

Two-Dimensional Conjugated Polymers Based on C–C Coupling

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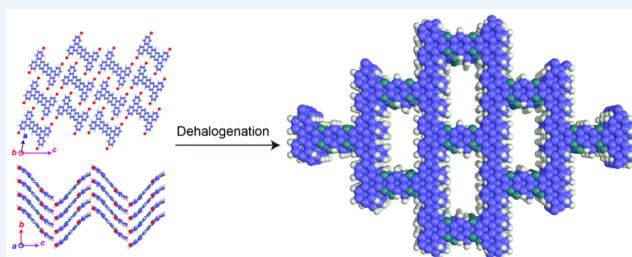
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ABSTRACT: The synthesis of a crystalline two-dimensional (2D) polymer linked by C–C bonds can be considered as one of the holy grails of synthetic chemistry. Possible routes may involve interface-confined polymerization at air–water or solid–solid interfaces or sterically constrained polymerization of prepacked crystalline monomers.



Graphene, an atomically thin sp^2 -hybridized carbon sheet, can be considered as a 2-D macromolecule comprising areal repeat units linked by strong carbon–carbon bonds. Since its successful discovery by Novoselov and Geim in 2004,¹ there has been interest in making structural analogs of graphene.^{2,3} Müllen and co-workers reported the bottom-up fabrication of 0-D (graphene quantum dot) and 1-D (graphene nanoribbon) graphene-like structures, which are interesting due to their promising optoelectronic properties, based on cyclodehydrogenation.^{4,5} However, challenges remain in the rational synthesis of graphene-like π -conjugated two-dimensional polymers (Figure 1b), which are expected to offer greater flexibility in terms of structure, topology, and physical properties compared to graphene. For example, theorists have predicted graphene analogs such as graphyne (GY) and graphdiyne (GDY), which are based on the dehydrobenzo[12]annulene and dehydrobenzo[18]annulene framework, respectively.⁶ From a structural viewpoint, these systems are highly attractive because their optical and electronic properties can be tuned by controlling the molecular structure of building units or the amount of double and triple bonds, or both, which is unique compared to the pure sp^2 hybridization of graphene. However, it is difficult to synthesize these at a scale similar to how graphene can be made.⁷ Conjugated porous polymers based on C–C coupling synthesized via solution chemistry methods, such as Sonogashira coupling, Suzuki coupling, Yamamoto coupling, etc., are typically produced in the form of amorphous fine powders.^{8,9} For graphyne, the simplest subunit is hexaethynylbenzene, which can be generated via intermolecular or intramolecular Sonogashira cross coupling, but extending the building blocks into a 2-D framework with long-range crystalline order is difficult experimentally, both in solution and via surface-templated approaches. Liu et al. grew vertically standing graphdiyne nanowalls using a modified Glaser–Hay

reaction, but a continuous 2-D crystalline film has not been made.¹⁰ From a synthetic perspective, the spatial control of C–C cross couplings between molecular building blocks in two dimensions is highly challenging. Due to the irreversible nature of the bond formation process in C–C linked macromolecular framework, the self-correction needed in crystal growth cannot occur readily.

Let us examine the possible approaches to achieve 2-D polymer, from physical confined polymerization to molecular control. Spatial confinement at surfaces, including air–water, liquid–liquid, or solid–solid interfaces can be used to limit the cross-talk (i.e., covalent bonding) between adjacent molecular layers.² Introducing amphiphilicity into the monomer allows it to phase segregate at the air–water interface; the higher rotational and diffusional mobility of these monomers on the surface of water allows error correction in self-assembled layers. In addition, the surface pressure can be controlled in a Langmuir–Blodgett trough to achieve liquid crystal-like packing, whereupon cross-linking between the organic layers can be induced by photochemical routes. In principle, we can also make use of periodic segregation of organic and inorganic assembled structures in hybrid organic–inorganic perovskite crystals. Inducing C–C coupling or cycloaddition among the organic chains that are spatially segregated by the inorganic section will naturally lead to confined polymerization in a 2-D space. Here the concept is not based necessarily on a layered aromatic system separated by weak interlayer forces, rather it relies on spatial segregation to separate the layers, and open up the possibility for a using a wider class of monomers where the cross-linking happens orthogonally to the main axis of the molecules. Examples of structural control at the molecular level

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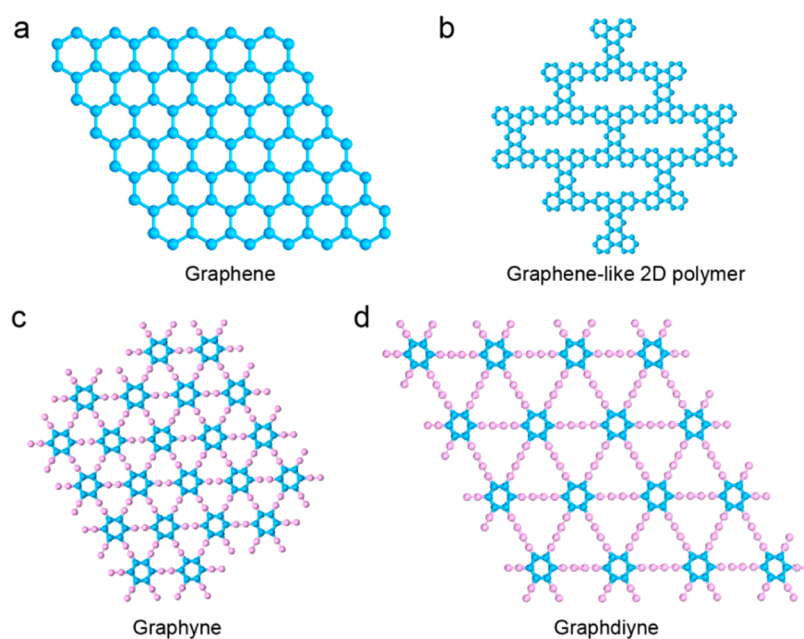


Figure 1. Schematic illustration of graphene, graphene-like 2-D polymer, graphyne, and graphdiyne (blue balls, sp^2 carbons; pink balls, sp^1 carbons).

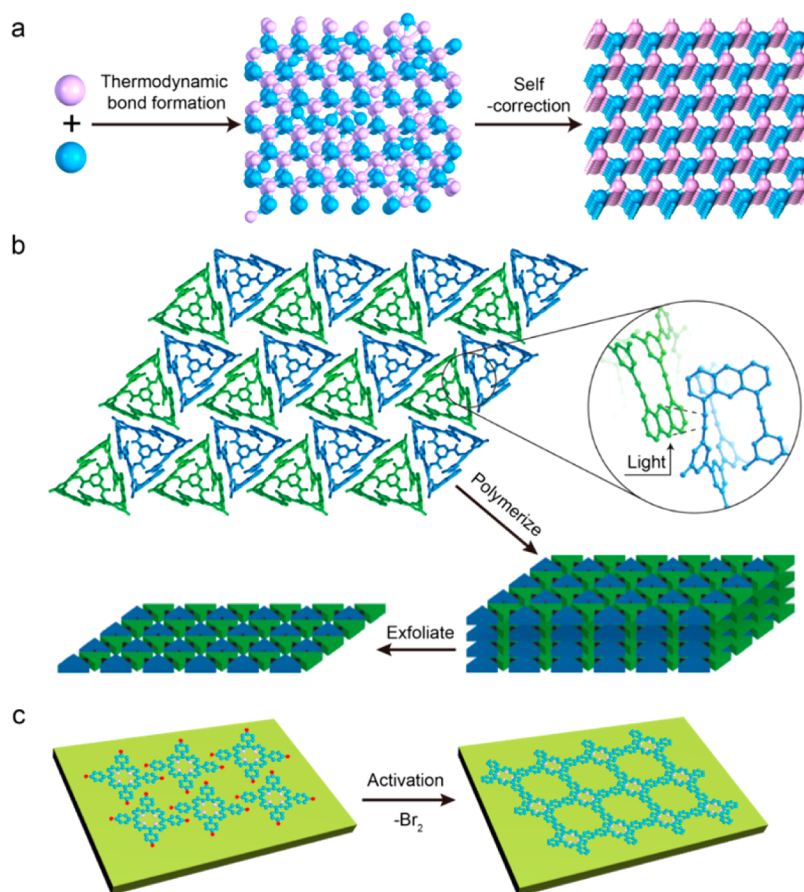


Figure 2. Two-dimensional polymerization strategies. (a) COFs via thermodynamic reactions; (b) topochemical polymerization of layered precursors via cycloaddition reaction between anthracenes and alkynes; (c) surface-mediated polymerization based on aryl–aryl coupling reaction. Panel b adapted with permission from ref 16. Copyright 2013 Macmillan Publishers Limited.

for layered aromatic systems are very limited. Some examples include crystalline 2-D covalent organic frameworks (COF) synthesized via thermodynamic linkages (such as boronate ester linkages, imine linkages, triazine rings),^{11,12} 2-D polymer single

crystals synthesized via topochemical polymerization from which few-layer to monolayer sheets can be exfoliated,¹³ and single layer 2-D polymers assembled on atomically flat surfaces,¹⁶ as shown in Figure 2. Utilizing thermodynamic

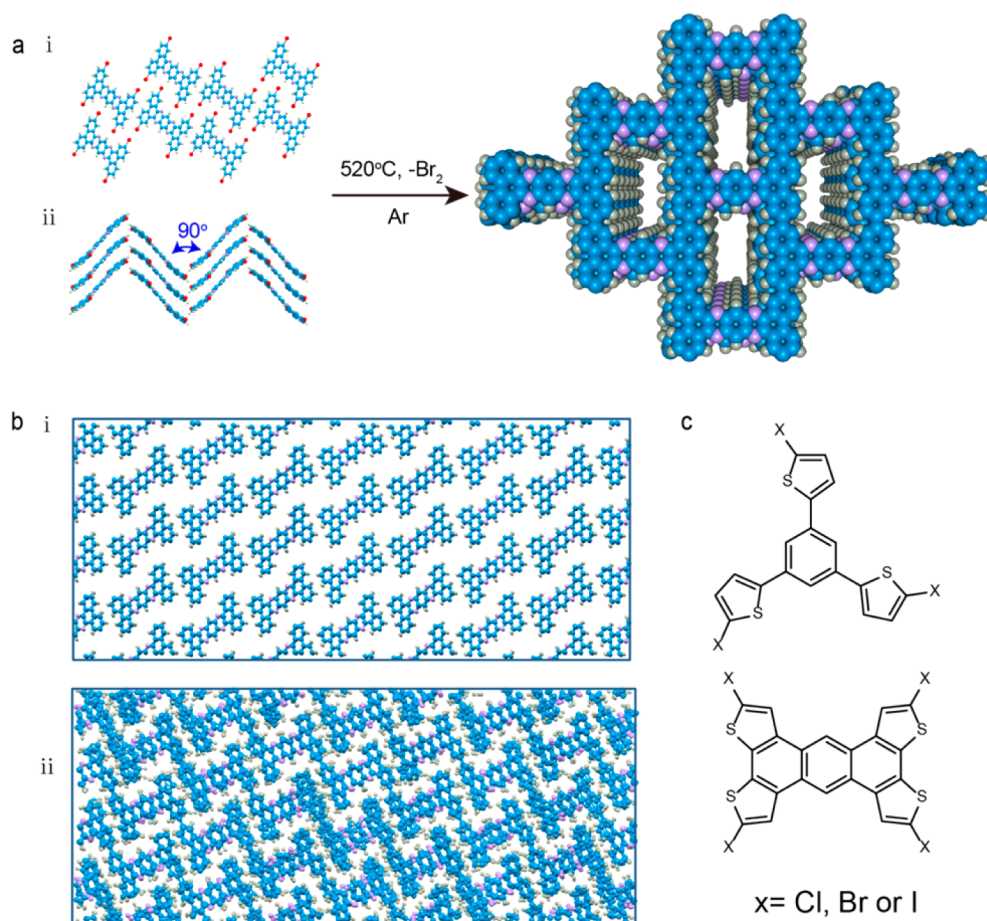


Figure 3. Example of 2D polymer via solid-state polymerization. (a, b) Molecular crystal with zigzag packing for 2D polymerization (a) and molecular dynamic simulation of 2-D polymerization (b). (c) Proposed halogenated thiophene derivatives for 2D polymerization. Panels a and b adapted with permission from ref 20. Copyright 2017 Macmillan Publishers Limited.

reactions on a relatively long time scale to allow self-correction, as is the case for COFs, is expected to improve long-range crystallinity (Figure 2a). The topology and dimensionality (2-D or 3-D) of the resulting framework is determined by the shape of precursor monomers and the propagation directions of the condensation reactions.¹⁶ Topochemical polymerizations have been shown recently to be an elegant approach to make nonconjugated 2-D polymers through intermolecular cycloaddition reactions between two-dimensionally confined monomers in single crystals.^{13–15}

A C–C coupling based 2-D polymer affords highly stable chemical bonds due to its “irreversibility” in bond formation but so far has only been realized via kinetically confined polymerization on an atomically flat metal surface.^{16,17} During thermal activation of chemical bonds, metal surfaces catalyze the cross-coupling reaction between monomers and confine the reaction to only occur at the substrate–molecule interface to produce a single layer 2D polymer. One problem is the strong binding of the monomers with the metallic substrate, which restrains their mobility and error-repairing ability. Defects common to such substrates also act as preferential nucleation centers, giving rise to nonuniform growth. In addition, the halogen atoms that are cleaved off from the monomers remain on the surface and aggregate into islands, which obstruct the 2-D growth of the polymer domains.¹⁸ The use of a metallic substrate also makes it necessary to transfer the grown film to a dielectric substrate for electrical measurements, which can be

nontrivial due to the mechanical stress the film is subjected to during the transfer process. Borrowing the experiences from 2-D materials research, a dielectric substrate such as hexagonal boron nitride (h-BN) can be a choice substrate because of its flat, inert honeycomb lattice with a low density of dangling bonds, which may be ideal for the growth of 2-D polymer from vaporized monomers. In view of the noncatalytic nature of h-BN, we like to suggest that a Cu-vapor-assisted chemical vapor deposition (CVD) process, with the copper vapor generated from an evaporating copper source, can be adapted to catalyze the growth. Due to the ease of desorption of copper atoms, no metal residues will remain on the dielectric surface. Copper-assisted CVD has been previously applied to the growth of graphene on amorphous SiO₂ substrate.¹⁹

Our recent study shows that to achieve macroscopically large C–C coupling based 2-D polymers, a viable strategy may lie in the endogenous solid-state polymerization (that is, without the presence of solvents, initiators, or catalysts) of structurally preorganized monomers in their crystalline state via thermal-initiated dehalogenation and concomitant C–C coupling, where the prearranged building blocks themselves could kinetically confine the propagation of the sheet in two dimensions.²⁰ Endogenous solid-state polymerization has the potential to achieve better structural order without the randomization effect of solvents and catalysts, inspired by the fact that linear polythiophenes with better crystallinity and conductivity have been achieved by this method.^{21,22} However,

thermally initiated C–C coupling based solid-state polymerization is constrained by the boundary conditions that the temperature of thermal dehalogenation has to be lower than the decomposition temperature of monomers. For example, the dehalogenation temperatures of halogenated aromatic hydrocarbon compounds could be as high as 700 °C, in which most organic materials are not stable. Comparing with monomers used in the polymerization of linear polythiophenes, monomers for 2-D polymers have at least three bond formation sites, leading to a higher degree of randomness in the coupling directions. Thus, to obtain 2-D polymers of good crystallinity, the molecular packing should impose steric hindrances and confine the propagation of C–C coupling in two dimensions. Figure 3a shows the crystalline structure of a tetrabrominated phenazine-ring fused molecule, where monomers are pre-arranged into a tightly packed zigzag crystal through a displaced face-to-face π – π interaction. Upon heating the molecular crystals to 520 °C to initiate debromination, radicals are produced for C–C coupling reactions. The as-synthesized polymer maintained the original shape of molecular crystals with the lamellar feature and can be mechanically exfoliated into ultrathin sheets as thin as 1 nm.²⁰ Molecular dynamic simulation suggests that in the monomer crystal, spatial selective C–C cross coupling favors the formation of a 2-D polymer (Figure 3b). One problem is that C–Br bonds may not be all cleaved at the same time, which will result in uneven propagation of the C–C coupling, giving rise to limited domain size in the polymer. In addition, molecular rotation is required to flatten the zigzag packed building units, which disrupts long-range structure order. The use of highly reactive aromatic structures such as thiophene derivatives (Figure 3c), in which the C–Br bonds can be cleaved at a much lower temperature, could promote a more uniform C–C cross-coupling to achieve a better structural order. Thiophene derivatives containing acetylene units may be useful for achieving 2D sp^x ($1 < x < 2$) structures (analogues of graphyne and graphdiyne structures) via endogenous solid-state polymerization. Although we have shown that solid-state polymerization of structurally pre-organized monomers is capable of producing 2-D conjugated polymers based on C–C coupling reaction, the generality of this method is still limited due to rotational freedom of these molecules, which makes the final structure difficult to predict. Steric hindrance introduced via side chains can be built in to limit rotation and discourage cross talk between layers. Due to contraction of the crystal during bond formation, cracks may form, and the monomers should be designed to accommodate mechanical stress. In this regard, the development of de novo computational methods to screen the monomers and simulate steric hindrance in the packed structure and strain propagation during bond formation will be highly useful.

Linking molecular building blocks by C–C cross coupling as opposed to imine or boronic ester functional linkages allows the strongest bonds to be formed in synthetic chemistry. C–C bonds can withstand hydrolysis of acids or bases and afford potentially the thermally most stable polymeric framework system. The robustness can make up for the lack of long-range order in the 2D polymer; in many instances, short-range local order, for example, functional groups, pore size, etc., can serve the desired functions in applications such as ultrafiltration, energy storage, or molecular separation processes.⁹ For example, a nanocrystalline 2D polymer synthesized by Liu et al. was found to contain pore size of 0.6 nm and was found to act as a highly effective energy storage medium in sodium ion

batteries.²⁰ In fact, processability and mechanical properties are often more important attributes in applications. One advantage of 2-D polymers based on C–C couplings is the potentially smaller pore size (<1 nm, for example, see pores in GDY where the distance between building units (hexaethynylbenzene) is only the length of a C–C bond), which are highly useful in molecular sieves or adsorption-type separation.²³ In addition, in fuel enrichment processes involving the separation of aromatics from linear alkanes, structural rigidity and thermal stability are more important requirements due to the high temperature processing conditions. For practical applications, the way forward may be forming a mixed matrix membrane of the 2-D polymer and some other polymers using conventional polymer extrusion techniques, where ultrathin sheets of the porous 2-D polymer act as a layered fillers in another polymer that serves the supporting and dispersing function. By controlling the density of the 2-D polymer sheets in the “transparent” polymer, it will create tortuosity for diffusion species. This may be a viable way to form ultrafiltration membranes. Alternatively, due to the higher thermal stability of C–C bonded 2-D polymer, they can be thermally impregnated on silicon oxide beads used in column chromatography and thus be used in adsorption-based molecular separation processes. Ultimately, the ease of scale up and identification of useful niche applications will decide if the 2-D polymer truly has any advantages over its 3D counterparts.

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Notes

The authors declare no competing financial interest.

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