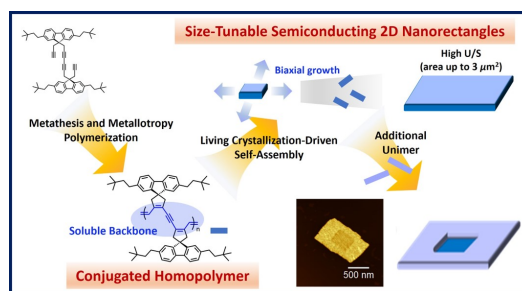


## Size-Tunable Semiconducting 2D Nanorectangles from Conjugated Polyenyne Homopolymer Synthesized via Cascade Metathesis and Metallotropy Polymerization

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Size-tunable semiconducting two-dimensional (2D) nanosheets from conjugated homopolymers are promising materials for easy access to optoelectronic applications, but it has been challenging due to the low solubility of conjugated homopolymers. Herein, we report size-tunable and uniform semiconducting 2D nanorectangles via living crystallization-driven self-assembly (CDSA) of a fully conjugated polyenyne homopolymer prepared by cascade metathesis and metallotropy (M&M) polymerization. The resulting polyenyne with enhanced solubility successfully underwent living CDSA via biaxial growth mechanism, thereby producing 2D nanorectangles with sizes precisely tuned from 0.1 to 3.0  $\mu\text{m}^2$  with narrow dispersity mostly less than 1.1 and low aspect ratios less than 3.1. Furthermore, living CDSA produced complex 2D block comicelles with different heights from various degrees of polymerization (DPs) of unimers. Based on diffraction analyses and DFT calculations, we proposed an interdigitating packing model with an orthorhombic crystal lattice of semiconducting 2D nanorectangles.



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