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Heteroligand and heteronuclear clamshell-type phthalocyanines: selective preparation, spectral properties, and synthetic application

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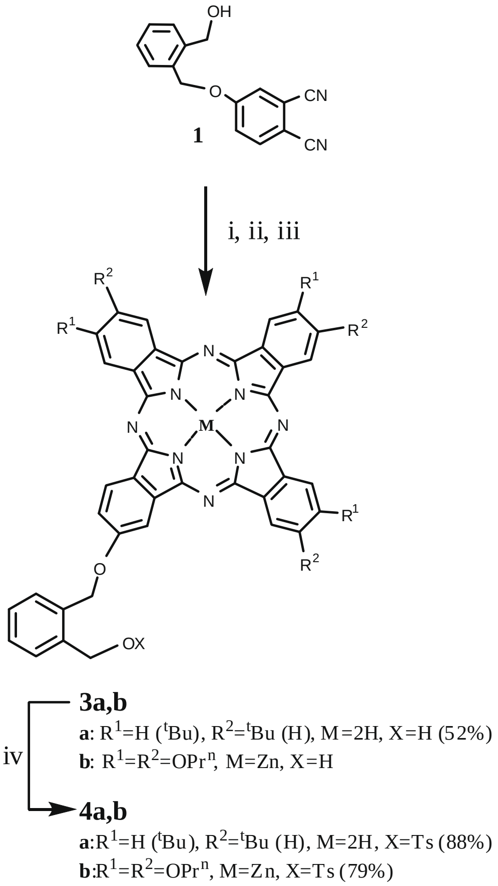
ABSTRACT

A direct synthetic method to produce heteronuclear and heteroligand *clamshell*-type binuclear phthalocyanines via a nucleophilic coupling reaction between A_3B-type monophthalocyanines is developed with the target compounds demonstrating the possibility to form sandwich-type heterocomplexes for the first time.

Binuclear phthalocyanines have become the subject of intensive research owing to their unique spectral and electrochemical properties resulting from a multicircuit-conjugated π-electronic system.[1–3] Significant attention has been paid to binuclear phthalocyanines bridged through rigid spacers (*clamshell*-type). Such bridges provide a specific geometry resulting in the macrocycles having a cofacial conformation in solution.[4] *Clamshell*-type metallophthalocyanines are both unique catalysts of biochemical processes[1,5] and components of ion-selective electrodes[6] for recognition of bifunctional organic molecules. Varying the nature of the complexing metals, as well as of the peripheral substituents, allows the selectivity of such recognition to be increased and widens appreciably the range of molecules under investigation. In this connection, the development of direct approaches to heteroligand and heteronuclear *clamshell*-type phthalocyanines is an important task.

Recently, we developed a selective method for preparing homonuclear *clamshell*-type phthalocyanines.[7] We now describe a new approach to heteroligand and heteronuclear *clamshell*-type phthalocyanines based on nucleophilic coupling of functionalized unsymmetrically substituted monophthalocyanines.

TMS-protection of phthalogen **1**[8] followed by cyclization of the isolated TMS-derivative with 4-*tert*-butylphthalonitrile (**2**)[9,10] in the presence of CH_3OLi in *n*-hexanol gave unsymmetrically substituted monophthalocyanine **3a**[11] after removal of the TMS-group using AcOH. Analogues have been described earlier, for example, zinc complex **3b**,[12] but the yields were poor. Reaction of phthalocyanines **3a, b** with TsCl gave the corresponding tosylates **4a, b**[13] (Scheme 1).



Scheme 1. The synthesis of starting tosyl derivatives **4a**, **b**. Reagents: (i) $[(CH_3)_3Si]_2NH$/THF, $(CH_3)_3SiCl$, 30 min; (ii) 4-*tert*-butylphthalonitrile (**2**), CH_3OLi/*n*-$C_6H_{13}OH$, 4 h; (iii), $AcOH/H_2O$; (iv) NaH/DMF, TsCl, 8 h.

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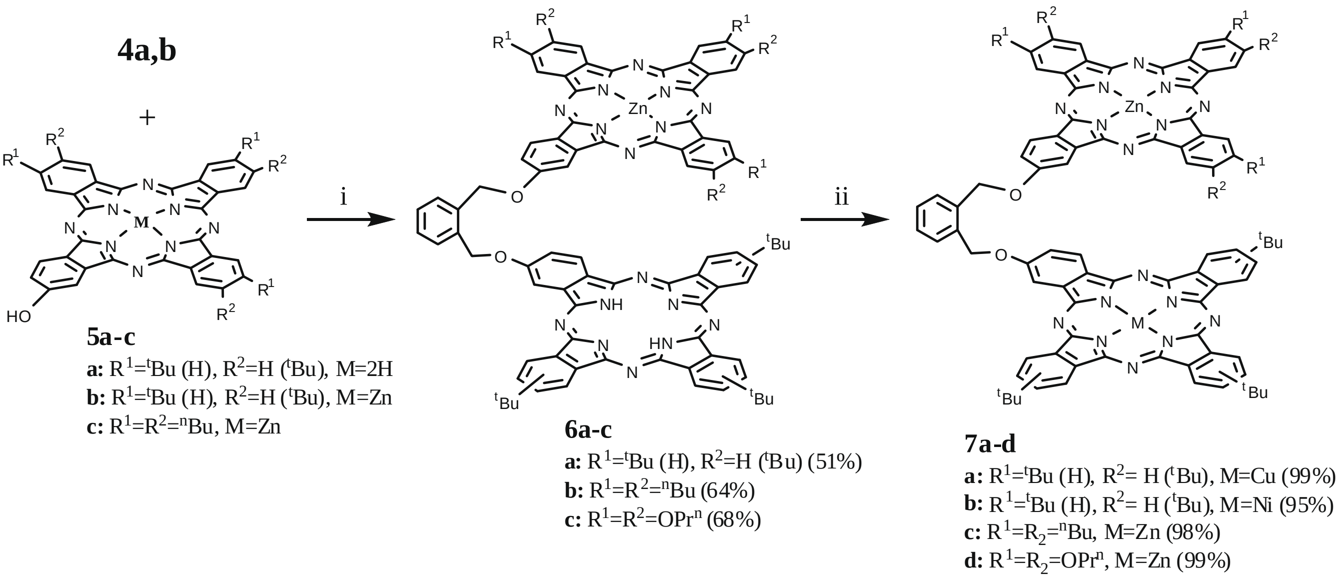
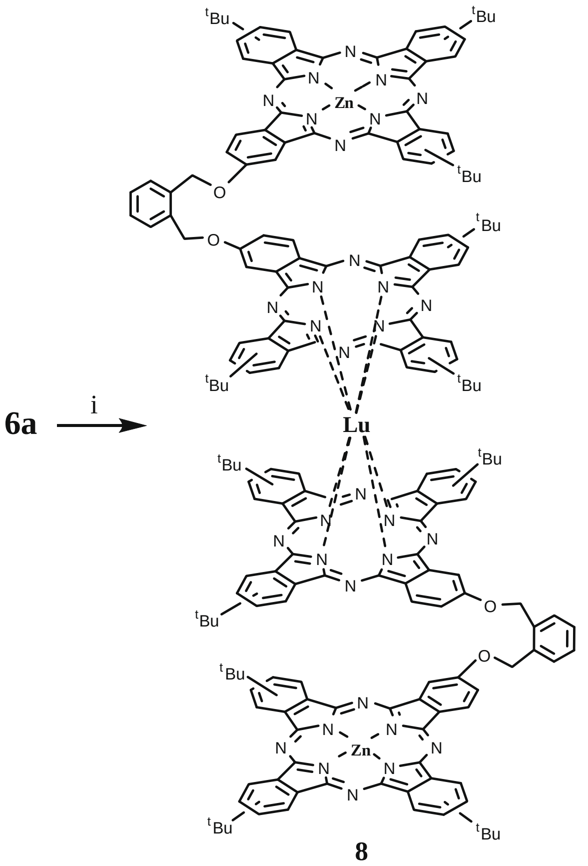


Scheme 2. The nucleophilic coupling reaction and synthesis of heteronuclear and heteroligand binuclear *clamshell*-type phthalocyanines **6a–c** and **7a–d**. Reagents: (i) K_2CO_3/DMF (20–48 h, 25–80 °C) or NaH/DMF (15–20 min, 60–80 °C); (ii) $M(OAc)_n \cdot mH_2O$, DBU/1,2,4-trichlorobenzene, 15 min.

Tosyl derivatives **4a, b** as well as 2-hydroxyphthalo-cyanines **5a–c**[14] were used to prepare the *clamshell*-type binuclear phthalocyanines **6–8**.

We found that the nucleophilic coupling reaction was sensitive to the nature of the base and the temperature (Scheme 2). Sodium hydride was found to be a good base for producing target compounds **6a–c**[15] in yields of 51–68% in comparison with milder K_2CO_3. As a result the reaction time was reduced. However, increasing the amount of strong base led to decomposition of the phthalocyanine compounds which was more pronounced upon increasing the reaction temperature. Complexes **7a–d**[16] were obtained by metal insertion reactions of **6a–c** with Zn, Cu, and Ni acetates.



Scheme 3. Synthesis of *sandwich-clamshell* tetraphthalocyanine **8**. Reagents: (i) $Lu(acac)_3 \cdot 3H_2O$, MeOLi/*n*-hexadecanol.

Furthermore, we have found phthalocyanines **6** to be suitable building-blocks for producing more complicated structures. Starting from **6a**, we obtained polynuclear phthalocyanine **8** consisting of two zinc(II) monophthalocyanine and one lutetium(III) bisphthalocyanine subunits (Scheme 3). This novel complex represents a *sandwich-clamshell-type* phthalocyanine.[17]

The structures of new mono- (**3a**, **4a**, **b**) and binuclear (**6**, **7**) phthalocyanines as well as of tetraphthalocyanine **8** were confirmed by mass spectrometry and ^1H NMR-spectroscopy data. The mass spectra (MALDI-TOF, matrix—DCTB[‡]) revealed molecular ion peaks $[M]^+$, $[M+nH]^+$ or $[M-nH]^+$ (n = 1–3) as well as signals characteristic of phthalocyanine fragment ions, in particular, phenoxide- or benzyl-type. It is important to note that changing the matrix to DHB[§] intensifies the fragmentation process and only fragment ion peaks were detected. All the ion peaks observed in the mass spectra have the characteristic isotope pattern corresponding to natural isotope distribution. The ^1H NMR spectra showed all the typical signals, but in the case of *tert*-butyl-substituted phthalocyanines, the asymmetry results in a higher amount of regioisomers and broadening of the aromatic signals. Variation of the solvent as well as the concentration and temperature did not affect the resolution of the spectra.

Unsymmetrical binuclear phthalocyanines **6–7** as well as tetraphthalocyanine **8** were also characterized from their UV–vis spectra. These spectra differed strongly from the spectra of the corresponding monophthalocyanines. Taking into account previous physico-chemical investigations of related compounds[4] we envisage that the binuclear phthalocyanines synthesized in the present investigation have 'partially-opened' conformations in solution.

[‡] DCTB—2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]-malonitrile.

[§] DHB—2,5-dihydroxybenzoic acid.

The UV–vis spectrum of **8** exhibits a split Soret band in the region 320–350 nm and a weaker absorption at 466 nm both typical of π-radical bisphthalocyanine species. The Q-band at 675 nm, showing superimposition of the mono- and bisphthalocyanine absorptions is widened and has a poorly resolved vibrational satellite as evidence of particular interactions between macrocycles, which is a subject for more detailed research.

Thus, we have developed a direct synthetic method to produce heteroligand and heteronuclear *clamshell*-type phthalocyanines for scientific investigations. A new tetraphthalocyanine di-Zn-Lu heteronuclear complex has been synthesized for the first time.

Acknowledgments

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Supplementary data

Supplementary data (mass spectra and UV–vis spectra of binuclear phthalocyanines **6**, **7,** and tetraphthalocyanine **8**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.048.

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11. To a solution of **1** (400 mg, 1.51 mmol) in THF (10 ml) hexamethyldisilazane (0.48 ml, 2.25 mmol) and several drops of trimethylchlorosilane were added. The mixture was heated at reflux for 30 min followed by evaporation of the solvent to give the crude TMS-derivative. This compound along with phthalonitrile **2** (2.8 g, 151 mmol) and CH_3OLi (860 mg, 22.6 mmol) was dissolved in *n*-hexanol (5 ml). The reaction mixture was heated at reflux for 3.5 h. After completion, the solvent was evaporated and the crude products were treated with a 10% solution of AcOH. After filtration of the phthalocyanine products and following washing with CH_3OH (2 × 50 ml) and H_2O (50 ml) the mixture was chromatographically separated (eluent–$CHCl_3$:THF 10:1) to give compound **3a** (642 mg, 52%). MS[¶] (*m/z*): 818 $[M-H]^+$ (11), 720 $[M-{}^tBu\text{-}2CH_3]^+$ (13), 697 $[M-C_8H_9O]^+$ (97). ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 1.66 (s, 27H, Me), 4.90 (s, 2H, CH_2), 5.69 (s, 2H, CH_2), 7.31–8.38 (m, 4H, Ar), 9.15–9.59 (m, 12H, Ar) ppm. UV–vis ($CHCl_3$), λ_{max}/nm: 345, 604, 644, 664, 699.
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13. *Typical procedure*: To a solution of phthalocyanine **3a** or **3b** (0.6 mmol) in DMF (10 ml), NaH (0.65 mmol) was added. Next, TsCl (0.9 mmol) was added followed by stirring for 8 h at room temperature (TLC). After the reaction was complete the product was precipitated by adding water. The solid residue was filtered and washed with CH_3OH (2×20 ml) to give compounds **4a**, **b**.*Data for* **4a**: Yield 88%. MS (*m/z*): 836 $[M-C_7H_7O_2S+H_2O]^+$ (38), 697 $[M-C_{15}H_{15}O_3S]^+$ (89). UV–vis ($CHCl_3$), λ_{max}/nm: 347, 604, 647, 665, 671.*Data for* **4b**: Yield 79%. MS (*m/z*): 1061 $[M-C_7H_7O_3S]^+$ (8), 1045 $[M-C_7H_7O_3S]^+$ (24), 939 $[M-C_{15}H_{15}O_3S]^+$ (92). UV–vis ($CHCl_3$), λ_{max}/nm: 356, 612, 680.
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15. *Typical procedure*. To a solution of **5a–c** (0.07 mmol) in DMF (2 ml), NaH (0.08 mmol) and **4a** or **4b** (0.05 mmol) were added. The mixture was heated to 60–80 °C for 15–20 min. After the reaction was complete (TLC) the products were precipitated by adding water followed by filtration and washing with CH_3OH (3 × 20 ml). After chromatographic separation (eluent–$CHCl_3$:THF 50:1) the target binuclear compounds **6a–c** were obtained.*Data for* **6a***:* Yield: 51%. MS (*m/z*): 1561 $[M-2H]^+$ (5), 759 $[M-C_{52}H_{49}N_8O]^+$ (49), 697 $[M-C_{52}H_{47}N_8OZn]^+$ (96). ^1H NMR (300 MHz, THF-d_8, 25 °C): δ 1.77 (s, 54H, Me), 4.81 (s, 2H, CH_2), 5.32 (s, 2H, CH_2), 5.38 (s, 2H, CH_2), 7.82–9.44 (m, 28H, Ar) ppm. UV–vis ($CHCl_3$), λ_{max}/nm: 341, 680.*Data for* **6b***:* Yield: 64%. MS (*m/z*): 1731 $[M]^+$ (99). UV–vis ($CHCl_3$), λ_{max}/nm: 338, 648, 671.*Data for* **6c***:* Yield: 68%. MS (*m/z*): 1743 $[M]^+$ (84), 1395 $2\times[M-C_{58}H_{59}N_8O_7Zn+H]^+$ (41), 1043 $[M-C_{44}H_{41}N_8O]^+$ (77), 940 $[M-C_{52}H_{49}N_8O]^+$ (62). UV–vis ($CHCl_3$), λ_{max}/nm: 347, 679.
16. *Typical procedure.* To a solution of **6a–c** (0.015 mmol) in DMF (2 ml), DBU (0.02 ml) and a stoichiometric amount of $Zn(OAc)_2{\cdot}2H_2O$, $Cu(OAc)_2{\cdot}H_2O$ or $Ni(OAc)_2{\cdot}4H_2O$ were added. The reaction mixture was refluxed for 20–30 min (TLC, UV–vis). After the reactions were complete the solvent was evaporated followed by addition of CH_3OH (15 ml) and water to precipitate target compounds **7a–d**.*Data for* **7a**: Yield: 99%. MS (*m/z*): 1624 $[M]^+$ (22), 911 $[M-C_{52}H_{47}N_8OZn+DBU]^+$ (86), 759 $[M-C_{52}H_{47}N_8OZn]^+$ (81). UV–vis ($CHCl_3$), λ_{max}/nm: 344, 680.*Data for* **7b**: Yield: 95%. MS (*m/z*): 1619 $[M]^+$ (24), 753 $[M-C_{52}H_{47}N_8OZn]^+$ (89). UV–vis ($CHCl_3$), λ_{max}/nm: 338, 641, 673.*Data for* **7c**: Yield: 98%. MS (*m/z*): 1795 $[M]^+$ (58), 929 $[M-C_{52}H_{47}N_8OZn]^+$ (82), 761 $[M-C_{64}H_{71}N_8OZn]^+$ (16). UV–vis ($CHCl_3$), λ_{max}/nm: 344, 638, 681.*Data for* **7d**: Yield: 99%. MS (*m/z*): 1807 $[M+H]^+$ (11), 941 $[M-C_{52}H_{47}N_8OZn]^+$ (96), 761 $[M-C_{58}H_{59}N_8O_7Zn]^+$ (9). UV–vis ($CHCl_3$), λ_{max}/nm: 342, 634, 676.
17. A mixture of Zn-free-base phthalocyanine **6a** (50 mg, 0.032 mmol) and $Lu(acac)_3{\cdot}3H_2O$ (8.5 mg, 0.016 mmol) was heated in *n*-hexadecanol (800 mg) under argon in the presence of MeOLi (0.6 mg, 0.016 mmol) for 30 min until the starting phthalocyanine had completely disappeared. The reaction was monitored by TLC (SiO_2, C_6H_6 as eluent) and UV–vis spectroscopy. The resulting solution was diluted with C_6H_6 (5 mL), rinsed through a glass filter, and the solvent was removed under reduced pressure. The residue was washed with boiling 80% aqueous MeOH (3 × 50 mL), filtered, and dried in a vacuum desiccator. The resulting powder was dissolved in C_6H_6 and chromatographed on a column (2.5 × 40 cm, Bio-Beads S-X1, C_6H_6 as eluent), to afford **8** as a green-colored fraction in 45% yield. MS (*m/z*): 3297 $[M+3H]^+$ (14), 2553 $[M-C_{44}H_{39}N_8Zn]$ (15), 2432 $[M-C_{52}H_{47}N_8OZn]$ (10), 1670 $[M-C_{44}H_{39}N_8OZn\text{-}C_{52}H_{47}N_8OZn]$ (98), 1566 $[M-2\times C_{52}H_{47}N_8OZn]$ (44), 760 $[M-C_{148}H_{133}LuN_{24}O_3Zn]$ (82). UV–vis ($CHCl_3$), λ_{max}/nm: 329, 347, 466, 615 sh, 675.

[¶] All of the mass spectra were recorded on an Autoflex II MALDI-TOF mass spectrometer.