# Supramolecular Assembly Formation in Monolayers of *tert*-Butyl Substituted Copper Phthalocyanine and Tetrabenzotriazaporphin

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**Abstract.** The effect is studied of the layer formation conditions on the molecular arrangement of copper tetra-*tert*-butyl phthalocyanine ($CuPctBu_4$) and copper tetra-*tert*-butyl tetrabenzotriazaporphin ($CuThptBu_4$) at the air–water interface. The decrease in initial surface concentration of these compounds is shown to affect the molecular orientation, as indicated by the increase in the area per molecule. The data are interpreted in terms of formation of $CuPctBu_4$ and $CuThptBu_4$ monolayers with a 'face-on' molecular arrangement when the initial surface concentration is sufficiently small ($N$ less than $1.6 \times 10^{-7}$ mole/m$^2$ for $CuPctBu_4$ and $N$ less than $4 \times 10^{-7}$ mole/m$^2$ for $CuThptBu_4$) and changes in the molecular orientation to 'edge-on' when the $N$ values are higher. It is emphasized that the 'edge-on' orientation on the water surface is not only a molecular but a collective property of the azaporphyrine supramolecular assembly.

**Key words:** azaporphyrins, monolayers, supramolecular assembly, Langmuir–Blodgett films

## 1. Introduction

Azaporphyrins are gaining in importance as a promising material for sensitive layers of gas sensors [1]. From the literature data one may infer that binding of a small molecule by an azaporphyrin film is controlled by both the donor–acceptor properties of the azaporphyrin and the supramolecular structure of the film. The latter factor often proves the most critical; a simple and convincing illustration thereof being the formation of the monoaqua-complexes by magnesium azaporphyrins. The beta modification of magnesium phthalocyanine (MgPc) is known

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to have compact packing and thus to be less active physicochemically than the labile alpha form. Therefore, MgPc binds a water molecule only in its alpha form [2]. On the other hand, the alpha-modification of magnesium naphthalocyanine (MgNc) is absolutely inert relative to water in spite of the loose crystal packing (which is evidenced by its high solubility in ether and acetone) [3]. However, beta-MgNc yields the thermally stable aqua-complex, indicating that some kind of synergism takes place between intermolecular donor–acceptor interactions and supramolecular effects.

These compounds, being related genetically to intermolecular charge migration, are mostly an object of conductivity investigations [4] but are usually underestimated in the design of gas sensitive layers. In most of the papers concerning organized azaporphyrin films, the octa-alkyl substituted phthalocyanines are employed [5–8] with the crystal structure controlled by mutual interaction of the long peripheral alkyl radicals rather than the azaporphyrin nuclei themselves. As a consequence, molecular assemblies of such phthalocyanines possess a column architecture, which does not create any advantage for intermolecular charge migration [4].

We assume that application of azaporphyrins bearing compact substituents – and therefore inclined to polymorphism – may allow creation of the supramolecular factors that will allow selective binding of molecules, thereby generating measurable physical effects in the films. The few papers [9, 10] dedicated to the variably structured LB films of azaporphyrins and their analogues refer only to binary compositions. So far it is not clear why the 'edge-on' orientation of the phthalocyanine nucleus prevails at the water–air interface despite four hydration $N$(meso)-centres situated symmetrically on the molecular contour. Our results on the LB films of mesomorphous crown ethers [11] show that the same compound can adopt both 'edge-on' and 'face-on' orientations at the water–air interface, provided the initial conditions of the film formation are appropriately modified. Our preliminary data [12] demonstrate that this approach is also applicable to forming azaporphyrin monolayers with variable orientation of the molecules on the interface.

The present work is believed to be a first step in discovering the factors controlling the molecular orientation in these layers of azaporphyrins substituted with compact groups. The objects are tetra-*tert*-butyl substituted copper phthalocyanine (CuPctBu$_4$) and tetrabenzotriazaporphin (CuThptBu$_4$). CuPctBu$_4$ was chosen because its LB films have been studied in regard to both their structure [13] and sensitivity [14]. The azaporphyrins under investigation are very similar, differing only in one atom (in CuThptBu$_4$, one methyne group occupies the meso-position).

## 2.  Materials and Methods

CuPctBu$_4$ and CuThptBu$_4$ were prepared from 4-*tert*-butylphthalonitrile according to the literature methods [15, 16], and purified chromatographically on aluminium

oxide with benzene as eluent. Their chemical authenticity was confirmed by NMR, IR and UV-visible spectra.

For the purpose of LB film formation, $CuPctBu_4$ dissolved in $o$-xylene ($6.25 \times 10^{-4}$ M) and $CuThptBu_4$ dissolved in benzene ($3.12 \times 10^{-4}$ M) were spread on triply distilled water. The measurements of surface pressures–area isotherms were performed on a Joyce–Loebel Langmuir trough (UK). Structural experiments were done using the small angle X-ray diffraction method on an Amur-K diffractometer (Russia) equipped with a position sensitive detector (angular resolution of 0.05 degree).

## 3. Results and Discussion

Figure 1 shows surface pressure–area isotherms of $CuPctBu_4$ and $CuThptBu_4$ when various amounts of the compounds are spread on the water surface. The isotherms are divided into parts with bends at pressures equal to 17 (weak), 23 and 50 mN/m for $CuPctBu_4$ and 13 (weak), 21, 27 and 44 mN/m for $CuThptBu_4$. The limiting areas ($A_{lim}$) determined for each part of the isotherms are given in Table I. Because the bend points correspond physically to changes in the monolayer structure, further discussion of the behaviour of azaporphyrins on the water surface concerns only the first part of the isotherms (before the first bend). Our approach is based on comparison of the area per molecule determined experimentally and the area calculated from the model within the projections of the molecular contour: $A_{face} = 2.35$ nm$^2$ and $A_{edge} = 0.78$ nm$^2$. In particular the changes in the molecular orientation due to variation of the initial surface concentration ($N$) may be reasonably discussed using the coverage values $C_\parallel$ and $C_\perp$, i.e., a ratio of the area covered by molecules (in 'face-on' or in 'edge-on' orientation, respectively) and the total area of the water surface before the layer compression.

At $N = 1.14 \times 10^{-7}$ mole/m$^2$ for $CuPctBu_4$ and $2.27 \times 10^{-7}$ mole/m$^2$ for $CuThptBu_4$ ($C_\parallel = 0.16$ and 0.32, respectively) both $A_0$ and $A_{lim}$ exceed $A_{face}$ indicating the 'face-on' orientation. In the intermediate cases, e.g., for $CuPctBu_4$, $N$ ranging between $1.5 \times 10^{-7}$ and $3.8 \times 10^{-7}$ mole/m$^2$ the tilted or both the 'face-on' and 'edge-on' orientation is assumed because both $A_0$ and $A_{lim}$ are lower than $A_{face}$. At $N > 3.8 \times 10^{-7}$ mole/m$^2$ ($C > 0.55$) $A_{lim}$ is slightly dependent on $N$. The layer seems to be tilted and densely packed because $A_{lim}$ is close to $A_{edge}$.

Figure 1 allows general observations of major importance to be made. First, the compressibility of the layers ($A_0 - A_{lim}$) depends on $N$, decreasing gradually as $N$ increases. The largest compressibility is observed for the 'face-on' monolayer: at $N = 1.14 \times 10^{-7}$ mole/m$^2$ its value exceeds 2 nm$^2$ per one molecule, which is 3–4 times greater than that for the layers formed at larger $N$. Second, the tilted orientation occurs only in the case when the $C_=$ values are sufficiently high ($C_= > 0.3$ for $CuPctBu_4$ and $>0.4$ for $CuThptBu_4$). The 'face-on' orientation prevails only at $C_= \leq 0.2$. This fact indicates that the azaporphyrin–azaporphyrin interactions in the monolayers already arise, even before pressure is applied, hindering the 'face-
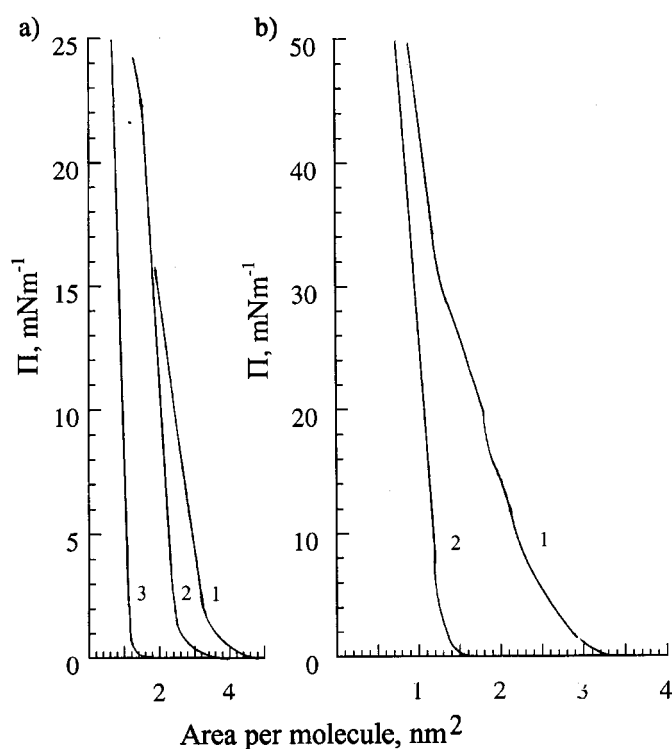
*Figure 1.* $\pi - A$ isotherms of CuPctBu$_4$, $c = 3.12 \times 10^{-4}$ M ($o$-oxylene), $N = 1.14(a_1)$, $N = 1.52(a_2)$, $N = 11.4 \times 10^{-7}$ mole/m$^2$ ($a_3$) and CuThptBu$_4$ $c = 6.25 \times 10^{-4}$ M (benzene), $N = 2.27(b_1)$ and $N = 6.06 \times 10^{-7}(b_2)$ mole/m$^2$.

on' orientation. Third, within the intermediate $N$ range, where the tilted orientation exists, the minimum $A$ value corresponding to the ideal 'edge-on' orientation is not achieved, even under the greatest pressure applied (Table I).

Considering the $A_{\text{lim}}$ and $A_{\text{edge}}$ values, one should bear in mind the geometrical nonuniformity of tetra-substituted azaporphyrins consisting of four randomers with various molecular symmetry. The lower the symmetry, the greater steric hindrances are expected for Pc—Pc interactions due to bulky *tert*-butyl radicals. Thus a molecule may be more easily squeezed out of the monolayer under compression within the high pressure range (other parts of isotherms – after the bends). It is this phenomenon that might explain the broad peaks detected on X-ray diffraction patterns in the case of sufficiently large initial surface concentrations used. The period of layer packing is equal to the values near 18 Å for both azaporphyrins under investigation.

Thus a model of the CuPctBu$_4$ monolayer formation is assumed to be as follows. After removal of solvent, a single CuPctBu$_4$ molecule tends to lie down on the water–air interface, as would be expected taking into account four $N$ (meso)-centres of hydration. Such orientation takes place in the rare layers and sustains

*Table I.* The areas ($A_0$ and $A_{lim}$) per molecule (in $nm^2$) when different initial surface concentrations ($N \times 10^{-7}$ mole/m$^2$) of CuPctBu$_4$ and CuThpBu$_4$ were used

| Compound | $N$ | 1.14 | 1.5 | 2.27 | 3.79 | 6.05 | 7.58 | 11.4 |
|---|---|---|---|---|---|---|---|---|
| solvent | $n$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| $c$ | | | | | | | | |
| CuThptBu$_4$ | | | | | | | | |
| *o*-xylene | | | | | | | | |
| $c = 3.12 \times 10^{-4}$ M | $A_0$ | 3.3 | 2.4 | 1.6 | 1.2 | | 1.2 | – |
| | $A_1$ | 2.7/16 | 2.2/18 | 1.4/19 | 1.1/19 | | 0.9/15 | 0.8/15 |
| | $A_2$ | | | | 1.3/40 | | 0.6/48 | 0.7/59 |
| | $A_3$ | | | | | | 0.7/70 | |
| CuThptBu$_4$ | | | | | | | | |
| Benzene | $A_0$ | | | 3.3 | | 1.5 | | |
| $c = 6.25 \times 10^{-4}$ M | $A_1$ | | | 2.5/12 | | | | |
| | $A_2$ | | | 2.3/20 | | 1.2/20 | | |
| | $A_3$ | | | 2.4/26 | | | | |
| | $A_4$ | | | 1.7/43 | | 1.15/34 | | |
| | $C_\parallel$ | 0.16 | 0.22 | 0.32 | 0.54 | 0.86 | 1.07 | |
| | $C_\perp$ | | | 0.11 | 0.18 | 0.29 | 0.36 | 0.53 |

$c$ = concentration of spread solutions.

$A_0$ = area per molecule in the beginning of the molecules interaction indicating at the points of surface pressure increasing.

$A_n/p$ = the limiting area per molecule in different parts of the isotherm and the corresponding surface pressure (under the line).

$C_\parallel$ = coverage value (area covered by molecules in 'face-on' orientation: total area of water surface before the layer compression).

$C_\perp$ = coverage value (area covered by molecules in 'edge-on' orientation: total area of water surface before the layer compression).

further compression up to 10 mN/m. So high compressibility of the 'face-on' monolayer seems to originate in variations in the mutual orientation of the aza-porphyrin molecules accompanied by successive creation and destruction of weak hydrophobic contacts of the *tert*-butyl groups.

At $N$ values higher than some critical level, the molecular orientation changes to 'edge-on' because azaporphyrin–azaporphyrin interactions arise and partly overcome hydration of the $N$(meso)-atoms. At this stage, the intermolecular contacts arise which are likely to be identical with those which control formation of the phthalocyanine polymorphous modifications, differing in tilt angle of molecules in the stacks [3]. We consider a change in the tilt angle to be a complementary and thus discrete process, taking into account the fact of inhibition of the alpha–beta transition in a ZnPc film by water vapour without diffusion into the film [2]. Pronounced stability of the tilted orientation on the water surface to compression also evidences

the complementary rather than statistical nature of the azaporphyrin–azaporphyrin interactions.

Comparison of the data on CuPctBu$_4$ and CuThptBu$_4$ indicates that the critical surface concentration of the assembly formation on the water surface is higher for the latter compound. Because CuThptBu$_4$ has a less favourable molecular structure for hydration than CuPctBu$_4$ (only three $N$(meso)-atoms) and a higher basicity (0.8 units on the Hammett acidity function scale [17]), the supramolecular assembly formation is not controlled by simple intermolecular interactions, such as hydrogen bonding or dispersion forces. This fact is not unexpected, taking into account data on the association of similar macrocyclic aromatic systems [18, 19]. However, the $\pi-\pi$ interaction concept proposed in [18], as explanation of a lack of donor–acceptor control over intermolecular interactions, does not stand up in the present case since it fails to explain the stability of the CuPctBu$_4$ staggered packing [13]. To discover the factors controlling azaporphyrin–azaporphyrin interactions and thereby the assembly architecture, it would seem fruitful to turn to the concept of the supramolecular continuum, as developed recently [20]. In accordance with this concept, the behaviour of the azaporphyrins on the water surface should be considered as a manifestation of supramolecular synthons differing in chemical nature, energy, energy gradient and a range of action. Data on other copper azaporphyrins isostructural to CuPctBu$_4$ are needed to be more precise (work in this direction is in progress). Here it should only be emphasized that the edge-on orientation on the water surface is not a molecular but rather a collective property of the azaporphyrin supramolecular assembly. In contrast to relatively small molecules, such as fatty acids, the ultimate assembly structure is controlled not only by the extent of compression but by the energy balance between the simple complexing (hydration) and supramolecular (azaporphyrin–azaporphyrin) interactions which already exist at the compression starting point.

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## References

1. G. L. Pakhomov, V. N. Spector, M. C. Anglada, J. M. Ribo, and C. Muller: *Mendeleev Commun.* 163–165 (1996).
2. B. Styme, F. X. Sauvage, and G. Wettermark: *Spectrochim. Acta* **35A**(10), 1195–1201 (1979).
3. F. H. Moser and A. L. Thomas: *Phthalocyanine Compounds*. Reinhold, New York/London (1963), p. 27.
4. P. G. Schouten, J. M. Warman, M. P. de Haas, C. F. van Nostrum, G. H. Gelink, R. J. M. Nolte, M. J. Copyn, J. W. Zwikker, M. K. Engel, M. Hanack, Y. H. Chang, and W. T. Ford: *J. Am. Chem. Soc.* **116**(5), 6880–6894 (1994).
5. M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown, and A. J. Thomson: *J. Chem. Soc. Chem. Commun.* 1148–1150 (1987).

6. S. Mukhopadhay, C. A. Hogarth, S. C. Thorpe, and M. J. Cook: *J. Mater. Sci. Mater. Electron.* **5**, 321–324 (1994).

7. K. E. Treacher, G. J. Clarkson, Z. Ali-Adib, and N. B. McKeown: *J. Chem. Soc. Chem. Commun.* 73–75 (1996).

8. J.-D., Kim, S.-R. Kim, K. H. Choi, and Y. H. Chang: *Sensors and Actuators B: Chemical Sensors* **40**(1), 39–45 (1997).

9. R. Azumi, M. Matsumoto, and Ya. Kawabata: *J. Am. Chem. Soc.* **114**(26), 10662–10663 (1992).

10. Ya. Fu, M. Forman, C. C. Leznoff, and A. B. P. Lever: *J. Phys. Chem.* **98**(36), 8985–8991 (1994).

11. L. A. Valkova, L. S. Shabyshev, L. A. Feigin, and O. B. Akopova: *Mol. Materials.* **6**(4), 363–368 (1996).

12. L. A. Valkova, L. S. Shabyshev, N. Yu. Borovkov, and L. A. Feigin: *Eighth Int. Conf. on Organized Molecular Films*, Asilomar, California (1997), P-1.14, 24-29.08.

13. J. R. Fryer and C. M. McConnell: *Phil. Mag. B.* **61**(5), 843–852 (1990).

14. B. A. Nesterenko and A. V. Kazantseva: *Int. J. Info Electronics* **78**(1), 129 (1995).

15. S. A. Mikhalenko, S. V. Barkanova, O. L. Lebedev, and E. A. Luk'yanets: *Zh. Obshch. Khim.* **41**(12), 2735–2739 (1971) (in Russian).

16. P. A. Barrett, R. P. Linstead, and G. A. Tuey: *J. Chem. Soc.* 1809 (1939).

17. P. A. Stuzhin, O. G. Khelevina, and B. D. Berezin: 'Azaporphyrins: Acid-base properties', in: C. C. Leznoff and A. B. P. Lever (eds.), *Phthalocyanines. Properties and Applications*, Vol. 4, VCH Publishers, New York (1996), p. 57.

18. C. A. Hunter and J. K. M. Sanders: *J. Am. Chem. Soc.* **112**(14), 5525–5534 (1990).

19. J. Zhang and J. S. Moore: *J. Am. Chem. Soc.* **114**(24), 9701–9702 (1992).

20. G. R. Desiraju: *J. Chem. Soc. Chem. Commun.* 1475–1482 (1997).