

Enhancement of Molecular Properties in Thin Films by Controlled Orientation of Molecular Building Blocks

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Modern surface chemistry is playing a key role in a large and diverse number of scientific areas, including heterogeneous catalysis, crystal design, and nanoscale- and molecule-level based devices.¹ Much attention and effort have been devoted to the understanding and quantification of self-assembled monolayers (SAMs) and thin films properties by deciphering intermolecular interactions.² As of yet, it is very difficult to predict material properties for a given molecular building block, and systematic studies aimed at understanding molecular orientation-dependent film properties of analogous compounds are uncommon. Commonly, an interface is considered as an inherent perturbation to the inversion symmetry of space. Therefore, it introduces a new spatial director that may provide a unique design mechanism.^{2a,3} For example, when thin films are formed by the assembly of molecular building blocks at an interface, minor structural differences that have negligible consequences in a homogeneous medium may be expressed and become prominent.

Here, we demonstrate the usage of an interface for triggering a pre-embedded structural difference in the constituent molecular units for the assembly of thin films with different physicochemical properties. This is especially important for many functional molecules where, for example, the different molecular axis dimensions show large diversity.^{4,5} In the present study, we describe the design and formation of porphyrin-based thin films having divergent physical and chemical properties by using two molecular building blocks with high chemical and optical resemblance (Figure 1a; T4PyP and B3PyP). We make use of functionalized porphyrins because the porphyrin's macrocycle has a rigid disklike shape with a large geometrical aspect ratio (thickness:diameter \approx 1:3; obtained using X-ray data for model compound tetra(phenyl)porphyrin).⁶ The variations of the pyridyl nitrogen position (*para* in T4PyP, and *meta* in B3PyP) cause only minor optical changes to the wavelength and intensity of the Soret ($\lambda_{\text{max}} = 416$ nm) and Q-bands in solution (Figure 1a). In contrast, the UV-vis optical absorbance measurements of the T4PyP-based films exhibit a large Soret red shift of 20 nm,⁷ whereas the B3PyP-based films exhibit a much smaller Soret red shift of only 7 nm (Figure 1d). Furthermore, the Soret band full-width half-maximum values of T4PyP and B3PyP films are about 48 and 23 nm, respectively, while the corresponding value in solution is 16 ± 1 nm for both species. The molecular assembly direction is dictated by the specific substitution position of the pyridyl nitrogens (Figure 1b,c). The different molecular orientations as expressed in the T4PyP- and B3PyP-based monolayers lead to a dramatic difference in intermolecular interactions (*vide infra*).

Coupling layers (CL) were prepared on freshly cleaned float glass and Si(100). Substrates were treated with a dry toluene solution of *p*-chloromethylphenyltrichlorosilane (1:50 v/v) at room temperature for 20 min under N₂.⁴ The substrates were then thoroughly washed with copious amounts of dry solvents and dried in 115 °C for about

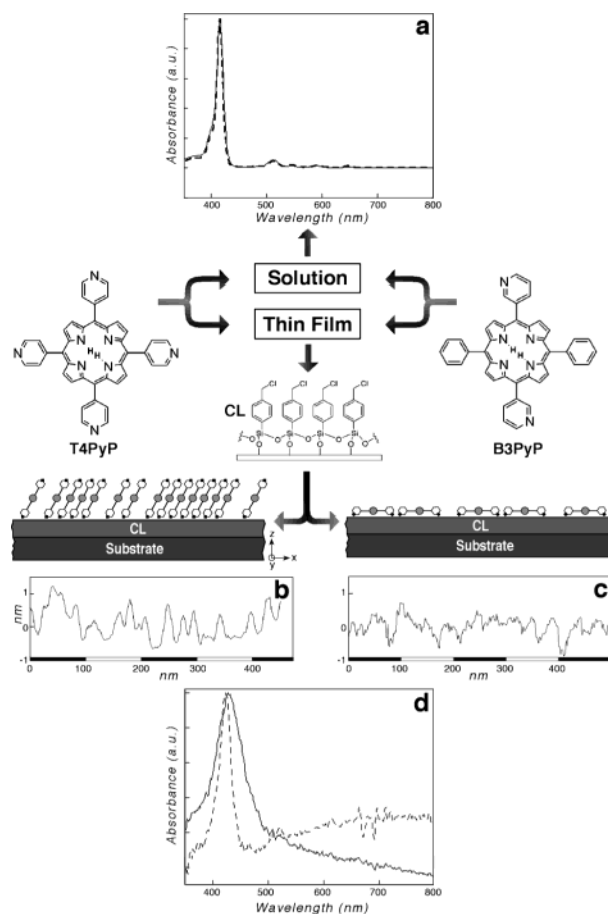


Figure 1. Molecular building blocks used in the present study: 5,10,15,20-tetra(4-pyridyl)porphyrin (T4PyP), and 5,10-bis(3-pyridyl)-15,20-diphenylporphyrin (B3PyP). (a) Solution UV-vis spectra and (d) monolayer UV-vis spectra are shown for T4PyP (solid line) and for B3PyP (dashed line). Monolayer spectra are shown after normalization of the B3PyP spectrum (dashed line) by a factor of 3.2. AFM cross-sections of the corresponding films on Si(100) are shown for (b) T4PyP (left) and for (c) B3PyP (right).

10 min. Subsequently, the colorless chlorobenzyl-functionalized substrates were fully immersed into 0.5 mM THF or MeOH/CHCl₃ (2:8 v/v) solutions of T4PyP and B3PyP, respectively, and heated at 85 °C under N₂ using pressure tubes. The resulting chromophore films were washed with copious amounts of solvent, sonicated (3 min), and dried under a gentle stream of N₂. Freshly prepared samples were characterized by a combination of noncontact atomic force microscopy (NC-AFM), optical (UV-vis) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The films strongly adhere to the glass and silicon substrates, are insoluble in common organic solvents, and cannot be removed by the “Scotch tape decohesion test”. Quaternization of the pyridyl moieties of T4PyP and B3PyP

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with the covalently anchored benzyl chloride coupling layer is revealed by XPS measurements. XPS spectra of both porphyrin-based films exhibit a N 1s signal at about 402.5 eV, indicative for pyridinium formation.^{4,8} Incomplete porphyrin films were used ($\theta < 1$) to determine the typical step size of the molecular assemblies on the surface by NC-AFM (Figure 1b,c).⁹ The typical step size for T4PyP-based films is about 1.2 nm, whereas the corresponding value for the B3PyP-based film is about 0.6 nm. The molecular dimensions of both porphyrins have been estimated to be approximately 1.8 and 0.5 nm for the long dimension and the diameter of the pyridyl or phenyl rings, respectively. Thus, the T4PyP molecules are oriented with the long molecular axis forming a tilt angle of approximately $47 \pm 7^\circ$ to the surface normal (z -direction).¹⁰ This kind of molecular orientation seems common for surface-bound porphyrin systems^{7,11} probably because of the strong intermolecular π interaction that is made possible in the tilted side-to-side conformation. In sharp contrast to the tilted molecular orientation of T4PyP, the B3PyP molecules are bound in a flat orientation to the surface with the long molecular axis lying in the xy plane (Figure 1c).

The different nature of the two types of monolayers is clearly expressed not only in their topological and optical properties, but also by their chemical and physical properties. For example, rinsing a T4PyP-based film with a solution of concentrated HCl (37%) resulted in a 10 nm blue shift of the Soret band due to protonation of the free pyridyl moieties.⁴ However, no optical changes were observed when B3PyP-based films are treated with HCl under identical conditions. Thus, the alignment of B3PyP molecules in the xy plane with both pyridyl sites bound to the coupling layer makes this system relatively inert toward acids. These markedly different properties are the result of the two different molecular orientations in the film. In the T4PyP-based film, neighboring π systems are in a side-to-side orientation that allows strong intermolecular π - π interactions (Figure 1d).⁴ In contrast, the B3PyP molecules are oriented such that the chromophores' π systems are aligned in the z -direction, prohibiting intermolecular interactions.

In conclusion, we have demonstrated that a predetermined variation in the molecular design can be efficiently transferred and even enhanced when constituting a two-dimensional film via control of molecular orientation. The expansion of the bottom-up design of thin films utilizing geometrical control as demonstrated here and the application to complex systems such as multilayers are expected to provide novel design means for achieving chemical control, reactivity, and specificity of such systems. Specifically, the pyridyl nitrogen position (*para* in T4PyP, and *meta* in B3PyP) has a significant impact resulting in distinctly different physicochemical properties of the corresponding film (i.e., film thickness, packing, optical properties, and reactivity). The conformational control of chromophore orientation is compelling for metalated derivatives because the porphyrin's core is tightly buried within the T4PyP-based films due to strong π - π interactions and packing, while it

is exposed to the environment in the B3PyP systems. The extension of the work presented here to films of metalated chromophore molecules as well as functionalized bacteriochlorophyll derivatives¹² is in progress.

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