

Accepted Manuscript

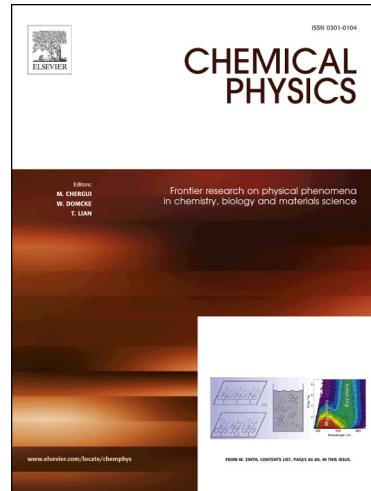
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PII: S0301-0104(18)30831-0

DOI: <https://doi.org/10.1016/j.chemphys.2018.09.028>

Reference: CHEMPH 10196



To appear in: *Chemical Physics*

Received Date: 30 July 2018

Revised Date: 18 September 2018

Accepted Date: 20 September 2018

Please cite this article as: Y. Miyauchi, R. Yukutake, K. Tsuchida, Y. Umemura, A. Tsukamoto, T. Suzuki, Observation by optical second harmonic generation of the mean tilt angle of cyanine dyes during compression with a phase transition in a Langmuir-Blodgett trough, *Chemical Physics* (2018), doi: <https://doi.org/10.1016/j.chemphys.2018.09.028>

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Title

Observation by optical second harmonic generation of the mean tilt angle of cyanine dyes during compression with a phase transition in a Langmuir-Blodgett trough

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Abstract

Optical second harmonic generation (SHG) signals from a cyanine dye during compression of a monolayer in a Langmuir-Blodgett trough were measured to investigate the mean tilt angle of the dye corresponding to the formation of an H-band. The pressure-surface area (π -A) isotherm for 3,3'-dioctadecyloxacarbocyanine molecules spread on an aqueous subphase showed a plateau region after a kink point in the isotherm characteristic, which suggests a phase transition from the liquid expanded (LE) phase to the liquid condensed (LC) phase. SHG signals from the monolayer were obtained as the surface area decreased for the input and output polarization combinations PP, MS, SP, PS, and SS, where the first and second letters denote the input and output polarizations, respectively, and M refers to the polarization midway between S and P. For polarization combination PP, the SHG signal increased steeply during compression, whereas for polarization combination MS, the signal increased gently. The SH field from the monolayer for polarization combination SP in the LC phase was almost inverted to the field in the LE phase. We estimated the mean polar angles from the SHG responses during compression. The angle decreased continuously by almost 5° from 28° with the growth of domains in the LC phase. Visible absorption spectra of monolayers transferred to glass substrates were also obtained. The area intensity of the peak in the spectra attributed to H-aggregates increased compared with that of the monomer as the surface area decreased in the LC phase. The results were consistent with the polar angle reduction in the LC phase observed by in situ SHG. The decrease of the angle in the LC phase probably allowed the cyanine dyes to pack together tightly and align side by side, promoting H-aggregation.

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