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Selective synthesis of *clamshell*-type binuclear phthalocyanines

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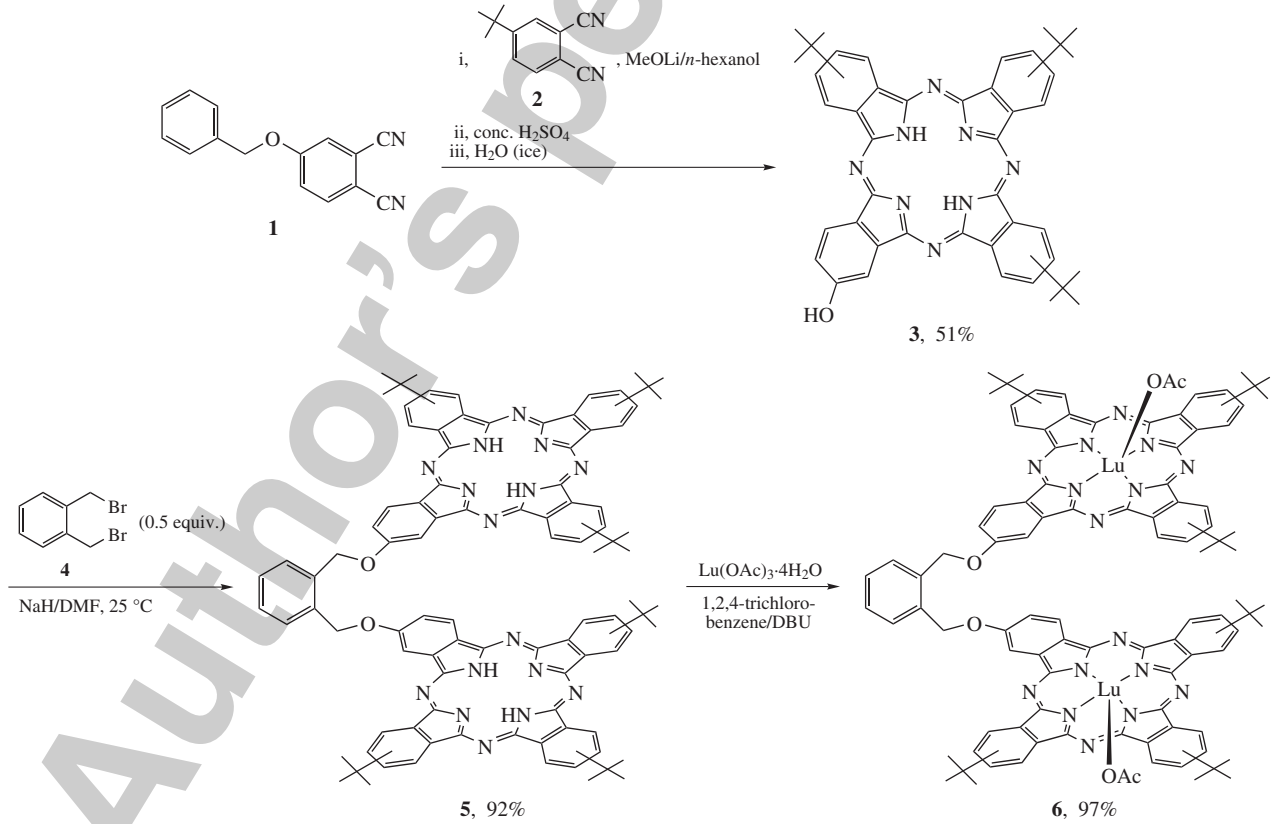
A direct selective synthesis of *clamshell*-type binuclear phthalocyanines *via* structural modification of monohydroxyphthalocyanines in up to 95% yield has been developed. Previously unknown *clamshell*-type Lu complex has been obtained. The spectral properties of the resulting binuclear phthalocyanines have been studied.

Interest in binuclear phthalocyanines increases every year. Owing to their specific structure, these compounds possess unique spectral, electro- and photocatalytic properties.[1–3] The majority of these properties result not only from the multiple-circuit aromatic conjugation system, which is also peculiar to monophthalocyanines, but mainly from the electronic interaction between the macrocycles that occurs either through an unsaturated spacer (planar binuclear phthalocyanines)[4,5] or through the space between the macrocycles (*clamshell*-type binuclear phthalocyanines).[6,7]

However, the synthesis of binuclear phthalocyanines is rather complicated limiting considerably the studies on these compounds and, all the more, their practical application. In most cases, binuclear phthalocyanines are obtained by mixed cyclisation of various phthalogens giving hard-to-separate mixtures of phthalocyanine products with extremely low yields of target compounds.[8] This is the reason that the search for selective methods of synthesising binuclear phthalocyanines with various structures currently attracts special attention. Such methods have already been developed for planar binuclear phthalocyanines with macrocycles linked through unsaturated aliphatic or aromatic spacers. Directed syntheses of such compounds are based on the Heck,[9] Wittig[10] or Diels–Alder[11] reactions; unsymmetrically substituted monophthalocyanines are used as starting compounds. At the same time, accesible synthetic techniques to *clamshell*-type binuclear phthalocyanines have not been developed yet. Therefore, the purpose of this study was to develop a method for selective synthesis that would increase the accessibility of these compounds.



Scheme 1 Selective synthesis of *clamshell*-type binuclear phthalocyanines.

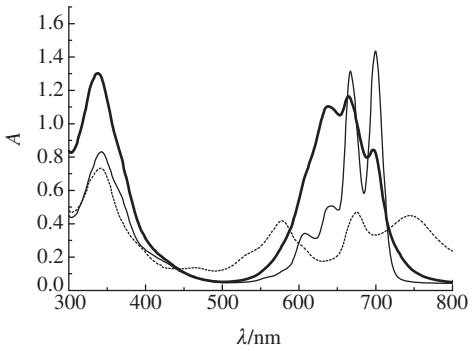


Figure 1 Electronic spectra of starting monophthalocyanine **3** (solid thin line), **3** + NaH (dashed line) and reaction product **5** (solid thick line) in DMF.

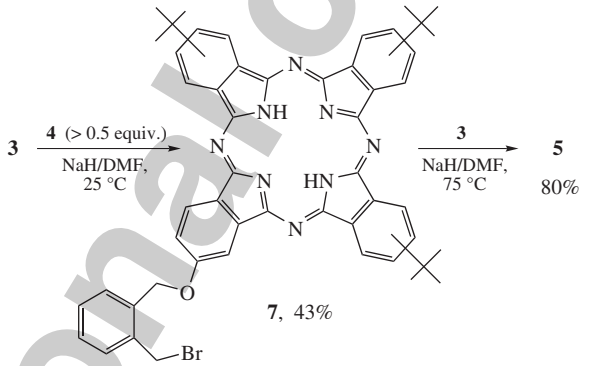
Retrosynthetic analysis of *clamshell*-type binuclear phthalocyanine structures allowed us to conclude that monohydroxy monophthalocyanines can be used as the starting compounds. This approach let us to perform the nucleophilic reaction under mild conditions and in a high yield (Scheme 1).

The reaction of 4-benzyloxyphthalodinitrile **1**[12] with 4-*tert*-butylphthalodinitrile **2**[13,14] in the presence of MeOLi in *n*-hexanol followed by treatment of the reaction mixture with concentrated sulfuric acid resulted in 2-hydroxy monophthalocyanine **3**† in 51% yield. Ligand **3** was used as the starting compound in the synthesis of *clamshell*-type binuclear phthalocyanines.

Due to the high reactivity of dibromide **4**, the reagent ratio should be taken into account in this synthesis. In fact, we succeeded to obtain binuclear ligand **5**‡ with high selectivity and in 92% yield using the ratio **3**:**4** = 1:0.5. The reaction was carried out in DMF in the presence of NaH. Initially, the treatment of compound **3** with NaH in the reaction mixture gave phenol-type alkoxy anions required for nucleophilic bonding. We also succeeded in detecting changes in their electronic spectra (Figure 1) accompanied by a change in the colour of monohydroxyphthalocyanine **3** from light-blue to dark-blue. The gradual addition of an exactly calculated amount of reagent **4** resulted in considerable changes in the reaction mixture electronic spectra, whereas an increase in the temperature (to 40 °C) accelerated the reaction. However, note that the yield of target binuclear phthalocyanine **5** drastically decreased upon a considerable increase in the reaction temperature due to the destruction of phthalocyanine macrocycles in the highly basic medium. This reaction gives a single product, namely, symmetric binuclear phthalocyanine **5**, involving quantitative conversion of starting compound **3**.

We have also demonstrated the versatility of the method developed previously[16] for the synthesis of rare-earth monophthalocyanines; a *clamshell*-type binuclear Lu complex was firstly synthesised as an example.§ The reaction of compound **5** with $Lu(OAc)_3 \cdot 4H_2O$ in the presence of DBU produced complex **6** in an almost quantitative yield (Scheme 1).

It was found that an increase in the amount of dibromide **4** above a stoichiometric quantity along with target binuclear phthalocyanine **5** also gives unsymmetrically substituted monophthalocyanine **7** (Scheme 2).¶ Compound **7** was further used to obtain ligand **5**.†† Obviously, this method may also be used to synthesise hetero-ligand binuclear phthalocyanines.



Scheme 2

The structures of phthalocyanines **3**, **5**–**7** were confirmed by mass spectrometry and NMR spectroscopy. The MALDI-TOF mass spectrum (2,5-dihydroxybenzoic acid – DHB as the matrix) of monophthalocyanine **3** contains only a protonated molecular ion peak with *m*/*z* 698. The mass spectra of binuclear phthalocyanines **5** and **6** contain, in addition to molecular ion peaks, also signals of fragment ions formed upon clevage of CH_2–OPc bonds. Figure 2 demonstrates the mass spectrum and molecular ion peak of binuclear ligand **5** as an example. For complex **6**, the molecular ion peak was not found in the spectrum, neither in the presence of DHB nor in the absence of the matrix. However, not only the molecular ion peak ($[M + 2H]^+$) but

† *Synthetic procedure*: MeOLi (0.86 g, 0.227 mol) was added to a solution of compounds **1** (0.40 g, 0.002 mol) and **2** (3.16 g, 0.017 mol) in *n*-hexanol (20 ml). The mixture was refluxed for 2 h; then, the solvent was evaporated followed by treatement of crude product with conc. H_2SO_4. The reaction mixture was kept for 5 min and poured onto ice. The phthalocyanine products precipitated were filtered off, repeatedly washed with water to a neutral pH, and chromatographed on silica gel ($CHCl_3$) to give 0.63 g (51%) of ligand **3**. IR (KBr, ν/cm^{-1}): 3200–3490 (OH). MS, *m*/*z*: 698 $[MH]^+$. ^{1}H NMR ([$^2H_8$]THF) δ: 1.71 (s, 27H, CMe_3), 9.21–9.48 (m, 12H, Pc). UV-VIS ($CHCl_3$, λ_{max}/nm): 347, 663, 700.

‡ *Synthetic procedure:* NaH (2 mg, 0.080 mmol) was added to a solution of compound **3** (50 mg, 0.072 mmol) in DMF (2 ml). Once the reaction was completed, reagent **4**[15] (11 mg, 0.030 mmol) was added to the reaction mixture with vigorous stirring, and the mixture was kept for 15–20 min at 25–30 °C (or for 5–7 min at 40 °C) with chromatographic monitoring of the reaction. The reaction mixture was treated with water; the precipitated product was filtered off, washed with water (2×20 ml), then with methanol (2×30 ml), and purified by chromatography on silica gel (Merck, 40×63 μm, $CHCl_3$) to give 100 mg (92%) of ligand **5**. MS, *m*/*z*: 1500 $[MH]^+$, 1395 $2[M - C_{52}H_{49}N_8O - H]^+$, 802 $[M - C_{44}H_{41}N_8O]^+$, 698 $[M - C_{52}H_{49}N_8O]^+$. ^{1}H NMR ([$^2H_8$]THF) δ: 1.8 (s, 54H, CMe_3), 5.6 (s, 4H, OCH_2), 7.2–9.3 (m, 28H, Ar). UV-VIS (CH_2Cl_2, λ_{max}/nm): 337, 635, 661, 696.

§ *Synthetic procedure*: DBU (0.025 ml, 0.167 mmol) and $Lu(OAc)_3 \cdot 4H_2O$ (14 mg, 0.033 mmol) were added to a solution of compound **5** (25 mg, 0.017 mmol) in 1,2,4-trichlorobenzene (1 ml). The mixture was kept for 1 h at 190 °C. Once the reaction was completed, the reaction mixture was diluted with benzene and non-phthalocyanine admixtures were filtered off. The filtrate was concentrated (2 ml) at reduced pressure and diluted with hexane (20 ml); product **6** was filtered off and dried at 30–40 °C to give 32 mg (97%) of the target complex **6**. MS, *m*/*z*: 1969 $[M + 2H]^+$, 1909 $[M - OAc - H]^+$, 1676 $[M - Lu - 2OAc]^+$. ^{1}H NMR ([$^2H_8$]THF) δ: 1.6 (s, 54H, CMe_3), 6.0 (s, 4H, OCH_2), 7.3–7.6 (m, 4H, Ar), 7.8–8.3 (m, 6H, Ar), 9.1–9.6 (m, 18H, Ar). UV-VIS (CH_2Cl_2, λ_{max}/nm): 347, 680.

¶ *Synthetic procedure*: NaH (0.125 mmol) was added to a solution of compound **3** (0.115 mmol) in DMF (4 ml). Once the reaction was completed, reagent **4**[15] (343 mg, 1.152 mmol) was added to the reaction mixture with vigorous stirring, and the mixture was kept for 10 min at 40 °C with chromatographic monitoring of the reaction. The reaction mixture was treated with water; the precipitated product was filtered off, washed with water (2×20 ml), then with methanol (30 ml), and purified by chromatography on silica gel (Merck, 40×63 μm, $CHCl_3$) to give phthalocyanine **7** in 43% yield. MS, *m*/*z*: 801 $[M - Br - H]^+$, 697 $[M - C_8H_8Br]^+$. UV-VIS (DMF, λ_{max}/nm): 342, 667, 701.

†† *Synthetic procedure*: NaH (1 mg, 0.042 mmol) was added to a solution of ligand **3** (15 mg, 0.021 mmol) in DMF (0.5 ml). Once the reaction was completed, phthalocyanine **7** (18 mg, 0.020 mmol) was added to the reaction mixture. The solution was heated to 75 °C and kept for 20 min at the same temperature. The reaction mixture was treated by the above procedure‡ to give 25 mg (80%) of binuclear ligand **5**.

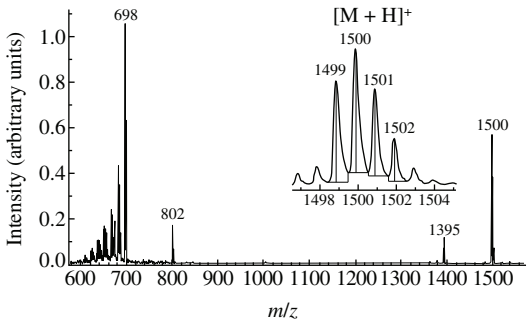


Figure 2 Mass spectrum (MALDI-TOF, DHB) and molecular ion peak of binuclear phthalocyanine **5**.

also characteristic peaks of fragment ions $[M - OAc - H]^+$ and $[M - Lu - 2OAc]$ were found in the mass spectrum using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malonitrile (DCTB) as the matrix. Unlike phthalocyanine **5**, no fragmentation of benzyl bonds is observed with the use of this matrix. The molecular ion peak in the MALDI-TOF mass spectrum (DHB) of bromide **7** is almost not observed due to its intense decay to give the $[M - Br]^+$ secondary ion. The fragment ion $[M - C_8H_8Br]^+$ is also present, which is formed by removal of the peripheral substituent. Signals of all proton types were found in the ^{1}H NMR spectra of binuclear phthalocyanines **5** and **6**; it was also found that an increase in the solvent polarity resulted in a gradual resolution improvement of the spectrum with a constant number of scans (NS = 128) and a temperature of 294 K. It may be assumed that the sharpness of signals in ^{1}H NMR spectra is considerably affected by specific interactions of phthalocyanine molecules, which result in disaggregation in the case of polar solvents, and hence higher signal resolution.

Binuclear phthalocyanines **5** and **6** were also characterized by electronic absorption spectroscopy (Figure 3). The character of their UV-VIS spectra well correlates with published data and those we obtained previously for related compounds.[1,7,17] It was found that the shape of their *Q* bands changed considerably in comparison with the corresponding mononuclear analogues. It is known that the character of binuclear phthalocyanines electronic spectra differs from that of their mononuclear analogues, and this difference is the stronger the more efficient the interaction between the chromophore centers.[1] Taking this fact into account, we may assume that the intramolecular interactions in binuclear ligand **5** show themselves more strongly than in metal complex **6**, and this phthalocyanine exists in the 'closed shell' conformation. It is likely that incorporation of the metal ion increases the distance between the macrocycles, and as a result,

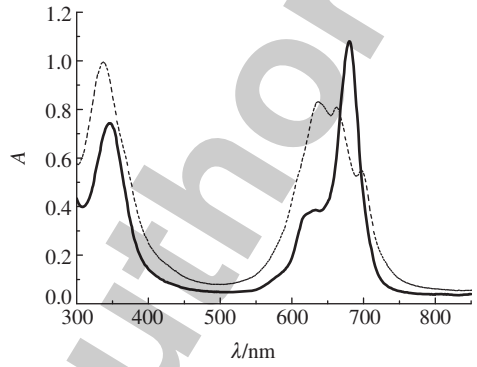


Figure 3 Electronic spectra of binuclear phthalocyanines **5** (dashed line) and **6** (solid thick line) in CH_2Cl_2.

the character of the spectra of complex **6** differs from that of mononuclear metal complexes less considerably than in the case of free ligands. Furthermore, attention should also be paid to the difference in the region of the vibrational satellite of metal complex **6**. In the case of the similar zinc complex that we obtained previously,[7] the satellite is rather flattened in comparison with lutetium complex **6**. Hence, it may be assumed that intramolecular interactions in complex **6** reveal themselves less strongly than those in the zinc analogue, which may be due to the presence of the bulky extra-ligand (OAc). This increases the distance between the macrocycles, so phthalocyanine **6** apparently has the 'open shell' conformation. As to the zinc complex, it apparently occupies an intermediate position and its most probable conformation is a 'partially open shell'.

Thus, we have elaborated a selective method for synthesising *clamshell*-type binuclear phthalocyanines, including their rare-earth complexes, with Lu as an example. This method offers serious advantages over the classical mixed cyclisation of phthalogens with various structures,[6] since it is selective and results in high yields of target binuclear phthalocyanines. Phthalocyanines **5** and **6** may serve as building blocks for synthesising new nano-sized structures with interesting and useful properties.

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