AFM-IR Nanospectroscopy of Aggregated Thin Porphyrin Films: Correlating Morphology with Intermolecular Stacking

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A comprehensive understanding of hierarchical self-assembly of low-dimensional supramolecular systems at multiple lateral length scales is of fundamental importance for applications in the field of nanobiology and biomedicine [1]. Metalloporphyrins serve as active components in a wide range of biological systems. The optical and electronic properties of metalloporphyrins can be varied by changing the molecular structure, including the size, metal center, ligands, and specific side groups. Their capability to self-organize over a wide range of length-scales spanning from a few nanometers up to hundreds of micrometers highlights the importance of porphyrin-based organic systems as multifunctional building blocks for synthesis of novel tailored materials for biosensing, molecular electronics, and thin-film photovoltaics [2,3]. Although the morphology of porphyrin aggregates which includes fractal or dendritic patterns has been studied extensively [4,5], their formation mechanisms have remained unclear up till now.

For the first time, we show IR nanospectroscopic evidence that the particular morphologies cannot be described purely as diffusion limited aggregation of single porphyrin molecules and different stacking is the underlying cause of different supramolecular morphological patterns in aggregated thin porphyrin films. In this work, we apply the AFM-IR technique and link intermolecular stacking interactions to nanoscale heterogeneous environments by analyzing infrared resonance shifts and broadening effects. This nanoscale spectroscopic technique is based on photothermal induced resonance and measures the thermal expansion of the sample resulting from IR absorption in a non-destructive fashion. This can be achieved by sending low-power laser pulses at a repetition frequency that is synchronized to the mechanical vibrational eigenfrequency of the AFM cantilever [6].

We compare the AFM-IR results to standard far-field FT-IR microscopic measurements of large-area porphyrin aggregates.

References

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