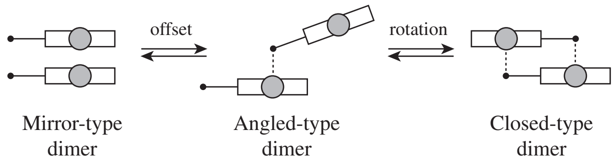


Figure 5 Hypothetical equilibriums in the test system on the conversion of dimers with different arrangements of the macrocycles.

rence of other macrocycle arrangements. Figure 4 shows the structures of the most probable isomers and the electronic absorption spectra calculated by the TDDFT method in the Q-band region.

The dimerization energy is 5.3 kcal mol^{-1}. The difference in the stability of these dimeric species is less than 0.5 kcal mol^{-1}, and the rough scanning (to within 0.2 Å) of the potential energy surface demonstrated comparatively low macrocycle rotation barriers (0.9–2.5 kcal mol^{-1}). These data are consistent with the experimental results on the high stability of the obtained dimer. Previously, with the use of the PRIRODA program[14] for calculating electronic absorption spectra in the Q-band region (TDDFT method), we found that the experimental character of UV-VIS spectra could be reproduced.[15] Differences were observed only in the positions of absorption maxima, which were hypsochromically shifted by 45–49 nm in the calculated spectra. Analogously, comparing the absorption spectrum of dimer **2** (Figure 1) with the calculated spectra of model dimers (Figure 4), we can assume the equilibrium transition closed ↔ mirror, which occurs through a transition state with the angular orientation of macrocycles by their turn and shift. Indeed, the UV-VIS spectrum of dimer **2** exhibited the appearance of not only an additional absorption band in the red region due to a mirror-type isomer but also a gently sloping satellite characteristic of a closed-type isomer. To confirm the occurrence of these equilibriums, it is necessary to isolate either an angled-type dimer or the products of its subsequent conversion (oligomers and polymers), that is, to terminate the equilibrium process which is schematically shown in Figure 5.

To conclude, we were the first to found the dimerization of a phthalocyanine complex of zinc containing the hydroxy group. The complex electronic absorption spectrum of the obtained dimer was explained using a molecular simulation.

This work was supported by the Russian Foundation for Basic Research (grant nos. 12-03-00774 and 12-03-31125) and the Presidium of the Russian Academy of Sciences (programme ‘Development of a Strategy of Organic Synthesis and Creation of Compounds with Valuable and Applied Properties’). We are grateful to the Joined Supercomputer Center of the Russian Academy of Sciences (www.jscc.ru) for providing us with computing resources.

References

1 J. Janczak and R. Kubiak, *Polyhedron*, 2009, **28**, 2391.
2 S. Fukuzumi, T. Honda and T. Kojima, *Coord. Chem. Rev*., 2012, **256**, 2488.
3 S. Tonga, J. Zhang, Y. Yana, S. Hua, J. Yua and L. Yu., *Solid State Sci.*, 2011, **13**, 1967.
4 K. Kameyama, A. Satake and Y. Kobuke, *Tetrahedron Lett*., 2004, **45**, 7617.
5 K. Miyasue, T. Honma, S. Kurita, T. Sekiya, M. Nakajima and T. Suemoto, *J. Lumin.*, 2005, **112**, 416.
6 J. Bujdak and N. Iyi, *J. Colloid Interface Sci*., 2008, **326**, 426.
7 F. Cong, J. Li, C. Ma, J. Gao, W. Duan and X. Du, *Spectrochim. Acta A*, 2008, **71**, 1397.
8 J.-Y. Liu, P.-C. Lo and D. K. P. Ng, in *Functional Phthalocyanine Molecular Materials*, ed. J. Jiang, Springer-Verlag, Berlin, 2010, vol. 135, pp. 169–210.
9 P. J. Gonçalves, N. M. Barbosa Neto, G. G. Parra, L. de Boni, L. P. F. Aggarwal, J. P. Siqueira, L. Misoguti, I. E. Borissevitch and S. C. Zílio, *Opt. Mater*., 2012, **34**, 741.
10 X. Lia, D. Lia, M. Hana, Z. Chen and G. Zou, *Colloids Surf. A*, 2005, **256**, 151.
11 A. Günsel, M. N. Yaraşir, M. Kandaz and A. Koca, *Polyhedron*, 2010, **29**, 3394.
12 V. E. Pushkarev, A. Yu. Tolbin, N. E. Borisova, S. A. Trashin and L. G. Tomilova, *Eur. J. Inorg. Chem*., 2010, **33**, 5254.
13 V. E. Pushkarev, A. Yu. Tolbin, F. E. Zhurkin, N. E. Borisova, S. A. Trashin, L. G. Tomilova and N. S. Zefirov, *Chem. Eur. J*., 2012, **18**, 9046.
14 D. N. Laikov and Yu. A. Ustynyuk, *Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 820 (*Izv. Akad. Nauk, Ser. Khim.*, 2005, 804).
15 A. Yu. Tolbin, V. E. Pushkarev, E. V. Shulishov and L. G. Tomilova, *J. Porphyrins Phthalocyanines*, 2012, **16**, 341.

Received: 22nd January 2013; Com. 13/4052