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

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General methods

All solvents were of reagent-grade quality and were obtained directly from Aldrich. Phthalocyanine (Pc) ligands **1**,**2** were synthesized according to our previously published procedures.* UV-Vis spectra were recorded on a Hitachi U-2900 spectrophotometer in a range of 300–1100 nm in THF. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded using a Bruker AVANCE 500 spectrometer (500.20 MHz and 202.48 MHz for ^{1}H and ^{31}P, respectively) with the samples dissolved in $CDCl_3$ or DMSO-d_6. Triethylamine (NEt_3, 12 vol %) and sodium methoxide-d_3 (MeONa-d_3) were used as disaggregating additives: NEt_3/$CDCl_3$, MeONa-d_3/DMSO-d_6 and NEt_3/MeONa-d_3/DMSO-d_6 systems were applied. MeONa-d_3 was prepared immediately before use by adding a small piece of Na metal to methanol-d_4 at ambient conditions with the following evaporation of the residual solvent. Chemical shifts for ^{1}H and ^{31}P are given in ppm relative to $SiMe_4$ and H_3PO_4, respectively. MALDI-TOF/TOF measurements were performed on a Bruker ULTRAFLEX II TOF/TOF spectrometer using α-cyano-4-hydroxycinnamic (HCCA, Aldrich) acid as a matrix.

*S1 *(a)* A. Yu. Tolbin, V E. Pushkarev, L. G. Tomilova and N. S. Zefirov, *Mendeleev Commun.,* 2009, 19, 78;

(b) A. Yu. Tolbin, V. K. Brel, B. N. Tarasevich and V. E. Pushkarev, *Dyes Pigm.,* 2020, 174, 108095.

Synthetic Procedure for Monophthalocyanine 2

To a solution of low-symmetry ligand **1** (200 mg, 0.28 mmol) in THF (30 mL), sodium hydride (20 mg, 0.83 mmol) was added, and the reaction mixture was further kept under reflux for 20 min. Next, an excess of phosphonitrilic chloride trimer (300 mg, 0.88 mmol) was added, and the boiling was continued for 10 min. After the reaction was finished (TLC control), the solvent was evaporated *in vacuo* followed by washing of the residue with the mixture of methanol/water (1:1) and chromatographic purification on Bio-Beads SX-1 (BIORAD®) with THF as the eluent to remove high molecular weight by-products. Target compound **2** was obtained in 81% yield (235 mg). MALDI-TOF/TOF (matrix – DHB): *m/z* 1009.1136 $[M+2H]^+$, calcd for $[C_{44}H_{43}Cl_5N_{11}OP_3]$ 1009.1308. ^{1}H NMR (MeONa-d_3/DMSO-d_6, δ/ppm): 9.11–9.24 (group m, 8H, α-H^{Ar}), 8.06–8.10 (group m, 4H, β-H^{Ar}), 1.72 (br s, 27H, H^{tBu}). {^{1}H} ^{31}P NMR (NEt_3/$CDCl_3$, δ_P/ppm): 22.45 (d, 2P, PCl_2, A_2), 12.60 (t, 1P, PCl(OPc), X), $^2J_{P,P}$ = 59.6 Hz. UV-Vis (solvent), λ_{max}/nm (log ε): data for CCl_4: 337 (4.88), 660 (4.95), 695 (4.94); data for acetone: 341 (4.91), 607 (467), 658 (5.01), 689 (4.95); data for methanol: 328 (4.91), 607 (4.77), 654 (4.67), 690 (4.51). FT–IR (ZnSe): 3290 (NH), 2950–2860 (C_{Ar}–H), 1610 (C=N), 1200 (P=N), 1090 (P–O), 984 (P–O–C_{Ar}).

Synthetic Procedure for Bis-Phthalocyanine 3

To a solution of compound **1** (50 mg, 0.07 mmol) in absolute THF (5 mL), NaH (8 mg, 0.33 mmol) was added followed by ultrasonic irradiation for 10 min at room temperature. The prepared nucleophile was added dropwise to a solution of phthalocyanine **2** (85 mg, 0.08 mmol) in THF (25 mL) under reflux. After completion of the reaction (UV-Vis and TLC control), the solvent was evaporated *in vacuo*, followed by a quick wash of the residue with methanol and chromatographic purification on BIORAD® Bio-Beads SX-1 (eluent – THF) to remove traces of monomers and oligomers. The yield of **3** is 65%. *Analytical data*: *m/z* 1671.4641 $[M]^+$, calcd. for $C_{88}H_{82}Cl_4N_{19}O_2P_3$: 1671.4836; (HCCA matrix): *m/z* 1672.5208 $[M+H]^+$, 1651.8171 $[M–2Cl+2CN+H]^{+\cdot}$. ^{1}H NMR (NEt_3/MeONa-d_3/DMSO-d_6, δ/ppm): 9.11–9.29 (group m, 16H, α-H^{Ar}), 7.98–8.08 (group m, 8H, β-H^{Ar}), 1.70–1.73 (group s, 54H, H^{tBu}). ^{31}P{^{1}H} NMR (NEt_3/$CDCl_3$, δ_P/ppm): 23.41–26.27 (group t, 1P, PCl_2, A) [26.27 (t, PCl_2 of *trans*-isomer/first enantiomer, $^2J_{P,P}$ = 53.2 Hz), 25.90 (t, PCl_2 of *trans*-isomer/second enantiomer, $^2J_{P,P}$ = 54.4 Hz), 23.41 (t, PCl_2 of *cis*-isomer/mesoform/Pc *H*-dimer, $^2J_{P,P}$ = 54.6 Hz)], 13.89–15.20 (m, 2P, PCl(OPc), X_2). UV-Vis (THF), λ_{max}/nm (log ε): 333 (5.07), 630 (4.87), 659 (4.87), 692 (4.76).

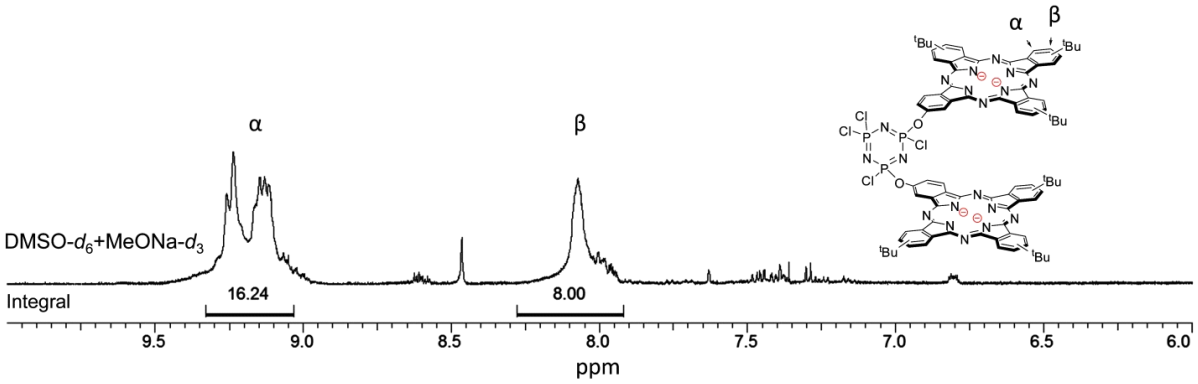

Figure S1. ^{1}H NMR spectrum of substance **3** (aromatic region).

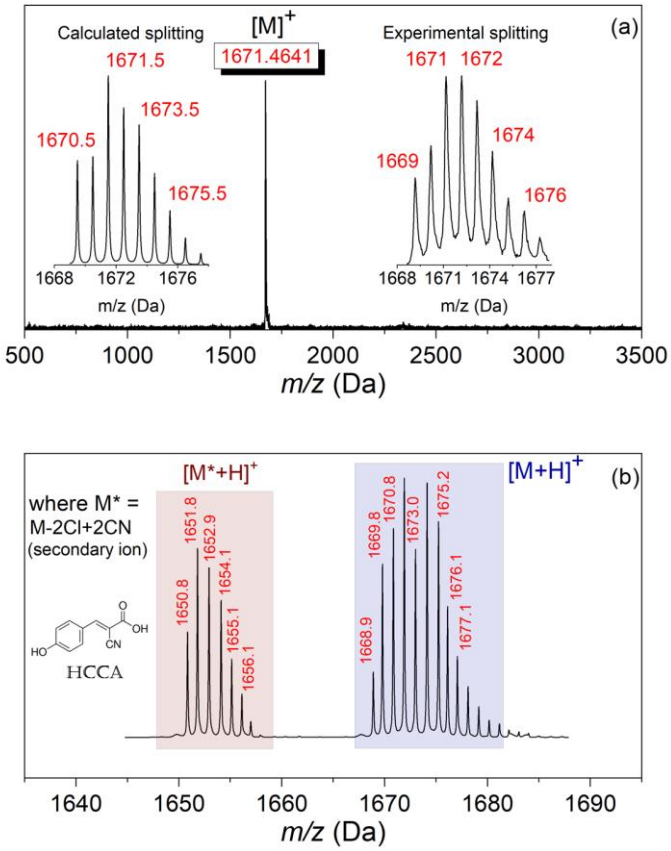

Figure S2. MALDI-TOF/TOF mass spectra of **3**: (*a*) no matrix;
(b) appearance of the secondary ion on interaction of $[M]^{+\cdot}$ with HCCA matrix.