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Selective synthesis of clamshell-type bis-phthalocyanine bearing tetrachlorocyclotriphosphazene intramolecular bridge

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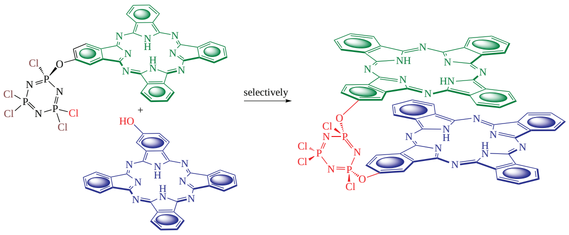
The selective synthesis of clamshell-type bis-phthalocyanine was performed using cyclotriphosphazene as a peripheral spacer. The spectral characteristics of the target dye are similar to those of most H-dimers, and the reaction can be considered conditionally selective with respect to the *cis*-isomer.



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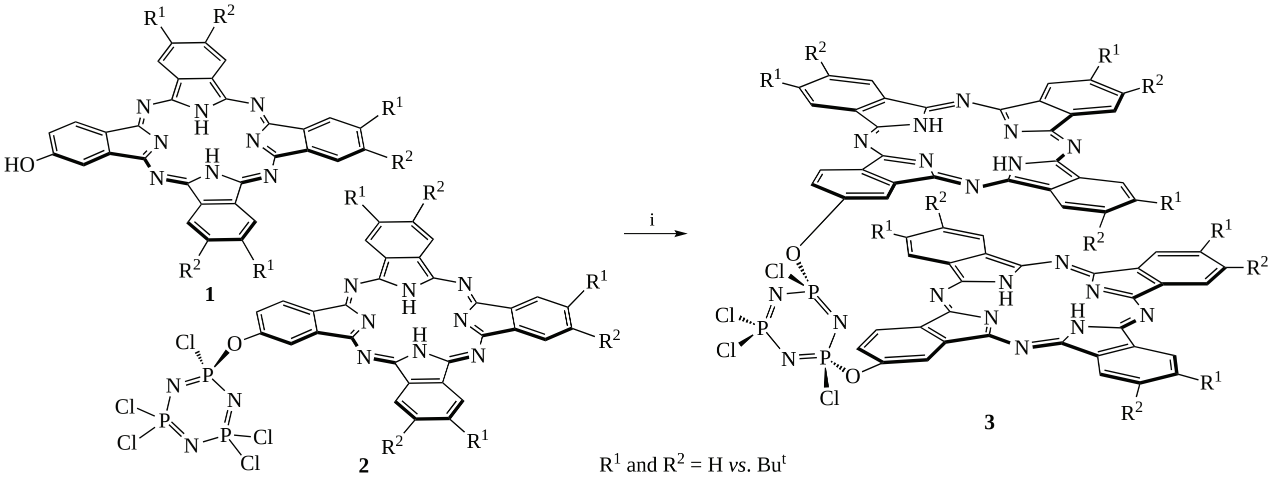
Dimeric phthalocyanines with parallel arranged macrocycles demonstrate effective intramolecular π–π interactions and are of interest for creation of nonlinear optical (NLO) materials.[1] Unlike the starting monomers,[2] these dyes exhibit unusual spectral properties in solutions and solid phases and can be used as low-threshold optical limiters.[3] Rigidly coupled co-facial bis-phthalocyanines are represented as stable H-type dimers; they exhibit an additional blue-shifted absorption band in UV-VIS spectra[4] as well as the low fluorescence quantum yields due to intramolecular self-quenching.[5] Chemical and physical properties of clamshell-type phthalocyanines depend on the nature of the bridging groups, which also determine the distance between subunits.[6] However, the synthesis of such dyes still remains a difficult task.

Due to high activity of chlorine atoms in hexachlorocyclotriphosphazene, this reagent can be conveniently used as a peripheral spacer, and we have already demonstrated this in the synthesis of low-symmetry A_3B-type monophthalocyanine.[7] In addition, the chlorine atoms provide this spacer with acceptor properties, which is important for the creation of NLO materials. It should be also noted that there are currently few examples of macrocyclic dyes with cyclotriphosphazene rings on the periphery (see ref. 8).

The synthesis that we have accomplished in this work is outlined in Scheme 1 depicting coupling of reactants **1** and **2** (for details, see Online Supplementary Materials). The formation of bis-macrocyclic derivative **3** is possible only when the reaction mixture is heated, and the reflux time strongly affects the selectivity of the nucleophilic cross-coupling. Thus, prolonged boiling causes formation of trimers and tetramers with the random position of macrocycles, according to mass spectrometry data.

Phosphazene-containing phthalocyanine **2** was used in a slight excess to reduce the chances of forming oligomeric products. The nucleophilic reaction leads mainly to a co-facial dimer with a *cis*-configuration of the macrocycles. This is evidenced from the UV-VIS spectrum (Figure 1), which shows



R^1 and R^2 = H *vs.* Bu^t

Scheme 1 *Reagents and conditions*: i, NaH/THF, 65 °C, 10 min.

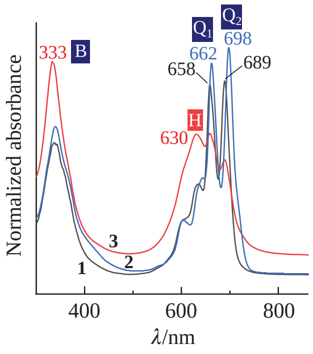


Figure 1 UV-VIS absorption spectra of low-symmetry monophthalocyanines **1**, **2** and the dimeric derivative **3** in THF ($C \sim 3 \times 10^{-5}$ M).

an additional band at 630 nm, in contrast to the starting monophthalocyanines **1**, **2**. In turn, the *trans*-isomer having an ‘open’ configuration of macrocycles should demonstrate a typical superposition of monophthalocyanine spectra, since it is deprived of co-facial arrangement of the macrocycles.

Purification of bis-phthalocyanine **3** was carried out on the Bio-Beads SX-1 (BIORAD®). As we pointed out earlier,[7] sorption carriers lead to the retention of dyes with a cyclotriphosphazene fragment due to a nucleophilic reaction taking place on the surface of silicon or aluminum oxides. When we tried to elute the adsorbed products with more polar systems, we obtained complex mixtures of products in which chlorine atoms were replaced by hydroxy groups.

Formation of the second macrocycle (**1** + **2** → **3**) makes the spin system more difficult: $A_2X \rightarrow AX_2$, and both PCl(OPc) groups in **3** are stereogenic, meaning that it should be formed as a mixture of three diastereomers, namely, achiral *cis*-isomer (*meso*-form) and two chiral *trans*-isomers (enantiomers). The ^{31}P NMR spectrum of substance **3** (Figure 2), indeed, contains three low-field PCl_2 triplets in the 23–27 ppm region with the most intense one at 23.41 ppm belonging to the *cis*-isomer. The PCl(OPc) signals, which should represent three higher-field doublets, are not fully resolved and are observed as a multiplet in a 14–16 ppm area. Therefore, it is evident that dimer **3** actually exists as a mixture of stereoisomers, and the *cis*-/*trans*-isomer ratio approximately amounts to 3 : 2 as follows from the integration of signals at 23.41 and 25.63/26.53 ppm, respectively. Note that it is the presence of the *cis*-isomer capable of intramolecular π–π interactions which is responsible for the appearance of the *H*-band in the UV-VIS spectrum of **3** (see Figure 1). The analysis of the phthalocyanine fragments in compound **3** is additionally supported by the ^{1}H NMR spectrum recorded in the MeONa-d_3/DMSO-d_6 disaggregating system (see Online Supplementary Materials, Figure S1), which reveals clear signals of α- and β-type phthalocyanine protons within 9 and 8 ppm regions, respectively.

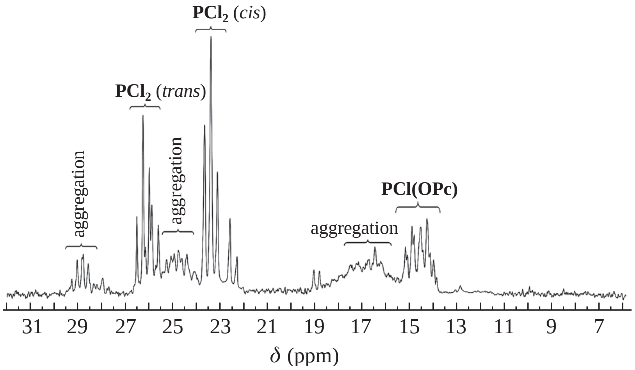


Figure 2 ^{31}P NMR spectrum of compound **3** in $CDCl_3$ with the addition of 1–2 vol% NEt_3.

In the MALDI-TOF/TOF mass spectrum without a matrix, only the molecular ion peak $[M]^+$ with *m/z* 1671.4641 is observed [Figure S2(*a*)]. The absence of fragmentation indicates the stability of the compound, despite the mobility of chlorine atoms in the phosphazene ring. Under ionization conditions, P–Cl bonds do not break. This becomes possible only under nucleophilic reactions, as demonstrated above. In the MALDI-TOF mass spectrometry, chlorine atoms can be lost if some matrices are used. Thus, in the case of the HCCA (α-cyano-4-hydroxycinnamic acid) matrix, it was possible to replace two chlorine atoms with a CN group, *i.e.*, the CN^- anion was formed during the destruction of the matrix and then acted as a nucleophile. For this reason, we observe the secondary ion with *m/z* 1651.8171 [Figure S2(*b*)].

In conclusion, we performed the directed synthesis of the clamshell-type bis-phthalocyanine **3**, with the macrocycles linked through a cyclotriphosphazene spacer. The spectral studies showed that, along with the *cis*-isomer, a certain amount of the *trans*-isomer was formed being a mixture of enantiomers. The obtained isomers of dimeric phthalocyanine **3** cannot be separated manually; however, the reaction (see Scheme 1) can still be considered selective for the *cis*-isomer, which is a strapped bis-phthalocyanine of the clamshell-type.

Looking ahead, the structure of dye **3** may be further modified since it contains four reactive chlorine atoms suitable for introduction of various groups and even small cyclic fragments. In this way, we can control the electronic properties of the clamshell-type phthalocyanines with their fine-tuning for the required purposes regarding the development of NLO materials, primarily optical limiters.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.01.029.

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