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# Supramolecular Phthalocyanine Dimers Based on the Secondary Dialkylammonium Cation/ Dibenzo-24-crown-8 Recognition Motif

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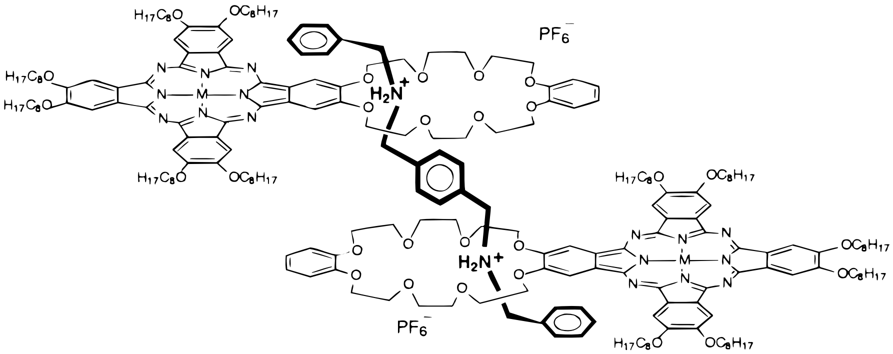
## ABSTRACT



**New unsymmetrically substituted DB24C8-phthalocyanines, which are able to form complexes with suitable dialkylammonium cations, have been prepared. These complexes most probably have a pseudorotaxane geometry.**

Supramolecular materials can be designed and created from simple molecular building blocks by self-assembly and self-organization using noncovalent interactions.[1] Phthalocyanines (Pcs)[2] have been employed extensively as subunits for the construction of functional materials since they exhibit special optical and electronic properties and self-organizing abilities to form columnar mesophases, Langmuir−Blodgett (LB) multilayers, or aggregates in solution.[3] The main forces that drive these self-assembly processes are the $\pi-\pi$ stacking interactions between the aromatic rings. The introduction of

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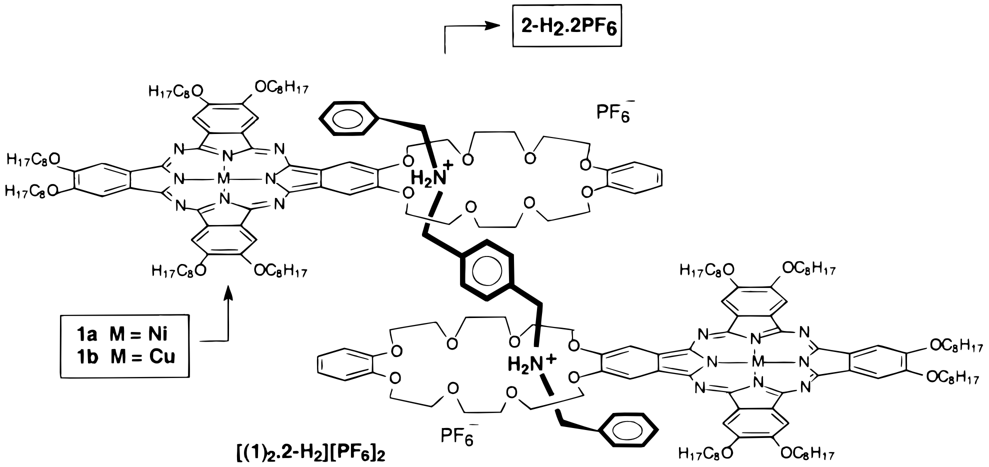

**Figure 1.** Structure of proposed pseudorotaxane $[(\mathbf{1})_2{\cdot}\mathbf{2}\text{-}H_2][PF_6]_2$.

either or both long aliphatic hydrocarbon chains or/and crown ether substituents at the periphery of the rigid phthalocyanine core can improve the organization properties of these molecules by exploiting either their mesogenic behavior[4] or the ability of their crown ether subunits to form complexes with alkali metal cations.[5,6] By contrast, hydrogen-bonding interactions have hardly been employed at all to self-assemble phthalocyanine molecules.[7]

In this communication, as a consequence of our interest in the organization features and physical properties of Pcs and related compounds,[8] we report a new strategy to produce discrete phthalocyanine oligomers based on the recognition motif developed by one of us, involving medium-sized crown ether macrocycles, such as dibenzo-24-crown-8 (DB24C8), and secondary dialkylammonium cations, e.g., dibenzylammonium ($DBA^+$) as its $PF_6^-$ salt.[9] These two components assemble in solution, forming stable hydrogen-bonded complexes with a pseudorotaxane geometry. The stoichiometry of the complex is determined by the number of ammonium centers that are present in the threadlike component. Furthermore, dethreading can occur[10] by adding a base to the solution so that the two reversible states can be switched by controlling the pH.

Here, we describe the synthesis of the novel unsymmetrically substituted phthalocyanines **1a,b** containing one DB24C8 unit and the formation of the supramolecular complex $[(\mathbf{1})_2{\cdot}\mathbf{2}\text{-}H_2][PF_6]_2$ (Figure 1), in solution, which consist on two crowned-phthalocyanines (**1a** or **1b**) and the bis(secondary dialkylammonium) dication **2**-$H_2^{2+}$.

The dicyano-DB24-crown-8 macrocycle **3** was prepared for the first time by following standard procedures.[5,11] The octyloxy chains were chosen as inert substituents on three of the isoindole units to increase the solubility of the final Pc compound in halogenated solvents. Thus, condensation of compound **3** with 3 equiv of 4,5-dioctyloxyphthalonitrile[4] (**4**) in the presence of $Ni(OAc)_2$ in *N*,*N*-dimethylaminoethanol (DMAE) at reflux temperature afforded the nickel(II) phthalocyaninato **1a** in 23% yield after purification on silica

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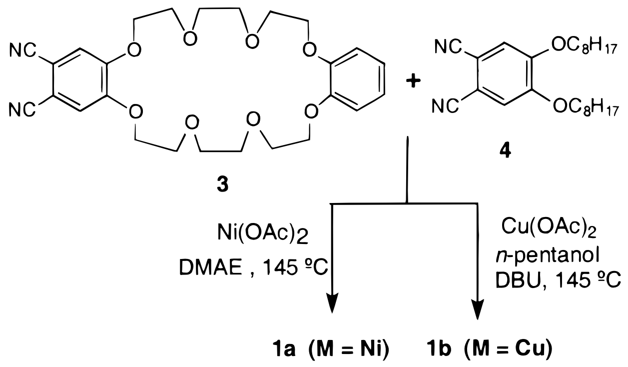
(12) Selected spectroscopy data. **3**: $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 7.11 (s, 2H, aromatic), 6.89, 6.88 (AA′BB′ system, 4H, aromatic), 4.2 (m, 8H, $OCH_2$), 3.9 (m, 8H, $OCH_2$), 3.8 ppm (s, 8H, $OCH_2$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 152.3, 148.8, 121.5, 115.4, 115.7, 114.0, 108.9, 71.6, 71.3, 70.0, 69.3 ppm; IR (KBr) $\nu$ 2231 $cm^{-1}$ ($C{\equiv}N$); FAB-MS (*m*-NBA) *m*/*z* 499 $[(M + H)^+]$. **1a**: $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.3, 8.2 (2× br s, 8H, Pc ring), 6.84, 6.83 (AA′BB′ system, 4H, aromatic), 4.7, 4.5, 4.3, 4.2, 4.1, 4.0 (6× m, 36H, $OCH_2$), 2.2, 1.8, 1.6, 1.4, 1.0 ppm (5× m, 90H, aliphatic); UV−vis ($CHCl_3$) (log $\epsilon$/ $dm^3mol^{-1}cm^{-1}$) $\lambda_{max}$ 289 (4.89), 310 (4.78), 411 (4.36), 605 (4.39), 643 (sh, 4.45), 671 nm (5.21); MALDI-TOF-MS (dithranol) *m*/*z* 1708.8 ($[M^+]$ **1a** requires 1708.96). **1b**: UV−vis ($CHCl_3$) (log $\epsilon$, $dm^3$ $mol^{-1}$ $cm^{-1}$) $\lambda_{max}$ 292 (4.87), 339 (4.85), 401 (4.68), 627 (4.66), 678 nm (4.79); MALDI-TOF-MS (dithranol) *m*/*z* 1713.9 ($[M^+]$ **1b** requires 1713.96).

gel using $CHCl_3$ and subsequently a mixture of $CHCl_3$/MeOH (100:1) as eluents (Scheme 1). Compound **1b** was obtained as depicted in Scheme 1 in a 22% yield, by crossover macrocyclization of the phthalonitrile **3** and **4** in a 1:5 ratio, using an excess of copper acetate in *n*-pentanol at 139 °C, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), followed by chromatography on silica gel with $CHCl_3$ and $CHCl_3$/MeOH (20:1) as eluents.

**Scheme 1.** Synthesis of Phthalocyanines **1a** and **1b**



All the new compounds were characterized by $^1H$ NMR and UV−vis spectroscopy and mass spectrometry.[12]

The $^1H$ NMR spectrum of **1a** in $CDCl_3$ (~3 mM) (Figure 2a) shows well-resolved sets of resonances easily assigned to the aromatic Pc nucleus and the crown ether moiety, suggesting that the DB24C8-phthalocyanines **1a** and **1b** are mainly monomers in solution. This result is consistent with their UV−vis spectra, which usually provide information on the type of aggregated structures that are present in solution: both compounds show the typical Q-band of monomeric phthalocyanines centered at 671 and 678 nm, respectively.

In a first complexation experiment, we investigated the formation of the complex [(**1a**)·DBA][$PF_6$] formed between the Pc **1a** and the dibenzylammonium DBA·$PF_6$ salt in solution. The DBA·$PF_6$ salt, which is highly insoluble in halogenated organic solvents, such as $CHCl_3$ or $CH_2Cl_2$ becomes soluble in a $CDCl_3$ solution containing the DB24C8-phthalocyanine **1a**. Since host−guest exchange is slow[9] on the $^1H$ NMR time scale at room temperature, the spectrum of a mixture of **1a** and DBA·$PF_6$ in $CDCl_3$ (Figure 2b) displays sets of resonances that correspond to the free species and the complex. Moreover, characteristic signals at $\delta$ 4.1, corresponding to the four $CH_2$ protons adjacent to the $NH_2^+$ group, in addition to the typical high field shift (0.1−0.3 ppm) of the resonances assigned to the catechol unit, indicate that complexation has taken place. Additionally, the signals assigned to the Pc core become nonequivalent and strongly high field shifted, suggesting an nonsymmetric $\pi-\pi$ interaction between the benzyl group of the ammonium salt and the aromatic Pc ring. Integration of the signals proves the formation of a 1:1 complex and evaluation of the signal intensities of the three species in equilibrium affords an association constant of 16 000 ± 2 000 $M^{-1}$. Furthermore, the formation of the 1:1 complex was supported by the matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) technique, using dithranol as the matrix. The spectrum displayed an intense peak at *m*/*z* 1906.8 (base peak) for the supramolecular ion [(**1a**)·DBA]$^+$ after loss of the $PF_6^-$ counterion.

Subsequently, we studied the formation of a noncovalent phthalocyanine dimer by complexation of each of the secondary ammonium centers present in **2**-$H_2$·2$PF_6$ with the DB24C8 void of two different Pc molecules **1a** or **1b**.

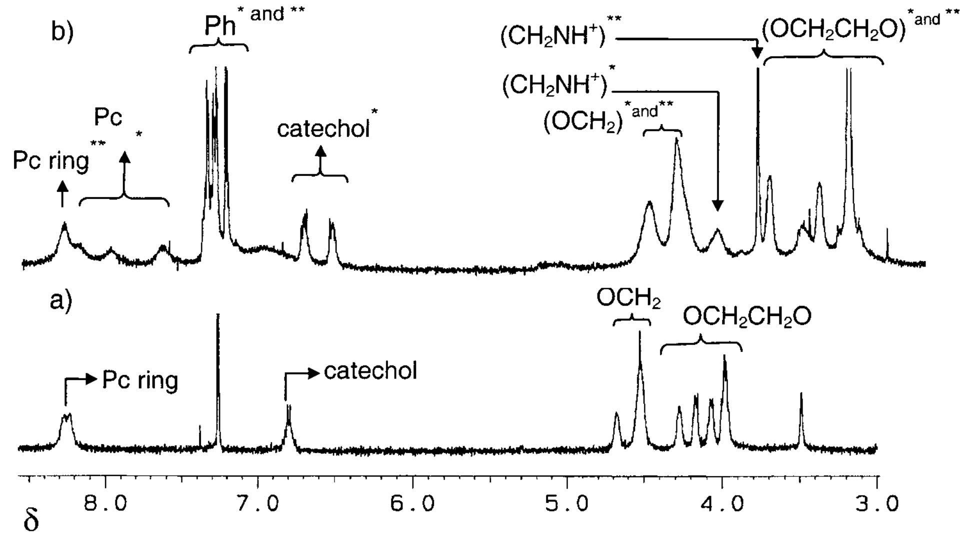


**Figure 2.** Partial $^1H$ NMR spectra (300 MHz, 298K, $CDCl_3$) of (a) Pc **1a** and (b) a mixture of **1a** and DBA·$PF_6$ (Asterisks indicate the following: (∗) complexed and (∗∗) uncomplexed).

Although it has been reported[9] that complexation constants between DBA•$PF_6$ salt and DB24C8 are larger in pure halogenated solvents, such as $CHCl_3$ or $CH_2Cl_2$, in this particular case it was necessary to add a more polar cosolvent, such as $CD_3CN$, to the $CDCl_3$ solution containing equimolar amounts of **1a** and **2**-$H_2$•$2PF_6$, to obtain a clear solution of the components. The $^1H$ NMR spectrum in a 4:1 mixture of $CDCl_3$ and $CD_3CN$ displayed a complex pattern of broad signals, that are reminescent to those obtained for the complex formed between **1a** and DBA•$PF_6$. This lack of resolution prevented us from determining the stoichiometry and association constants of the complex.

Intriguingly, a TLC on silica gel plates of a 1:1 mixture of **1a** and **2**-$H_2$•$2PF_6$ using a 4:1 mixture of $CHCl_3$ and MeCN as solvents, showed a new spot, with a remarkably higher $R_f$ value when compared with the monomeric compound **1a,** which could be interpreted as the formation of a supramolecular dimer. On the other hand, spots for the individual components were observed by addition of MeOH to the eluent or by using alumina as the chromatographic medium.

The MALDI-TOF mass spectrum of a 1:1 mixture of **1a** and **2**-$H_2$•$2PF_6$ showed a base peak at $m/z$ 1709.0 corresponding to the uncomplexed crowned-Pc **1a**. Additionally, peaks at $m/z$ 3734.8 (19%) and at $m/z$ 2026.0 (87%), which were assigned to the supramolecular ion [(**1a**)$_2$•**2**-H]$^+$ and to the 1:1 complex [(**1a**)•**2**-H]$^+$, respectively, were detected. We have carried out a control complexation experiment by MALDI-TOF spectrometry using DB24C8 and **2**-$H_2$•$2PF_6$ which also confirms that, in this case, the intensity of peak assigned to the 1:2 complex is low in comparison with the intensity of the peak attributed to the 1:1 complex. We interpret these results as reflecting a lack of stability of the dications in the gas phase, associated with the loss of an $HPF_6$ molecule and the concomitant loss of a crown ether macrocycle. The presence of the peak corresponding to the supramolecular ion [(**1a**)$_2$•**2**-H]$^+$ does not prove its pseudorotaxane geometry, but it is unlikely that any other structure other than a [3]pseudorotaxane would be stable enough to be detected under the conditions of the MALDI-TOF experiment. To obtain more information about the superstructure of the 2:1 complex formed between **1a** and **2**-$H_2$•$2PF_6$, a titration experiment was carried out. The UV−vis spectrum of a dilute solution ($4.6 \times 10^{-6}$ M) of **1a** in $CHCl_3$ does not show any significant difference upon addition of different amounts of a concentrated solution ($6.6 \times 10^{-4}$ M) of **2**-$H_2$•$2PF_6$ in MeCN. This result confirms that in the supramolecular dimer, the Pc rings are not electronically interacting with each other.[13] Moreover, EPR experiments,[14] carried out using the copper(II) phthalocyanine **1b** established the absence of Cu−Cu intra- or intercomplex interactions between cofacially arranged phthalocyanine nuclei. Related systems[15] showed characteristic triplet EPR spectra due to the ferromagnetic coupling of the Cu ions which is possible between cofacially stacked molecules. In the present work, such signals were completely absent for the complex of **1b** and **2**-$H_2$•$2PF_6$; only a slight broadening of the signals was observed, which is due to the mutual influence of the paramagnetic Cu ions without coupling, and is consistent with the proximity of the Cu ions in the complex and the absence of electronic interactions as proposed in Figure 1. Indeed, the distance between the two $NH_2^+$ centers of **2**-$H_2$•$2PF_6$ (7.2 Å), calculated from CPK molecular models is far too large to expect any intracomplex $\pi-\pi$ stacking between the Pc rings in the supramolecular dimer [(**1a**)$_2$•**2**-$H_2$][$PF_6$]$_2$. Taking into account the X-ray structure[9] of the [3]pseudorotaxane complex [(DB24C8)$_2$•**2**-$H_2$][$PF_6$]$_2$ and the similarities between the nonsubstituted DB24C8 and our DB24C8-Pc **1a**, whose binding abilities shoud not be much different, it seems reasonable to propose a geometry for the supramolecular complex [(**1a**)$_2$•**2**-$H_2$][$PF_6$]$_2$ like the one represented in Figure 1.[16]

In conclusion, new unsymmetrically substituted crowned-phthalocyanines **1a,b** which are able to form complexes with suitable dialkylammonium cations have been prepared. This strategy has been applied successfully for the first time to the preparation of supramolecular phthalocyanine dimers. The preparations of other related systems, which could be of interest as electron- and energy-tranfer models, are under investigation.

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(16) A recent paper describing the formation of a pseudorotaxane using the same dication **2**-$H_2$•$2PF_6$ and a bis-DB24C8 peptide has been published: Meillon, J.-C.; Voyer, N.; Biron, E.; Sanschagrin, F.; Stoddart, J. F. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 143.