ダイナミックチアヘリセン超分子ナノファイバーのメカニカル形成と電子回折による分子配列解析

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Mechanical Fabrication and Electron Diffraction Analysis of Supramolecular Nanofiber of Dynamic Thiahelicene.

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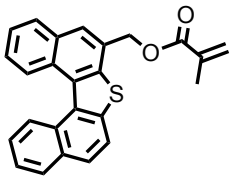
Dinaphtho[2,1-*b*:1′,2′-*d*]thiophene (**DNT**), a helical isomer of dinaphthothiophenes, is known to exhibit stereodynamic characteristics owing to its low energy barrier for enantiomerization. We have found that a methacrylate derivative of **DNT** (**6MDNTMA**) forms fibrous nanocrystals by ball milling, which was confirmed by SEM measurement. Although the determination of crystal structure of **6MDNTMA** by X-ray analysis was difficult, we were able to disclose the molecular arrangement of **6MDNTMA** nanofibers clearly by electron diffraction. The results suggest that **6MDNTMA** forms supramolecular nanofibers by the complementary growth of dense *P*- and *M*-columns toward the *b*-axis via the cooperative intermolecular π-π interactions between helical dinaphthothiophene cores and between methacryloyl groups, respectively.

Keywords : Dynamic Thiahelicene; Dinaphthothiophene; Ball Milling; Supramolecular Nanofiber ; Electron Diffraction

ダイナミックチアヘリセン構造をもつ種々のジナフトチオフェン誘導体のバルク結晶をボールミル粉砕したところ、メタクリレート型誘導体: **6MDNTMA**[1] において、SEM によりファイバー状のナノ集積体が観測された（図 1a, b）。各誘導体の電子回折による結晶構造解析の結果、**6MDNTMA** においてのみ、ステレオダイナミックなジナフトチオフェンコア間およびメタクリロイル基間の協奏的な分子間π–π相互作用により密な *P*-および *M*-体カラムが *b*-軸に沿って相補的に成長し、超分子ナノファイバーを形成することが示唆された（図 1c）。



6MDNTMA

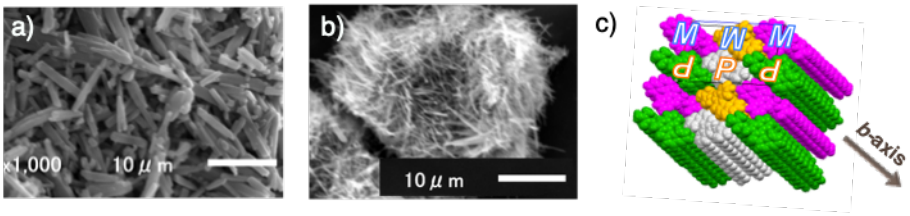


Fig. 1. a) SEM image of **6MDNTMA** bulk crystals, b) SEM image of nanofibers formed by ball milling, and c) packing arrangement of nanofibers drawn by CPK model.

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