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# Self-Assembly Polymorphism of Regioisomeric Diketopyrrolopyrrole Based $\pi$ -Conjugated organic Semiconductors

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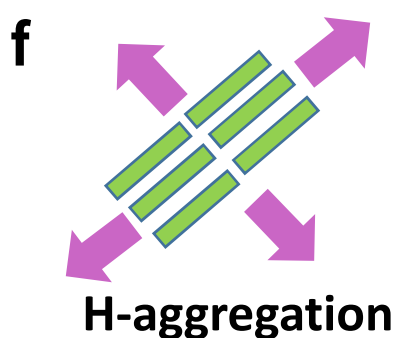
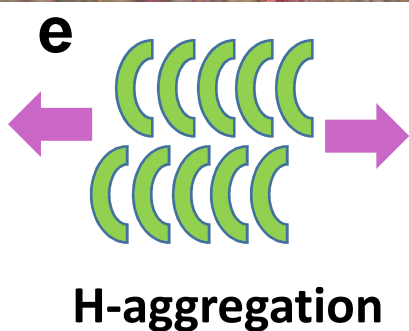
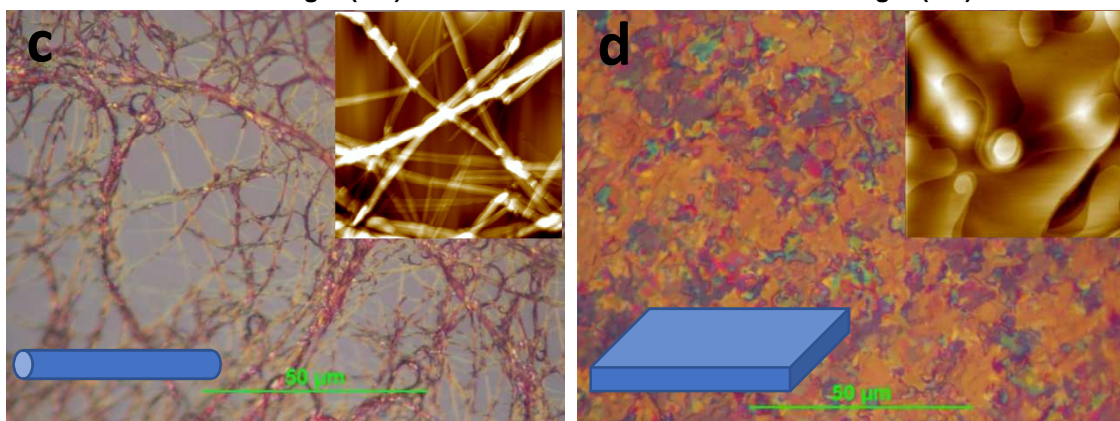
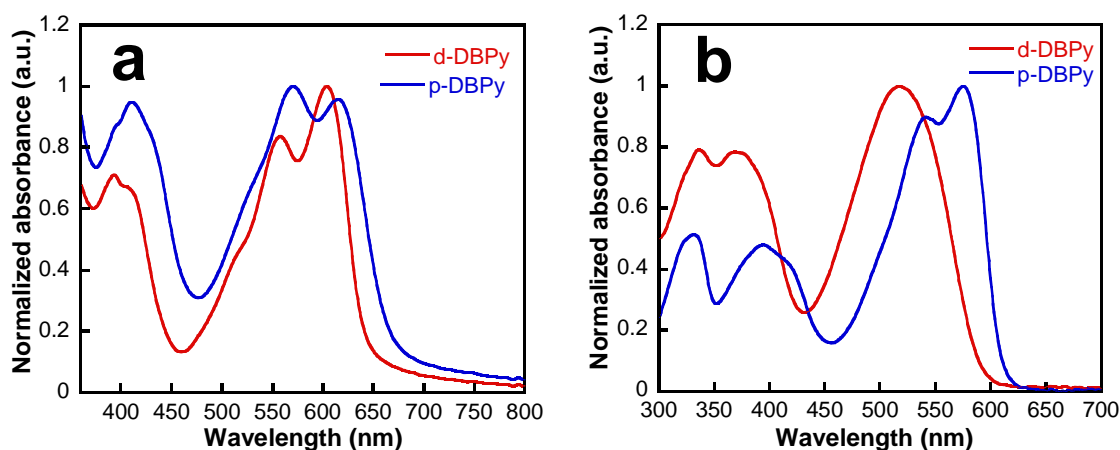
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## Abstract

The 2D molecular assemblies of two structural isomers *p*-DBPy and *d*-DBPy relevant to the field of organic electronics. These two molecules only differ in the position of pyridyl N-atoms. The solution concentration and solvent effects on the adlayer morphology are investigated using scanning tunneling microscopy (STM). Both kinds of molecules could exhibit obviously different molecular conformations and packing patterns, which demonstrate that the variation of the N-atom position in the pyridyl leads to different intermolecular interactions and stacking styles. Positioning the pyridyl N-atoms *proximal* to the central conjugated core could change the molecular conformation into a banana shape by bending the molecule, however, the *d*-DBPy molecule in which pyridyl N-atoms are *distal* to the central conjugated cores keep a linear shape in the monolayer. This work illustrates that altering the position of N-atoms in pyridyl could influence the film morphology and provides a deeper insight from molecular scale to understand the molecular conformation in different packing patterns, which are benefit for the rational design of future advanced optoelectronic devices.

## Discussion

STM shows that *p*-DBPy and *d*-DBPy molecules self-assemble into different patterns under different solution concentrations at the 1-phenyloctane/HOPG interface. At low concentration the powder color is purple black for *p*-DBPy, whereas it is orange for *d*-DBPy molecules. At high concentration the powder color is purple red for the two molecules. The color change indicates that molecular aggregation or packing has been modified (REFERENCE). STM data previously showed that *p*-DBPy molecules can adopt different conformations. The color change can also reflect the variation of molecular conformation. The conformation for the conjugated core of *p*-DBPy is linear in solution, however, the conformation is curve in solid states (solid powder and film). However, for *d*-DBPy, the colors for the solution and solid state has not obviously significant change, indicating the molecules keep the same linear molecular conformation.



**Figure 6.** (a,b) UV-vis absorption spectra of *p*-DBPy and *d*-DBPy molecules as thin films (a) and in toluene (b). (c,d) Polarized optical microscopy (POM) images showing the aggregations of *p*-DBPy (c) and *d*-DBPy (d) on mica surfaces. Insets are the AFM images showing the morphology of the films. The samples were prepared with an air-drying method. (e,f) Proposed models showing the aggregation modes.

Figure 6a shows the UV-vis spectra of the molecular thin films, whereas the UV-vis spectra of the molecules in solutions is presented in Fig.6b. The spectra reveal that the adsorption peaks of *p*-DBPy and *d*-DBPy films are blue-shifted in comparison with the peaks measured in solutions (**Figure 6b**). Ref.[47,48] propose that this shift results from different H-aggregation. **Molecular aggregation is investigated using** Polarized optical microscopy (POM) and atomic force microscopy (AFM), (**Figure 6c,d**). AFM and POM images reveals that the *p*-DBPy molecules form linear fibers (Fig.6c), whereas *d*-DBPy molecules form multilayer flat films. *p-DBPy form the linear aggregation in the films owing to the intra- and intermolecular interactions, so the H-aggregation is formed when the molecules stack by a parallel arrangement with the banana-like conformation (Figure 6e). d-DBPy with the linear conformation form the lamellar structure with the H-aggregation (Figure 6f).* According to the models, the film of *p*-DBPy molecules grows fast along two directions as the pick arrows indicated, while the *p*-DBPy film extends towards four directions. Because the films are prepared with relative high solution concentration, the self-organization of molecules in the films are the same with 2D molecular self-assembly obtained at high solution concentration. Thus, the STM results could interpret the nature of molecular packing and morphologies of the films from the molecular scale. It can be concluded that the 2D assembly of *p*-DBPy and *d*-DBPy is supported by different intermolecular interactions and two regio-isomers favor entirely different molecular arrays not only in the solid phase but also at the solid-liquid interface.

## Conclusion

In summary, we have carried out a systematical investigation of 2D self-assembled monolayers for the regio-isomeric DPP derivatives (*p*-DBPy and *d*-DBPy) formed at 1-phenyloctane /HOPG interface and 1-octanoic acid/HOPG interface using STM, respectively. Our aim is to explore how the slight difference in position of N-atoms in pyridyl influences the molecular packing. It is interesting to find that the orientation of pyridyl unit relative to the DPP moiety has absolutely impact on the resulting self-assembled patterns. At the 1-phenyloctane/graphite surface, the conjugated cores of *p*-DBPy molecules adopt different conformations at different solution concentrations resulting from different intermolecular interactions. Although the conjugated moieties of *d*-DBPy display the same conformations, *d*-DBPy forms different nanopatterns at different solution concentrations, in which the side chains of *d*-DBPy exhibit different adsorbed fashions due to the molecular packing density. At the 1-octanoic acid/graphite surface, the *p*-DBPy and *d*-DBPy self-assemble into a dislocated segmented and wavy-like pattern, respectively, because of the polarity of the solvent. The identification of intermolecular interactions by STM can be utilized to explore the nature of the different morphology of the films. What is learn from STM results is therefore relevant for understanding the structure and local environment in the active layers of organic optoelectronic devices.

## ASSOCIATED CONTENT

**Supplementary Information** Available: Additional STM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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