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RPPR Final Report
as of 08-Jun-2021

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Proposal Number: 70702MS **Agreement Number: W911NF-17-1-0339**
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Final Report for Period Beginning 15-Jul-2017 and Ending 14-May-2021
Title: Theoretical Description of Two-Dimensional Covalent Organic Frameworks (2D COFs)
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Submitted By: Dr. Jean-Luc Bredas Email: jlbredas@arizona.edu
Phone: (520) 626-3050

STEM Degrees: 0 **STEM Participants:**

Major Goals: We aim at gaining a better understanding of the growth dynamics as well as the structural and mechanical properties of 2D covalent organic frameworks (COFs). We focus on the following two topics:

1. Description of the microscopic processes involved in the growth of 2D COFs in solution. The ability to synthesize COFs in solution is appealing from simplicity and low-cost viewpoints. However, the quality of COFs prepared in this way remains poor. In order to understand the growth mechanism of 2D COFs in solution, our goal was to develop and apply kinetic Monte Carlo (KMC) models to investigate these processes. In particular, we paid attention to the factors influencing the nature of the COF final products, such as bond formation and bond breakage, as well as stacking and destacking among oligomers.

2. Investigation of the structural properties of 2D COFs. Understanding the structural conformations and dynamical motions of 2D COFs is critical to their design, fabrication, and application. While 2D COFs have been generally perceived as flat sheets, this does not necessarily hold true since strictly 2D materials are not present in nature. Our goal here was to investigate the COF structures and motions using molecular dynamics (MD) simulations. We included the effect of solvation and impact of defects, in order to simulate at best common experimental conditions.

Accomplishments: Please see the attached file.

Training Opportunities: Our efforts provided training of a postdoctoral scholar.

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Results Dissemination: All our results were/are being published in top-tier scientific journals and presented at international conferences.

(a) Papers published in peer-reviewed journals

- Li, H. Y.; Chavez, A. D.; Li, H. F.; Dichtel, W. R.; Bredas, J.-L. “Nucleation and Growth of Covalent Organic Frameworks from Solution: The Example of COF-5” J. Am. Chem. Soc. 2017, 139, 16310.

- Li, H. Y.; Bredas, J.-L. “Large Out-of-Plane Deformations of Two-Dimensional Covalent Organic Framework (COF) Sheets” J. Phys. Chem. Lett. 2018, 9, 4215.

- Li, H. F.; Li, H. Y.; Dai, Q. Q.; Li, H.; Bredas, J.-L. “Hydrolytic Stability of Boronate Ester-Linked Covalent Organic Frameworks” Adv. Theory Simul. 2018, 1, 1700015.

- Chen, C.; Joshi, T.; Li, H. F.; Chavez, A. D.; Pedramrazi, Z.; Liu, P.-N.; Li, H.; Dichtel, W. R.; Brédas, J.-L.; Crommie, M. F. "Local Electronic Structure of a Single-Layer Porphyrin-Containing Covalent Organic Framework" ACS Nano 2018, 12, 385.

- Li, H. Y.; Bredas, J.-L. “Two-Dimensional Covalent Organic Frameworks Form Nanoscrolls” Chem. Mater. 2019, 31, 3265.

- Castano, I.; Evans, A. M.; Li, H. Y.; Vitaku, E.; Strauss, M. J.; Bredas, J.-L.; Gianneschi, N. C.; Dichtel, W. R. “Chemical Control over Nucleation and Anisotropic Growth of Two-Dimensional Covalent Organic Frameworks” ACS Cent. Sci., 2019, 5, 1892.

.• Thomas, S.; Li, H.; Zhong, C.; Matsumoto, M.; Dichtel, W. R.; Bredas, J.-L. "Electronic Structure of Two-Dimensional Pi-Conjugated Covalent Organic Frameworks" Chem. Mater. 2019, 31, 3051.

- Thomas, S.; Li, H.; Bredas, J.-L. "Emergence of an Antiferromagnetic Mott Insulating Phase in Hexagonal Pi-Conjugated Covalent Organic Frameworks" Adv. Mater. 2019, 31, 1900355.

- Joshi, T.; Chen, C.; Li, H.; Diercks, C. S.; Wang, G.; Waller, P. J.; Li, H.; Bredas, J.-L.; Yaghi, O. M.; Crommie, M. F. "Local Electronic Structure of Molecular Heterojunctions in a Single-Layer 2D Covalent Organic Framework" Adv. Mater. 2019, 31, 1805941.

- Li, H.; Li, H.; Xun, S.; Brédas, J.-L. “Doping Modulation of the Charge Injection Barrier between a Covalent Organic Framework Monolayer and Graphene" Chem. Mater. 2020, 32, 9228.

- Jhulki, S.; Evans, A. M.; Hao, X.-L.; Cooper, M. W.; Feriante, C. H.; Leisen, J.; Li, H.; Lam, D.; Hersam, M. C.; Barlow, S.; Brédas, J.-L.; Dichtel, W. R.; Marder, S. R. "Humidity Sensing through Reversible Isomerization of a Covalent Organic Framework" J. Am. Chem. Soc. 2020, 142, 783.

- Li, H. Y.; Evans, A.; Castano, I.; Strauss, M.; Dichtel, W. R.; Bredas, J.-L. “Nucleation-Elongation Dynamics of Two-Dimensional Covalent Organic Frameworks” J. Am. Chem. Soc. 2020, 142, 1367.

- Li, H. Y.; Evans, A.; Dichtel, W. R.; Bredas, J.-L. “Quantitative Description of the Lateral Growth of Two-Dimensional Covalent Organic Frameworks Reveals Self-Templation Effects” ACS Mater. Lett., 2021, 3, 398.

- Li, H. Y.; Bredas, J.-L. “Impact of Structural Defects on the Elastic Properties of Two-Dimensional Covalent Organic Frameworks (2D COFs) under Tensile Stress” Chem. Mater. 2021, DOI: 10.1021/acs.chemmater.1c00895.

(b) Papers published in non-peer-reviewed journals

None

(c) Presentations

i. Presentations at meetings, but not published in Conference Proceedings

• Li, H. Y.; Bredas, J.-L.: “Modeling of actual-size organic electronic devices from efficient molecular-scale simulations”, The 13th World Congress on Computational Mechanics, New York City, July 22-27, 2018.

ii. Non-Peer-Reviewed Conference Proceeding publications (other than abstracts)

None

iii. Peer-Reviewed Conference Proceeding publications (other than abstracts)

None

(d) Manuscripts

None

Honors and Awards: • Jean-Luc Bredas: Appointed Member of the World Cultural Council (2019-present); member of the Committee in charge of selecting the Laureate of “The Albert Einstein World Award of Science”.

• Jean-Luc Bredas: Research Award of the Alexander von Humboldt Foundation, 2019.

• Jean-Luc Bredas: Ranked as one of the 500 most cited scientists (among > 100,000 top scientists) in: “A standardized citation metrics author database annotated for scientific field”, by Ioannidis JPA, Baas J, Klavans R, Boyack KW, PLoS Biol 17(8): e3000384 (2019). See: https://doi.org/10.1371/journal.pbio.3000384.

• Jean-Luc Bredas: 2020 Materials Theory Award of the Materials Research Society.

• Jean-Luc Bredas: 2021 Centenary Prize of the Royal Society of Chemistry (UK).

• Jean-Luc Bredas: Ranked as one of the 500 most cited scientists (among > 100,000 top-cited scientists) in: “Updated science-wide author databases of standardized citation indicators”, by J.P.A. Ioannidis, K.W. Boyack, J. Baas, PLoS Biol 18(10): e3000918 (2020). See: https://doi.org/10.1371/journal.pbio.3000918.

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Participant Type: PD/PI
Participant: Jean-Luc Bredas
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
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Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Qingqing Dai
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Staff Scientist (doctoral level)
Participant: Haoyuan Li
Person Months Worked: 3.00 **Funding Support:**

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Project Contribution:
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Participant Type: Faculty
Participant: Hong Li
Person Months Worked: 4.00 **Funding Support:**
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Participant: Xiaojuan Ni
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Article Title: Nucleation and Growth of Covalent Organic Frameworks from Solution: The Example of COF-5
Authors: Haoyuan Li, Anton D. Chavez, Huifang Li, Hong Li, William R. Dichtel, Jean-Luc Bredas
Keywords: covalent organic frameworks
Abstract: The preparation of two-dimensional covalent organic frameworks (2D COFs) with large crystalline domains and controlled morphology is necessary for realizing the full potential of their atomically precise structures and uniform, tailorable porosity. Currently 2D COF syntheses are developed empirically, and most materials are isolated as insoluble and unprocessable powders with typical crystalline domain sizes smaller than 50 nm. Little is known about their nucleation and growth processes, which involve a combination of covalent bond formation, degenerate bond exchange, and noncovalent stacking processes. A deeper understanding of the chemical processes that lead to COF polymerization and crystallization is key to achieving improved materials quality and control. Here, we report a kinetic Monte Carlo (KMC) model that describes the formation of a prototypical boronate-ester linked 2D COF known as COF-5 from its 2,3,6,7,10,11-hexahydroxytriphenylene and 1,4-phenylene bis(boronic acid) mono
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Date Submitted: 4/16/19 12:00AM Date Published: 3/1/19 5:00AM
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Article Title: Emergence of an Antiferromagnetic Mott Insulating Phase in Hexagonal ?-Conjugated Covalent Organic Frameworks
Authors: Simil Thomas, Hong Li, Jean-Luc Bredas
Keywords: density-functional theory calculations
Abstract: While the search for 2D organic semimetallic Dirac materials displaying, like graphene, a Dirac cone at the Fermi level remains active, attention is also being paid to the quantum phase transition from semimetal to antiferromagnet. Such a transition in graphene?like materials is predicted based on theoretical investigations of the 2D honeycomb lattice; it occurs (within a Hubbard model) when the on?site electron–electron Coulomb repulsion (U) is much larger than the nearest?neighbor inter?site electronic coupling (t). Here, monomers carrying long?lived radicals are considered and used as building blocks to design 2D hexagonal ??conjugated covalent organic frameworks (COFs). Both the nonmagnetic semimetallic phase and magnetically ordered phases are evaluated. It is found that the electronic coupling between adjacent radical centers in these COFs is more than an order of magnitude smaller than in graphene while the on?site Coulomb repulsion is reduced to a lesser extent. The resulting l
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Article Title: Nanoscrolls Formed from Two-Dimensional Covalent Organic Frameworks
Authors: Haoyuan Li, Jean-Luc Brédas
Keywords: colvalent organic frameworks
Abstract: Two-dimensional (2D) covalent organic frameworks (COFs) represent an emerging class of nanomaterials with building blocks precisely connected in-plane through covalent bonds. Gaining insights into their structure and stabilities is critical to both their preparation and applications. Here, via atomistic molecular mechanics simulations and free-energy calculations, we investigate 2D COFs both under vacuum conditions and in solution, taking representative boronate ester-based and imine-based COFs as examples. Rather than remaining flat, single-layer 2D COF sheets with at least their length larger than ?15–?20 nm are found to preferably form nanoscrolls. These nanoscrolls display a finite number of configurations and represent open structures due to the large pores present in the 2D sheets; this feature distinguishes them from nanoscrolls formed by dense 2D materials such as graphene. Density functional theory calculations indicate that the intrasheet interactions in the nanoscrolls make
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
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Date Submitted: 4/16/19 12:00AM Date Published: 3/1/19 5:00AM
Publication Location:
Article Title: Electronic Structure of Two-Dimensional ?-Conjugated Covalent Organic Frameworks
Authors: Simil Thomas, Hong Li, Cheng Zhong, Michio Matsumoto, William R. Dichtel, Jean-Luc Bredas
Keywords: covalent organic frameworks
Abstract: Increasing attention is being given to the development of covalent organic frameworks (COFs) that are based on monolayers of fully ?-conjugated structures. At first glance, such two-dimensional (2D) polymer networks could simply be viewed as a mere extension into a second dimension of the quasi-one-dimensional (1D) conjugated polymers at the origin of the field of organic electronics. However, such a view misses essential characteristics coming specifically from 2D lattice symmetry. Our aims in this Perspective are twofold. We seek (i) to provide a conceptual, chemistry-oriented theoretical description of the impact on the electronic structure of this extension from 1D to 2D and (ii) to establish chemical structure–symmetry–electronic property relationships for this class of 2D ?-conjugated COFs.
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Publication Location:
Article Title: Large Out-of-Plane Deformations of Two-Dimensional Covalent Organic Framework (COF) Sheets
Authors: Haoyuan Li, Jean-Luc Brédas
Keywords: covalent organic frameworks
Abstract: Flexibility and deformability are important factors influencing the assembly and application of two-dimensional covalent organic frameworks (2D COFs). On one hand, the formation of stable, extended 2D sheets is a prerequisite for the fabrication of high-quality 2D crystals. On the other hand, characterizing these properties will eventually provide a path toward the inclusion of electron-vibration couplings when evaluating their electronic properties such as their band structures. Here, atomistic molecular dynamics simulations are used to investigate the mechanical properties of 2D COF sheets, taking the prototypical COF-5 as a representative example. Large out-of-plane deformations are found, about 400% higher than those encountered in graphene. In addition, structural defects lead to significantly larger twists and deformations, which underlines the challenges in fabricating stand-alone, large-size 2D COF sheets. Stacking, on the other hand, effectively reduces the out-of-plane deform
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as of 08-Jun-2021

Partners

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I certify that the information in the report is complete and accurate:
Signature: Jean-Luc Bredas
Signature Date: 6/8/21 4:15AM

Scientific Progress and Accomplishments

1. **Kinetic Monte Carlo simulations of 2D COFs**

We have carried out kinetic Monte Carlo (KMC) simulations to model the growth of COF-5 from its monomers in solution. The theoretical model is based on data from transition-state searches, reaction pathway analyses, molecular dynamics simulations, and free-energy calculations, as well as experimental kinetics data from the William Dichtel group. The model is able to describe accurately the COF growth measurements and to reproduce the dependence of the size of the COF-5 crystals on H_2O concentration. Major findings from the kinetic Monte Carlo model are: (i) the nuclei in the growth process are small, multi-layer structures; (ii) nucleation occurs in several stages (**Fig. 1**); (iii) the formation of the precursors is the first stage and influences the length of the induction period; (iv) there are multiple nucleation pathways; (v) extensions in the lateral (in-plane) and vertical (stacking) directions are both seen to be linear with respect to time; (vi) small monomers dominate the lateral growth; and (vii) the vertical growth is related to stacking with oligomers. This work has been published in ***J. Am. Chem. Soc.***, **2017**, 139, 16310.

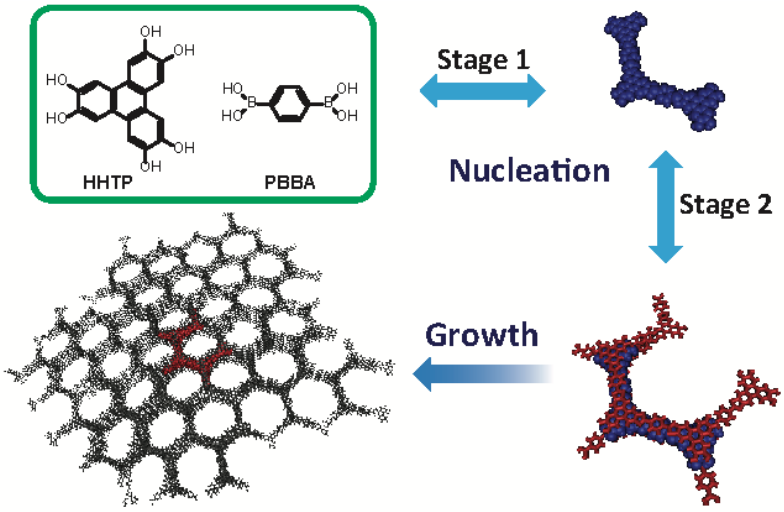

Figure 1. Illustration of the different stages of COF-5 formation from the KMC simulations.

2. **Hydrolytic stability of COF-5**

We have put forward a comprehensive understanding of the hydrolytic stabilities of COF-5 oligomers and crystals based on the reaction pathways. Besides acting as the reactant, H_2O is also found to catalyze bond dissociation and significantly reduce the reaction barrier from ca. 22 kcal mol^{-1} to only 6.5 kcal mol^{-1} (**Fig. 2**). In addition, in the crystalline environment, the linkages have reaction pathways different from those for isolated

oligomers and display increased hydrolytic stabilities, leading to some 3-6 orders of magnitude decrease in hydrolysis rate. This work has been published in ***Adv. Theory Simul.***, **2018**, 1, 1700015.

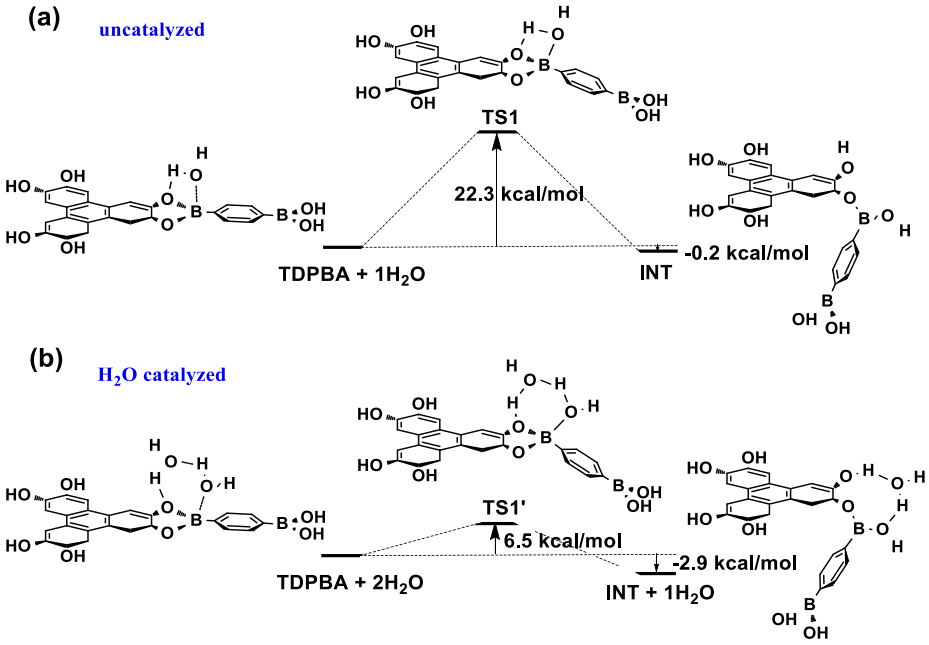

Figure 2. Reaction pathways for the first B-O bond dissociation in TDPBA, in the presence of (a) one molecule and (b) a second water molecule acting as catalyst.

3. Quantitative analysis of the nucleation and growth rates of 2D COFs

We have expanded our kinetic Monte Carlo (KMC) model, in order to investigate the nucleation and growth rates of 2D covalent organic frameworks (COFs). The KMC model has provided us with a first quantitative understanding of the monomer consumption rates related to nucleation and growth of 2D COF crystals. We found that nucleation and growth have a second-order and a first-order dependence on monomer concentration, respectively. The different dependences mean that there always exists a threshold monomer concentration below which growth is faster than nucleation (**Fig. 3a**). This is consistent with the recent experimental findings that nucleation can be suppressed by reducing the monomer addition speed (Austin Evans *et al*., ***Science***, **2018**, *361*, 52).

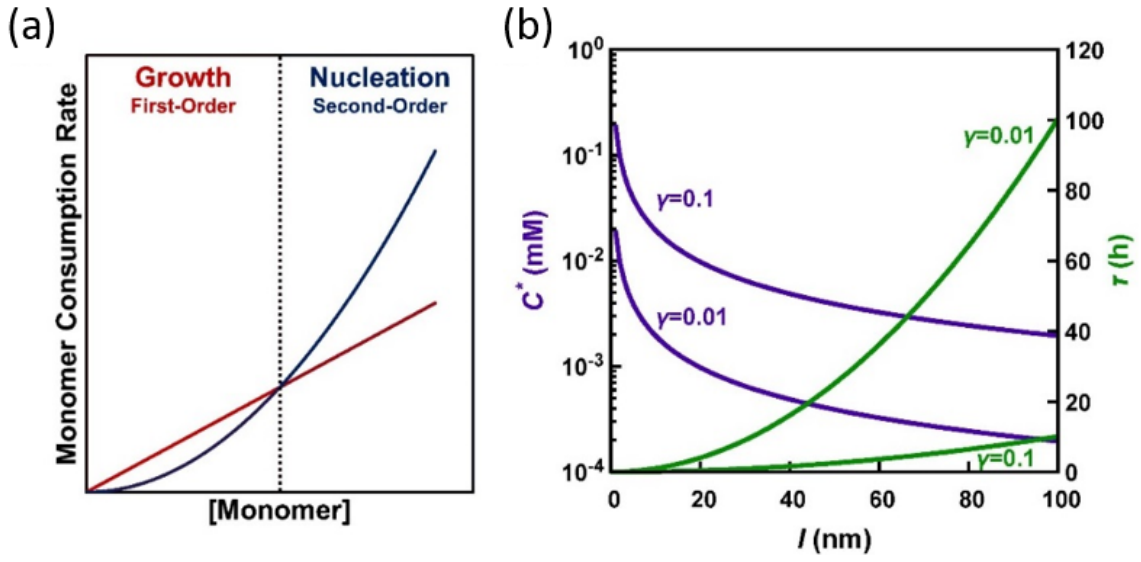

Figure 3. (a) Comparison of the monomer consumption dynamics of nucleation and growth. (b) Illustration of the critical monomer concentration and reaction time at different desired crystallite expansion (*l*). The value of the initial nuclei concentration is assumed to be 3.3×10^{-5} mM.

With the objective of suppressing nucleation, we define γ as the number of newly nucleated species divided by the initial seed crystals during a growth process in which the diameter of the existing crystals is extended by *l*. There exists a critical monomer concentration (C^*) that represents the upper theoretical limit for a specific combination of γ and *l*. We find that C^* depends on the initial nuclei concentration ($C_{nuc,0}$) and can be expressed as:

$$C^* = \frac{\gamma C_{nuc,0} k_{growth,in-plane}}{l k_{nucleation}} \quad (1)$$

For practical 2D COF growth, the reaction time is also an important factor to be considered. The use of too low a monomer concentration should be avoided as it results in undesirably slow growth. The shortest time for crystal growth is achieved when using $C_{monomer} = C^*$. In this case, the time required for the desired crystal expansion *l* is calculated to be:

$$\tau = \frac{k_{nucleation} l^2}{k^2_{growth,in-plane} \gamma C_{nuc,0}} \quad (2)$$

A graphical illustration of **Eqs. (1)** and **(2)** is shown in **Fig. 3b**. This work has been published in ***J. Am. Chem. Soc.***, **2020**, 142, 1367.

4. Quantitative description of the lateral growth of 2D COFs

We applied KMC simulations to calculate the lateral growth rates of 2D COFs formed from monomers for different combinations of rate parameters describing (microscopic) bond formation, bond breakage, stacking, and destacking. Our results show that the lateral growth rate evolves linearly with the bond formation rate constant. By further considering that the bond formation rate depends on the detailed microscopic molecular environment, we were able to derive an equation for the in-plane growth rates ($g_{lateral}$) of 2D COFs under homogeneous solution conditions:

$$g_{lateral}\left(\lambda_2, \lambda_3, k_{bf1}, \kappa, C_A\right) = \sqrt{\frac{\lambda_2^2 \lambda_3 \kappa}{\mathrm{A}_1 \lambda_2 + \mathrm{A}_2 \lambda_3}} \mathrm{S} k_{bf1} C_A \qquad (3)$$

Here, κ represents the lateral area divided by the number of vertices in the 2D lattice; A_1 and A_2 are unitless constants with values of 0.70 and 1.60, respectively. S is a geometrical factor and defined to be 1 for disk-shaped crystals; For square- and hexagon-shape crystals, S takes values of $\sqrt{\pi/4}$ and $\sqrt{\pi/2\sqrt{3}}$, respectively; $\lambda_2 = k_{fb2} / k_{fb1}$. $\lambda_3 = k_{fb3} / k_{fb1}$; k_{bf1}, k_{bf2}, and k_{bf3} are the bond formation rate constants between the reactive functional groups of core and linker monomers, along the lateral face of a 2D COF particle, and at a cleanly cut multilayered crystalline facet, respectively; C_A is the concentration of **core** monomers.

Fig. 4 shows the in-plane growth rates calculated by **Eq. (3)** for various λ_2 and λ_3 values. It can be seen that increasing either λ_2 or λ_3 leads to faster lateral growth rates. However, λ_2 has a larger influence on the in-plane growth rate than λ_3. Within the calculated parameter range in **Fig. 4**, the lateral growth rate can increase by over an order of magnitude as λ_2 evolves. Our proposed analytical model provides a feasible way to estimate the growth rate of 2D COFs, which is expected to be useful in their molecular design and the optimizations of their synthesis conditions. This work has been published in ***ACS Mater. Lett.***, **2021**, 3, 398.

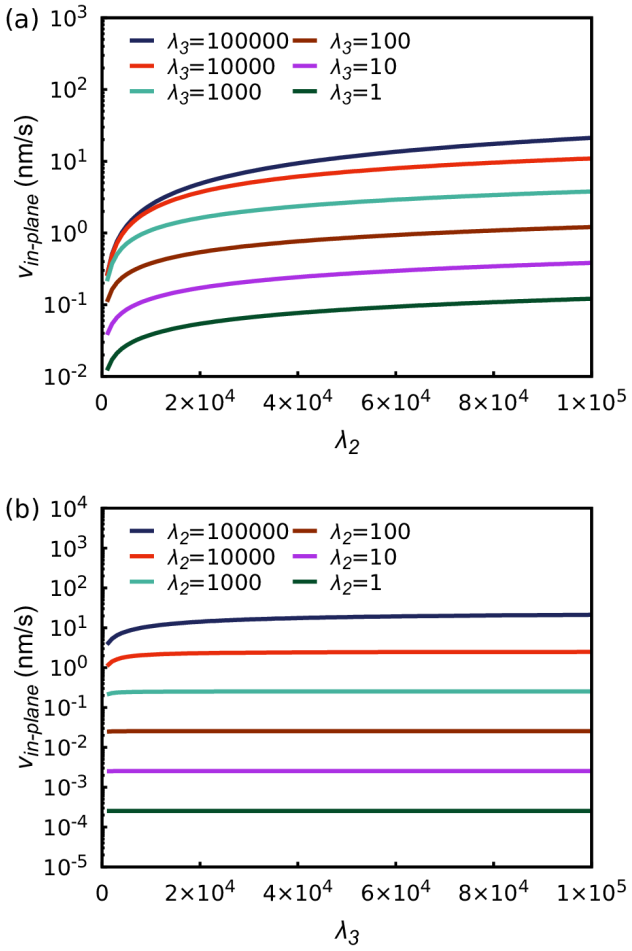

Figure 4. Lateral growth rates of COFs as a function of: (a) λ_2 and (b) λ_3, as calculated via **Eq. (3)**. The κ and C_A values are set to 3.9 nm^2 and 0.4 mM, respectively, which are similar to the conditions used for the synthesis of COF-5.

5. Investigation of the impacts of TCAT on the nucleation and growth of COF-5

In an effort to break the limitations of the 2D COF crystalline size, the Dichtel group has found that adding TCAT (which has a chemical structure corresponding roughly to 1/3 of HHTP), effectively suppresses nucleation and growth and leads to smaller diameter-to-height ratios. In order to understand the underlying mechanism, we have carried out simulations based on a modification of our KMC model, with the goal to study the early stage of nucleation by considering the oligomerization of HHTP and PPBA in the presence of TCAT.

Fig. 5 shows the evolution of the simulated average oligomer size from the simulation for different amounts of TCAT. It can be seen that adding TCAT slows the elongation of

oligomers and limits them to small sizes. Excess TCAT molecules react with the PBBA units and need to be removed before oligomers can grow, which leads to slow oligomer growth. From the thermodynamics perspective, adding TCAT shifts the equilibrium oligomer size to smaller values by stabilizing the fragments from bond breakage. These trends are also seen in **Fig. 5b**, which shows the evolution of the size of the largest oligomer in the simulation. In the case of 15 equivalents of TCAT, the oligomers do not exceed 7 monomer units throughout the simulation of an hour. This size is close to the critical nucleus (in-plane) size (6-7) from our previous KMC simulations and explains why nucleation is fully suppressed at high TCAT loading. This work has been published in ***ACS Cent. Sci.***, **2019**, 5, 1892.

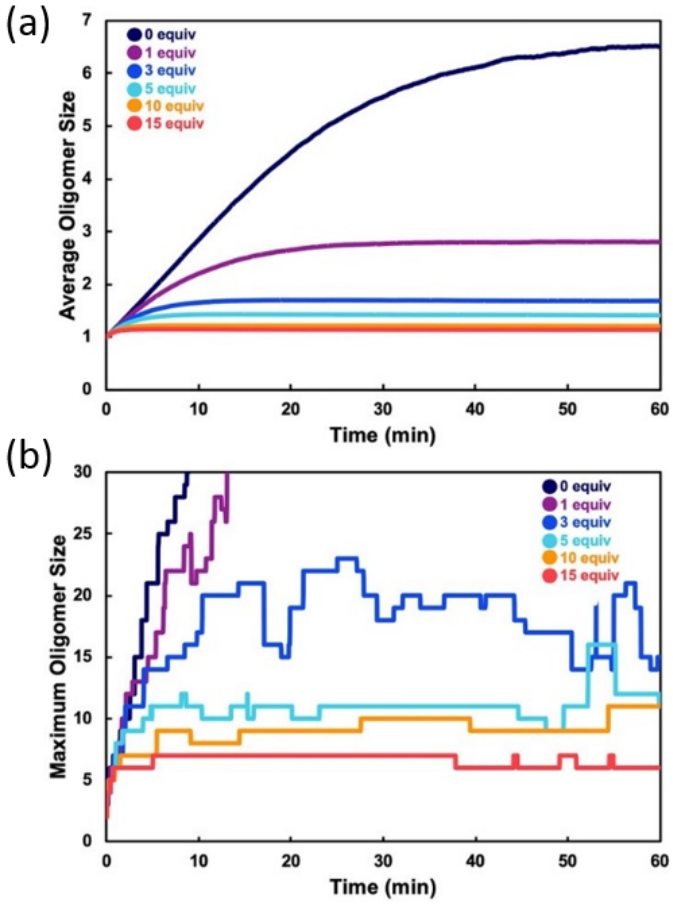

Figure 5. Kinetic Monte Carlo simulation of oligomerization of HHTP and PBBA in the presence of TCAT. Evolution of the A) average oligomer size and B) the size of the largest oligomer (excluding TCAT unit) as a function of time.

6. Investigation of the flexibility of 2D COF sheets

We have performed atomistic molecular dynamics simulations to investigate the out-of-plane motions of COF-5 sheets, see **Fig. 6**. Large out-of-plane deformations are found, about 400% higher than those encountered in graphene. In addition, structural defects lead to significantly larger twists and deformations, which underlines the challenges in fabricating stand-alone, large-size 2D COF sheets. Stacking, on the other hand, effectively reduces the out-of-plane deformations and suppresses the role of defects, two aspects beneficial to the lateral extension of 2D COF sheets. This work has been published in ***J. Phys. Chem. Lett.***, **2018**, 9, 4215.

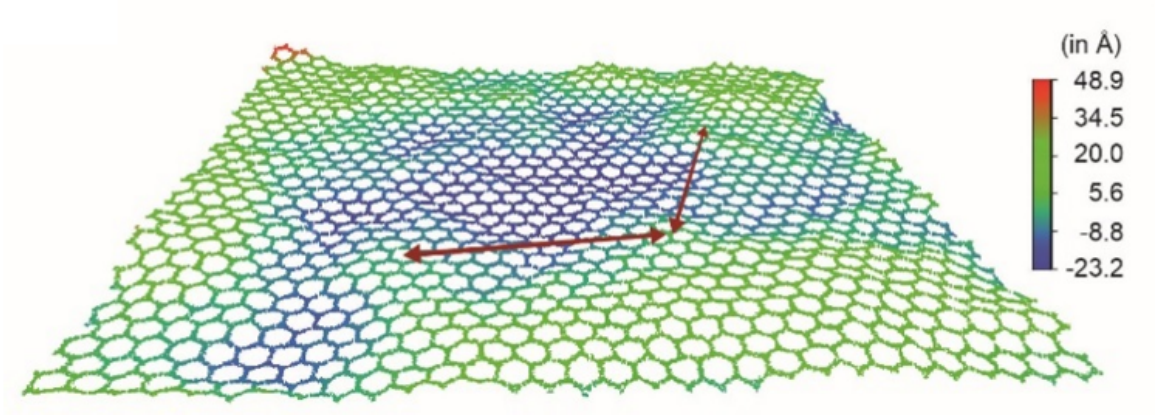

Figure 6. A representative snapshot from the MD trajectories. The color bar represents the out-of-plane displacement. The red arrows correspond to 30 nm.

7. Simulations of 2D COF nanoscrolls

We have performed molecular dynamics simulations on COF-5 and TAPB-PDA COF nanoscrolls. The results show that single-layer COF-5 [TAPB-PDA COF] sheets with at least a length larger than ~15 nm [~20 nm] form stable nanoscrolls in both vacuum and solution conditions (**Fig. 7**). They can only exist in a finite number of configurations (from a 2D sheet with a fixed size) and represent open structures stemming from the large pores present in the 2D sheets. The formation of nanoscrolls from flat sheets or the switching from a stable nanoscroll structure to another one can require activation. These features distinguish them from the nanoscrolls formed by "dense" 2D materials such as graphene, MoS_2, or hexagonal boron nitride (*h*-BN). Density functional theory calculations show that these nanoscrolls have optoelectronic properties different from single-layer sheets.

One important implication of these results is that, when exfoliating monolayers from stacked sheets in solution, mild experimental conditions (*e.g.*, avoiding sonication) should

be used in order to retain the (metastable) flat structure of the 2D sheet. On the other hand, when targeting nanoscrolls, external stimuli (*e.g.*, sonication) should be used to facilitate sheet bending. It is also worth noting that nanoscroll formation can provide a strategy for the helical extension of 2D COFs or the realization of porous nanotubes. This work has been published in ***Chem. Mater.***, **2019**, 31, 3265.

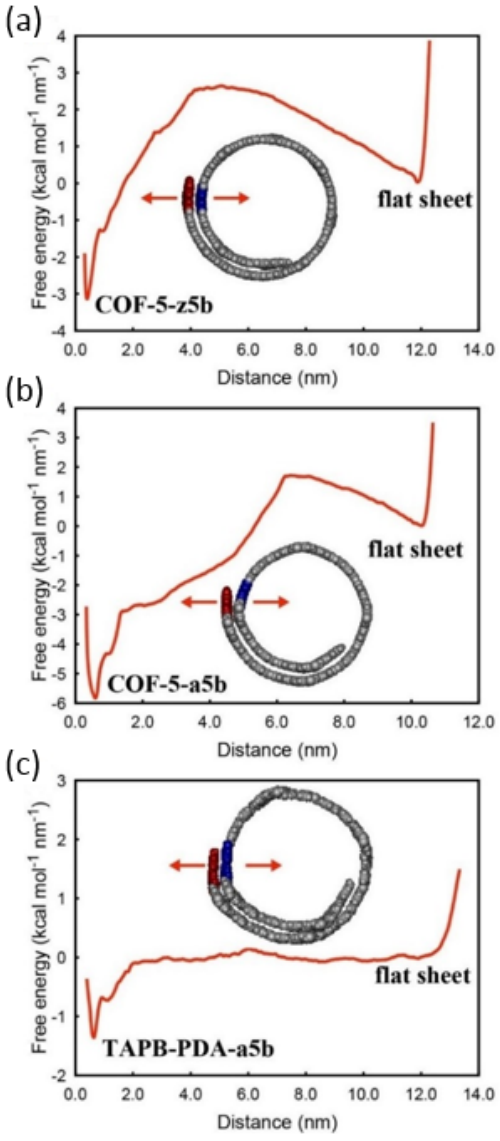

Figure 7. (a) Free energy per unit of length in the armchair direction for the unrolling of nanoscroll COF-5-z5b in the zigzag direction; (b) free energy per unit of length in the zigzag direction for the unrolling of nanoscroll COF-5-a5b in the armchair direction; (c) and free energy per unit of width in the zigzag direction for the unrolling of nanoscroll

TAPB-PDA-a5b in the armchair direction. The *x*-axis corresponds to the center-of-mass distance between the red and blue parts. Simulations are in solution conditions (where the solvent is taken as a 4:1 dioxane/mesitylene mixture) at 298 K.

8. Investigation of the mechanical properties of 2D COFs

We have applied molecular dynamics (MD) simulations to investigate the mechanical properties of COF-5 and TAPB-PDA COF sheets under tensile stress (**Fig. 8**), which represent two types of the most widely studied 2D COFs. In both systems, the Young's moduli are found to be dependent on the stretching direction and range from 4 GPa to 24 GPa. A large Poisson's ratio of 0.9-1.1 is found, which suggests that 2D COFs have a large contraction in the transverse direction when stretched. These results point to 2D COFs as anisotropic elastic materials. Importantly, the presence of structural defects is found to significantly impact the mechanical properties of 2D COFs. For instance, the presence of 3% vacancies can lead to a ~50% decrease in Young's modulus. Our work provides a comprehensive understanding of the elastic properties of representative 2D COFs, a useful stepping stone when considering these systems for a variety of applications. This work has just been accepted in ***Chem. Mater.***

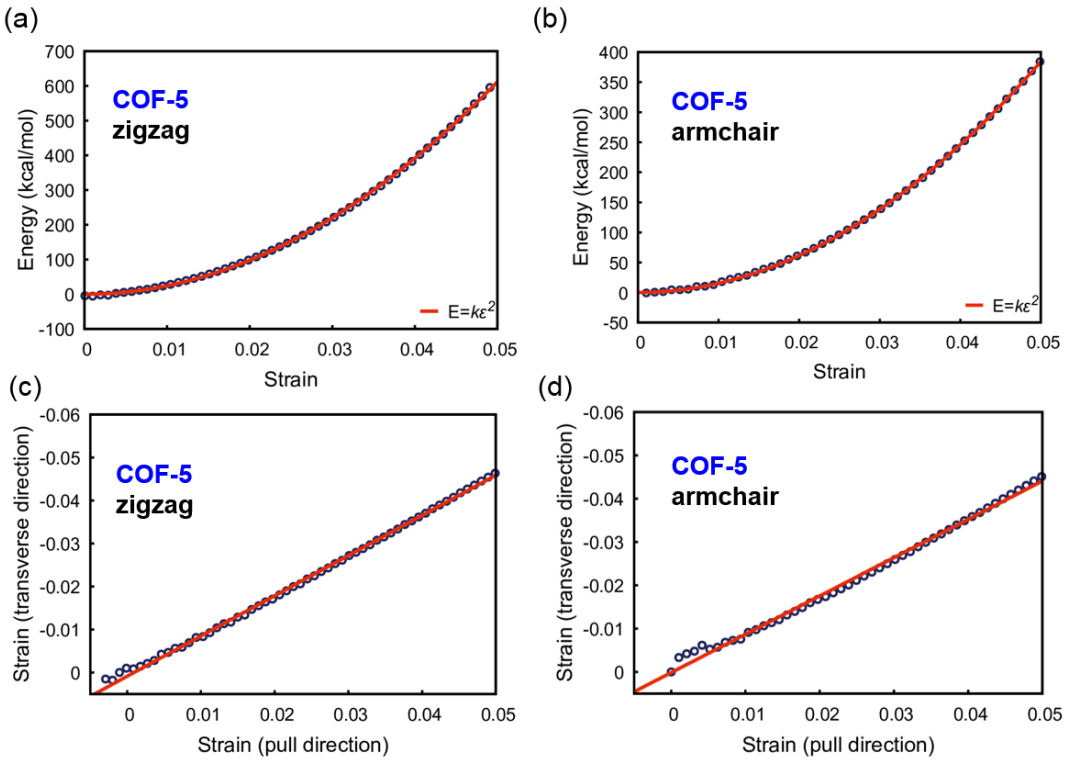

Figure 8. Evolution of the potential energy of a COF-5 monolayer when stretched in the (a) zigzag and (b) armchair directions. Evolution of the strains upon stretching in the (c) zigzag and (d) armchair directions.