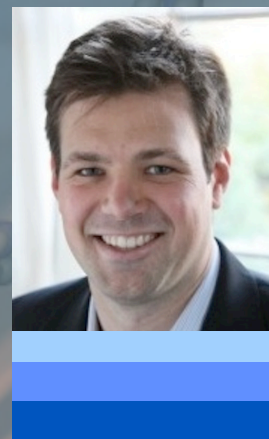


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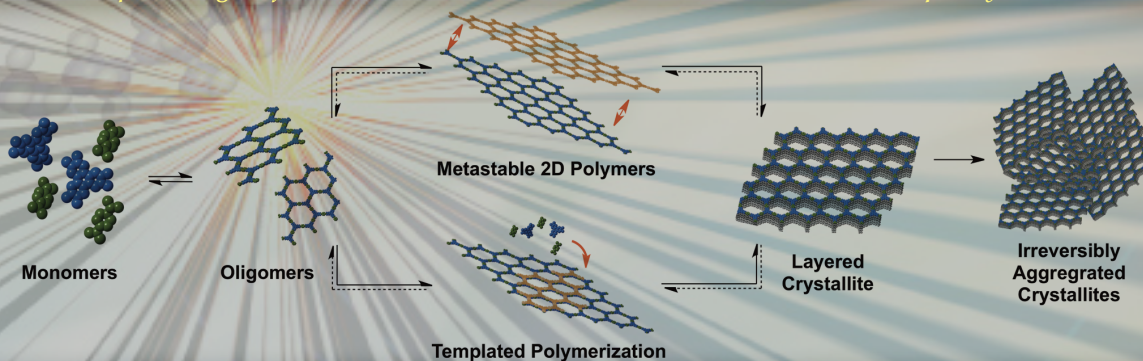
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“Polymerization Across Multiple Dimensions”

Summary

Covalent organic frameworks (COFs) are periodic 2D and 3D polymer networks with high surface areas, low densities, and predictable structures. Despite intense interest in framework materials, the nucleation and growth processes of COFs, and even of more established metal-organic frameworks (MOFs), are poorly understood. The COF growth rate's sensitivity to reaction conditions provides mechanistic insight needed to improve their crystallinity and rationally access new materials. Such kinetic measurements are unprecedented and are difficult to perform on typical heterogeneous COF reaction mixtures. The synthesis of 2D boronate ester-linked COFs under conditions in which the monomers are fully soluble will be presented. These homogenous growth conditions provide equal or better material quality compared to any previous report and enable the first rigorous studies of the early stages of COF growth. 2D COFs form within minutes, and their formation rate is readily quantified from optical turbidity measurements. For example, COF-5 formation follows an Arrhenius temperature dependence between 60–90° C with an activation energy of 22–27 kcal/mol. A rate law includes a second order in both boronic acid and catechol moieties, and inverse second order in MeOH concentration. A monofunctional catechol competitor slows COF-5 formation but does not redissolve already precipitated COF, indicating both dynamic covalent bond formation and an irreversible precipitation. Finally, stoichiometric H₂O provided a four-fold increased crystallite domain areas, representing the first rational link between reaction conditions and material quality.



WED. OCT. 29th, 2014 • **ROOM 4-231**

SEMINAR 3:30 - 5:00 PM • REFRESHMENTS 3:00 PM

<http://polymerscience.mit.edu>

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