

Conjugated Polymer Nanoparticles in Aqueous Media by Assembly with Phospholipids via Dense Alkyl Chain Packing

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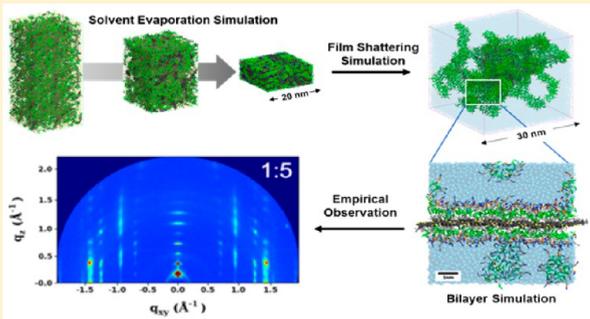
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Supporting Information

ABSTRACT: Revealing the nature of chain packing in conjugated polymer nanoparticles (CPNs) is one of the important issues to polymer physics research. Surfactant-stabilized CPNs in water show significantly enhanced luminescence intensity in comparison to small molecular organic dyes and single polymer chains dissolved in solvents. The importance of the conjugated polymer structure in nanomaterials is undoubted. However, details of the relationship between alignment of conjugated polymer backbone in CPNs and its luminescent property have not been established. Furthermore, there are yet no methods that can predict the atom-resolved structure of conjugated polymer in the CPNs. Herein, we employ coarse-grained (CG) molecular dynamic simulations to investigate the structure of phase-separated film and the film shattering process for a mixture of poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) and 1,2-dioctanoyl-*sn*-glycero-3-phosphocholine (D8PC). The π - π stacked structure of PCPDTBT is significantly enhanced when the ratio of D8PC increases in both dried and water exposed film. We also show that the amount of D8PC is at least 2.5 times larger than that of PCPDTBT to wrap the conjugated polymer chain, and the direct retrieval of atomistic details is achieved through back-mapping from the morphology of CG. Finally, we confirmed that conjugated backbones inside the nanoparticles were completely shielded from the aqueous solution by the dense layers of alkyl chains, resulting in remarkably enhanced chain packing. These simulated results are correlated with experimentally observed structure through UV-vis-near-infrared (UV-vis-NIR) spectrometry, scanning electron microscopy (SEM), particle size analyzer (PSA), transmission electron microscopy (TEM), and grazing-incidence X-ray diffraction (GIXD).



1. INTRODUCTION

Conjugated polymers as semiconductors, which have band gaps between their valence and conduction bands, can absorb energy upon light irradiation, exciting electrons from the valence to the conduction band. Consequently, the absorbed energy can be emitted as light, heat, or charge carriers (electrons and holes) and can be transferred to the surroundings to participate in photocatalytic reactions.^{1,2} When conjugated polymers are in the form of nanomaterials, such as nanodots, nanoparticles, and nanowires, one can further expect significantly enhanced luminescence intensity in comparison to small molecular organic dyes and single molecular polymer chains dissolved in solvents.³ Thus, conjugated polymer nanomaterials have attracted significant attention for applications in aqueous media, such as fluorescence imaging, photoacoustic imaging, photothermal therapy in biomedical fields,^{3–10} and photocatalytic reactions such as water splitting for hydrogen generation and organic pollutant degradation. Although there is a noticeable

improvement in the luminescence of conjugated polymer nanoparticles (CPNs) in comparison to single molecules, there remains room to improve the luminescence of these conjugated polymer nanomaterials. To improve their luminescence property, the importance of the conjugated polymer structure in nanomaterials is undoubted. Atomic force microscopy (AFM) has been employed to unravel the size and shape of phase-separated domains. However, this result does not provide any information on molecular structure inside CPNs. Furthermore, details of the relationship between the molecular structure of conjugated polymer in CPNs and their luminescent property have not yet been established.

In this paper, we focus on the morphologies of CPNs prepared by shattering phase-separated films of a conjugated polymer and a phospholipid. As recently reported,³ in the

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