

COFs Meet Graphene Nanoribbons

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2D covalent organic frameworks (COFs) have received considerable attention because of their crystallinity, permanent porosity, and tunability, yet they exhibit low in-plane conductivity. In this issue of Chem, Fischer and co-workers report an approach for growing 2D COF thin films featuring high in-plane conductivity for potential use in organic electronics.

Chemists have been driven to continuously adapt and alter experimental protocols in order to overcome challenges and achieve the ultimate goal: total control over a chemical reaction. Whereas control can be considered simply as anticipating the outcome of a reaction on the basis of the reactivity and structure of the reactants, these days control over a chemical reaction also refers to accurately predicting the structure-property relationships of target materials on the basis of precisely tuned synthetic procedures. In fact, achieving total control has proved to be an elusive feat for chemists, and this was nicely highlighted in a book about R. Hoffman and his view on the philosophy, art, and science of chemistry:

Organic chemists are masterful at exercising control in zero dimensions. ... One subculture of organic chemists has learned to exercise control in one dimension. These are polymer chemists, the chain builders. ... But in two or three dimensions, it's a synthetic wasteland.¹

Especially in organic materials science—a field that is concerned with designing new materials for cutting-edge technologies such as organic light-emitting diodes (OLEDs), solar cells, and batteries—complete control over the morphology, structure, and chemical

nature of a material is crucial for establishing a structure-property relationship. Although the first crystalline "organic" 2D material—graphene—was first discovered in 1962 with an electron microscope,² it wasn't until 2004 that it was isolated from graphite via the "Scotch tape method."³ Graphene is a 2D single-atom-thick hexagonal lattice of sp²-bonded carbon atoms and features high π -surface area, high electrical and thermal conductivity, and mechanical stability. Subsequently, several studies have focused on the development of bottom-up synthetic strategies for the preparation of graphene on various surfaces and of graphene-derived materials ranging from graphene nanoribbons to graphene nanodots, endowing the resulting materials with new structural features. Despite the significant advances in this area, most preparations of these materials are based on sophisticated processes (such as chemical vapor deposition) or require multistep syntheses. A breakthrough in the area of 2D materials was made with the bottom-up synthesis of crystalline 2D materials named covalent organic frameworks (COFs), which were first reported by Yaghi and co-workers⁴ in 2005, thus introducing a highly effective and modular strategy for accessing this exciting class of 2D materials. The formation of COFs involves reversible dynamic covalent-bond formation under solvothermal conditions to induce crystallinity to the resulting materials.

COFs exhibited many of the intriguing physical properties previously found only in graphene—a layered crystalline structure based on π - π stacking, high surface area, and thermal stability. Notably, the nature of organic linkers used in the synthesis of COFs dictates the property and function of the resulting material, an important advantage over other 2D materials. To date, a plethora of new COFs based on a variety of different synthetic strategies, covalent linkages, and dimensionality have been reported, and each affects the properties of the resulting COF in a very specific way. Because of the modularity and crystallinity of COFs, they have already found applications in membranes, heterogeneous catalysis, gas storage and sequestration, adsorbents, battery materials, OLEDs, and photocatalytic water splitting. Whereas COFs feature a multitude of sought-after properties, especially in the field of organic electronics, an inherent problem prevails: the charge-carrier transport in COFs mainly occurs (Figure 1A) by an interlayer hopping mechanism rather than in plane as a result of the types of linkages (e.g., imine, imide, and boroxine), giving rise to semiconductors with large band gaps, which are undesirable for advanced electronic applications.^{5,6}

Besides the "conventional" approach toward COF synthesis—designing small organic monomers of suitable functionality and polymerizing them under specific conditions—more recent publications have focused on the possibility of using functionalized 1D macromolecular building blocks and their post-polymerization to form 2D COFs. Yaghi and co-workers recently demonstrated this approach by preparing 1D

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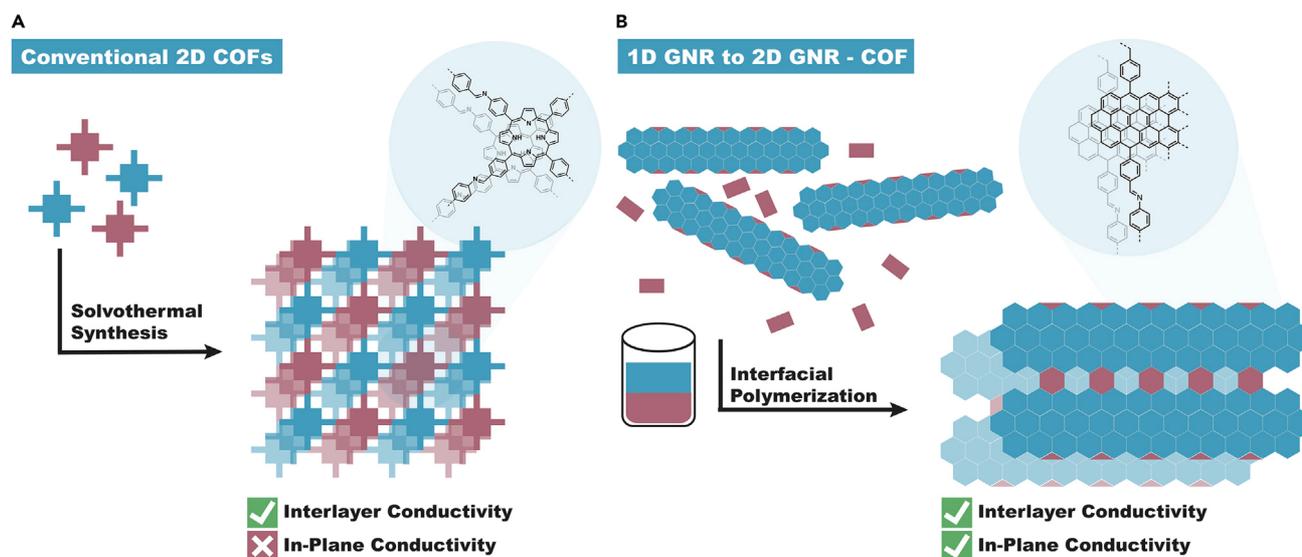


Figure 1. Graphical Representation of the Synthetic Strategies for Conventional 2D COFs and 2D GNR-COF Films

(A) Porphyrin-based COF synthesized under solvothormal conditions. Magnification: imine linkages often employed in COF chemistry result in wide band gaps and low in-plane conductivity.

(B) Synthesis and structure of 2D GNR-COF and illustration of the formation of GNR-COF via interfacial polymerization. Magnification: imine-linked GNRs featuring extended conjugation result in improved conductivity.

ribbons having unreacted, frustrated amine functional groups on the backbone and linking them by reacting them with aldehydes or anhydrides in order to obtain imine- or imide-linked 2D COFs, respectively.⁷

In this issue of *Chem*, Fischer and co-workers report the efficient growth of a 2D COF film from highly conjugated macromolecular building blocks, such as graphene nanoribbons (GNRs), through interfacial polymerization (Figure 1B).⁸ GNRs, which are essentially small strips of graphene, can be tuned through modification of their length, width, dopants, edge modification, or functional groups, thus rendering them interesting building blocks for COF synthesis. To achieve these precise structures, however, a bottom-up synthetic approach based on a multi-step organic synthesis involving several cyclization reactions is usually employed.⁹ Conventionally, such GNRs do not feature reactive functional groups, which are necessary for linking them together to form 2D materials. Hence, the authors used an acetal pro-

tected precursor in order to perform the Diels-Alder cycloaddition polymerization and subsequent cyclodehydrogenation reaction to form the GNR before deprotecting in the final step, resulting in aldehyde-functionalized GNRs (CHO-GNR). In order to convert a highly conductive GNR macromolecule into a 2D COF, they employed interfacial polymerization—a technique that is often used for preparing large thin films of conductive polymers for electronic devices—to obtain the desired polymer as relatively large-area macroscopic films ($>1,000 \mu\text{m}^2$), as verified by optical microscopy analysis. However, it should be noted that GNRs cannot be converted into COFs under conventional solvothormal reaction conditions, presumably because of their low solubility and affinity to form aggregates. Accordingly, Fischer and co-workers grew the target GNR-COF films via Lewis-acid-catalyzed interfacial polymerization (Figure 1B). They prepared two solutions—one containing the reactants and the other containing the catalyst—and over the course of several days, a polymer film

formed at the interface; the authors could remove this film simply by dipping a suitable substrate into the solution and coating it with the GNR-COF. The choice of reaction solvents enabled the polymerization reaction as well as protection of the amine precursors from oxidation. In order to showcase the enhanced conductivity of GNR-COFs, the authors prepared an Al_2O_3 substrate patterned with Pt electrodes, and even without applying a gate bias, they could measure drain currents at a very low source drain bias. To achieve such thin layers of GNR-COF, they employed a liquid-phase exfoliation by ultrasonication of the GNR-COFs and casting them onto a Si/SiO₂ support. Subsequent atomic force microscopy measurements revealed that films with a thickness corresponding to bilayers or trilayers were obtained.

In a broader context, the combination of GNRs and COFs provides a first glimpse into the world of highly conductive 2D materials featuring structurally tunable mechanical, electrical, and optoelectronic properties.

Moreover, these highly conductive COFs can also find applications as electrode materials in Li-ion batteries¹⁰ and in organic photovoltaics, organic electronics, and photocatalysis.

1. Kovacs, J., and Weisberg, M. (2012). *Roald Hoffmann on the Philosophy, Art, and Science of Chemistry*, First Edition (Oxford University Press).
2. Boehm, H.P., Clauss, A., Fischer, G.O., and Hofmann, U. (1962). Das Adsorptionsverhalten sehr dünner Kohlenstoff-Folien. *Z. Anorg. Allg. Chem.* 316, 119–127.
3. Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V., and Firsov, A.A. (2004). Electric field effect in atomically thin carbon films. *Science* 306, 666–669.
4. Côté, A.P., Benin, A.I., Ockwig, N.W., O’Keeffe, M., Matzger, A.J., and Yaghi, O.M. (2005). Porous, crystalline, covalent organic frameworks. *Science* 310, 1166–1170.
5. Dogru, M., and Bein, T. (2014). On the road towards electroactive covalent organic frameworks. *Chem. Commun.* 50, 5531–5546.
6. Joshi, T., Chen, C., Li, H., Diercks, C.S., Wang, G., Waller, P.J., Li, H., Bredas, J.L., Yaghi, O.M., and Crommie, M.F. (2019). Local electronic structure of molecular heterojunctions in a single-layer 2D covalent organic framework. *Adv. Mater.* 31, e1805941.
7. Nguyen, H.L., Gropp, C., and Yaghi, O.M. (2020). Reticulating 1D ribbons into 2D covalent organic frameworks by imine and imide linkages. *J. Am. Chem. Soc.* 142, 2771–2776.
8. Veber, G., Diercks, C.S., Rogers, C., Perkins, W.S., Ciston, J., Lee, K., et al. (2020). Reticular growth of graphene nanoribbon 2D covalent organic frameworks. *Chem* 6, this issue, 1125–1133.
9. Jordan, R.S., Wang, Y., McCurdy, R.D., Yeung, M.T., Marsh, K.L., Khan, S.I., Kaner, R.B., and Rubin, Y. (2016). Synthesis of graphene nanoribbons via the topochemical polymerization and subsequent aromatization of a diacetylene precursor. *Chem* 1, 78–90.
10. Li, X., Wang, H., Chen, H., Zheng, Q., Zhang, Q., Mao, H., Liu, Y., Cai, S., Sun, B., Dun, C., et al. (2020). Dynamic covalent synthesis of crystalline porous graphitic frameworks. *Chem* 6, 933–944.