Recent Advances in Covalent Organic Frameworks for Molecule-Based Two-Dimensional Materials

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ABSTRACT: Covalent organic frameworks (COFs), newly emerging crystalline and porous materials, have been widely studied in many fields because of their unique periodic porous structures, high surface area, and strong interlayer π−π interaction when they are formed into a layered structure. Among the various types of COFs, highly oriented COF thin films with a layered structure have received great attention as one of the most promising organic-based two-dimensional (2D) materials due to their modifiability, flexibility, and multifunctional properties. In this mini-review, we aim to provide information on recent advances in highly oriented 2D COF thin films, which have one molecular thickness level to tens of nanometers. We first discuss the preparation of high-quality 2D COF thin films in terms of interfacial synthesis and exfoliation methods, which are representative methods for bottom-up and top-down approaches, respectively. Also, we summarize the applications of 2D COF thin film focusing on semiconducting devices, membranes, and highly sensitive and selective sensors.

1. INTRODUCTION

Covalent organic frameworks (COFs) formed by chemical linkages through strong covalent bonds of light atoms such as carbon, nitrogen, and oxygen have been widely studied as new organic robust two-dimensional (2D) or three-dimensional (3D) crystalline polymers since their first report in 2005.1 Due to their uniform porous structure and high thermal/chemical stability, they have been investigated as potential materials of various applications including energy storage, optoelectronic devices, gas adsorption, chemical catalysts, and sensors.2 Especially, 2D COFs, being regarded as a new source of layered materials, have received great attention because they can be obtained in not only highly oriented multilayers but also one molecular level thick layer. Different from conventional atomic-level 2D materials such as graphene, transition metal dichalcogenides (TMDs), or hexagonal boron nitride (h-BN), molecule-based 2D COFs can be obtained as desired crystal structures with specific functional groups using various types of precursors. Such structure and property variation of 2D COFs facilitates control of optical and electrical properties as well as other physical properties, which is a big advantage in their potential applications. However, randomly oriented 2D COFs in powder form obtained by conventional solution-phase synthesis methods such as solvothermal,1 microwave,3 and sonochemical4 methods are not suitable for confirming intrinsic properties of 2D COFs due to the irregular orientation and numerous grain boundaries caused by small particle size. Therefore, to take advantage of the interesting properties of 2D COF films, highly oriented and well-defined films become needed. To date, various approaches have been reported, and this mini-review focuses mainly on two representative synthesis methods: (1) interfacial growth on a liquid surface and (2) exfoliation method using external forces. Also, we summarize the investigated applications of 2D COF thin films that show outstanding semiconducting, separating, and sensing properties according to their functional groups, pore sizes, and crystal structures.

2. SYNTHESIS OF HIGHLY ORIENTED 2D COF FILMS

Synthesis of COFs is mainly based on the dynamic covalent chemistry (DCvC) which is one of the efficient synthetic strategies used to obtain a thermodynamically stable structure through reversible covalent bond formation. Through chemical reactions of various precursors having specific functional groups and highly symmetric structure, various types of COFs can be synthesized. To obtain a high-quality COF successively, covalent bond formation has to occur reversibly, which enables an “error-checking” or “self-healing” process, resulting in a thermodynamically stable and highly symmetrical crystal structure. Among the various reactions used in DCvC for COF formation, two representative dehydration reactions have been widely used. The first is the dehydration reaction of boronic acid and catechol, and the other is the Schiff base reaction of aldehyde and amine functional groups. Based on these reactions, various synthetic approaches for 2D COF films have been developed as follows.

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Figure 1. (a) Chemical reaction of dialdehyde (1) and triamine (2) for obtaining a polyimine COF (3), which are reacted on the air/water interface. (b) Atomic force microscope (AFM) height image of a polyimine COF monolayer on a SiO$_2$/Si substrate. (c) Height profiles of lines shown in (b) indicating monolayer thickness of COF. Reproduced with permission from ref 5. Copyright 2016, Wiley-VCH. (d) Chemical structures of monomers (1, 2, and 3) and target two-dimensional polymers (2DPs) (4 and 5) synthesized by imine condensation reaction between precursors (e). Photograph of a 2DP monomer on a 4 inch SiO$_2$/Si substrate. (f) Transmission electron microscope (TEM) image of a multilayer 2DP showing clear lattice fringes of 2DP. Inset: selected area electron diffraction pattern of the film. Reproduced with permission from ref 6. Copyright 2016, Nature Communications.

2-1. Interfacial Synthesis. Liquid surfaces are one of the most uniform and flat surfaces suitable for obtaining molecule-based 2D materials. Different from conventional 2D crystalline materials synthesized at the gas–solid interface at high temperature, molecular precursors for COFs are less mobile on a solid substrate and easily decomposed at high temperatures. Therefore, liquid surfaces that can increase the mobility of molecular precursors and induce 2D-confined reaction at mild synthetic conditions would be a more appropriate substrate for the synthesis of 2D COF films.

In 2006, Zhang and co-workers synthesized an imine-linked monolayer COF at the air/water interface using a Langmuir–Blodgett trough method that has been widely used to obtain various monolayer films by monitoring the surface tension of liquid layers. They used a Schiff base formation reaction between terephthaldehyde and 1,3,5-triformylphloroglucinol (Tp) and four different types of PTSA salts that interact with the amine precursor and slow the liquid–solid interface condensation reaction between precursors. After the reaction, they used a salt-mediated technique using amine–p-toluene sulfonic acid (PTSA) salts that interact with the amine precursor and slow down the diffusion rate. In addition, the obtained 2DPs were examined as a thin-film transistor exhibiting mobility of 1.3 × 10$^{-6}$ cm$^2$ V$^{-1}$ S$^{-1}$. Also, the cobalt-containing 2D films show outstanding electrocatalytic hydrogen evolution characteristics. Recently, our group reported a light-promoted synthesis of scalable 2D COF film on the surface of polarity-controlled precursor solution. We focused on the simple and rapid synthesis of the target COF as a 2D structure without using complex instruments other than the ordinary apparatus for wet chemistry and elucidated the importance of the solvent polarity of the reaction precursor solution. The highly uniform layer of the precursor solution on the water surface makes it possible to control not only the size of the resulting 2D COF film but also the number of layers at a level of single molecular thickness with a 4 inch wafer size.

Also, the liquid–liquid interfacial growth uses immiscible liquid interfaces that enable spatially confined growth of COFs. In general, water is used as one liquid layer, and nonpolar solvents such as chloroform, toluene, or hexane are used as the other layer. Banerjee and co-workers synthesized four types of free-standing 2D COF films (Tp-Ta, Tp-Tba, Tp-Bpy, and Tp-Azo) at the liquid–liquid interface through Schiff base reactions. Control of the growth rate of reaction, which affects the crystallinity of product, was achieved through use of a salt-mediated technique using amine–p-toluene sulfonic acid (PTSA) salts that interact with the amine precursor and slow down the diffusion rate. They used the dichloromethane–water interface as a reaction substrate, which dissolved 1,3,5-triformylphloroglucinol (Tp) and four different types of PTSA–amine precursors, respectively. After 72 h, free-standing and transparent thin films having uniform...
surface and crystalline structure with a thickness in the range from ∼50 to 90 nm were obtained (Figure 2c). More recently, Li et al. synthesized two different 2D COF films, 2DCCOF1 and 2DCCOF2, both of which show highly crystalline structures and have flat and uniform surfaces.9 Different from the conventional synthesis reactions of COFs, they used Suzuki reaction between boronic groups and highly symmetric halogen-containing precursors for the sp2−sp2 carbon bond formation. For the reaction, a precursor solution dissolved in toluene with Pd(PPh3)4 was dropped on the K2CO3 aqueous solution and stored in a refrigerator for a month. The resulting free-standing films show clear electron diffraction patterns that are well-matched with the simulated results. Using the geometrical advantage of large-scale and uniform 2D materials, they fabricated 2DCCOF1-based FET devices. Due to the 2D extended conjugated structure, the resulting device shows a carrier mobility of 3.2 × 10−3 cm2 V−1 s−1, which is one of the highest values in the reported 2D COF films. Also, they confirmed the hydrogen evolution reaction activity of 2DCCOF1 film, which shows an overpotential of 541 mV at a current density of 10 mA cm−2 and Tafel slope of 130 mV/decade.

2-2. Exfoliation/Delamination Method. Because layered materials interact through strong covalent bonds on their planes, while held together by weak van der Waals interactions along the out-of-plane direction, they can be isolated into thin 2D films. Similar to other conventional layered materials, there have been efforts to isolate COF thin films from their bulks by breaking the π−π interaction between layers by mechanical force, sonication in various solvents, and chemical intercalation. Although the small grain size of the parent COF powder limits the large-scale formation of 2D COF films, it is a simple, efficient, intuitive method to obtain mono- or multilayer 2D COF films. In 2013, Banerjee and co-workers synthesized seven different bulk crystalline COF powders, TpPa-2, TpPa-NO2, TpBD-Me2, TpPa-F4, TpPa-1, TpBD-(OMe)2, and TpBD, that show chemical stability in aqueous, acidic, and basic environments.10 After grinding the as-synthesized COFs in a mortar with a small amount of methanol for 30 min, they could obtain 2D COF thin films with thickness of a few nanometers (Figure 3a). The resulting 2D COF films show identical chemical bonds and crystal structures with bulk COFs, which means mild mechanical force efficiently delaminates the COF layers without changes or degradations of chemical bonds and crystal structures. Besides the mechanical delamination method, solvent-assisted exfoliation is one of the simplest and most widely used methods to obtain desired thin-film materials. However, low structural and chemical stability of COFs in various solvents brought difficulties in applying to solvent-assisted exfoliation method. Therefore, Dichtel and co-workers used a newly synthesized acyl-hydrazone containing COF-43 that shows improved chemical/thermal stability and has weak interlayer interactions that are favorable for exfoliation in solution11 (Figure 3b).
They confirmed that the crystal structure and chemical bonds of COF-43 are well-preserved in THF, CHCl₃, PhMe, and MeOH, while the crystallinity is lost in dioxane, H₂O, and DMF due to hydrolysis. After soaking and sonicating bulk COF-43 powder in various solvents for 2 h, the dispersed COF-43 layers were obtained. The resulting COF-43 films have thickness ranging from 3.3 Å to several tens of nanometers according to the solvents, and the obtained films dispersed in dioxane and THF show high crystallinity especially when dissolved in dioxane or THF (Figure 3c and d).

Figure 3. (a) Packing diagrams and HR-TEM images (before and after grinding) of the representative four types of COFs obtained by the aldehyde–amine Schiff base condensation reaction. Reproduced with permission from ref 10. Copyright 2013, American Chemical Society. (b) Schematic representation of exfoliation of COF-43 that yields a suspension of few-layered 2D COF-43 films. TEM images of COF-43 suspensions in (c) THF and (d) dioxane. Insets of c and d are SAED patterns of each film that indicate high crystallinity of COF-43 nanosheets. Reproduced with permission from ref 11. Copyright 2017, American Chemical Society.

Figure 4. (a) Schematic representation of the exfoliation process of DaTp through inducing a bulky functional group using Diels–Alder reaction. (b) SEM image of thin DaTp films on a silicon wafer (scale bar, 5 mm) having a smooth surface. (c) AFM image of a uniform thin film produced from DCM suspensions with high concentrations of DaTp-CON. Reproduced with permission from ref 12. Copyright 2016, Wiley-VCH.
More recently, Banerjee et al. reported a new strategy for obtaining anthracene-containing 2D covalent organic nano-sheets (CONs), DaTp-CONs, using a postmodification-derived chemical exfoliation method. The \([4 + 2]\) cycloaddition reaction of \(N\)-hexylmaleimide molecules and anthracenes in DaTp disturbs the \(\pi-\pi\) interaction of DaTp layers and facilitates their separation (Figure 4a). The postmodified DaTp (DaTp-CON) has almost identical vibrational bands with original DaTp, and additional C−H vibrational bands are newly observed at 2937 and 2857 cm\(^{-1}\) in IR spectra. Different from the morphology of DaTp having a ribbon-like aggregated morphology, after cycloaddition reaction, DaTp-CON shows a thin-sheet-like morphology having a width, length, and thickness of 200, 500, and 17 nm, respectively. Also, they used not only exfoliation methods through additional chemical reactions but also the interfacial method to obtain thin films as large-scale and free-standing structures with tunable thickness. A suspension of DaTp-CONs dissolved in dichloromethane (DCM) was slowly added on the water surface, and after 60 s, transparent, flat, and robust DaTp-CON films having uniform thickness were successfully obtained (Figure 4b and c).

**2.3. Other Methods.** Highly oriented COF films have also been obtained on conventional 2D materials. The atomically flat and ordered atomic structure of the conventional 2D materials allows oriented assembly of organic molecules. In 2011, Dichtel and co-workers synthesized COF-5, the first COF reported by O.M. Yaghi, on a large-scale graphene. They used a conventional solvothermal method for condensation reaction of 1,4-phenylenebis(boronic acid) (PBBA) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) in the presence of graphene on various substrates (Cu, SiC, SiO\(_2\)) in a mixture of mesitylene and dioxane. After 1 h of reaction at 90 °C, COF-5 was obtained in the form of an insoluble powder in the reaction solution and a film on the graphene surface, respectively. Although the thickness of the resulting films was much thicker than the ones prepared by other synthesis methods, they exhibit vertical alignment with a long-range order that is important for their intrinsic electrical and optical properties. Besides graphene, another 2D material, hexagonal boron nitride (h-BN), was also used as a dielectric substrate to...
confirm the electronic property of COF-366 film. Wang et al. synthesized COF-366 films on h-BN through imine-condensation reaction of tetra(p-aminophenyl)porphyrin (TAPP) and terephthaldehyde (TPA) in the presence of exfoliated h-BN transferred to the SiO2 substrate.14 They confirmed that few-layer (5−8 layers) COF-366 films were selectively grown on the h-BN substrate, and the absorption edge of the films red-shifted compared to the bulk COF-366 powder. The resulting COF-366 films on h-BN exhibit p-type semiconducting properties with an on/off ratio of 105 and mobility of 0.015 cm2 V−1 S−1. In addition to the aforementioned synthesis methods, other methods using solvent or precursor including solvent vapor were reported for a simple and efficient method to obtain COF films consisting of unoriented and polycrystalline powder with a thickness of several micrometers.15,16

3. VARIOUS APPLICATIONS OF 2D COF FILMS

Different from bulk COF powders that have been widely studied as gas adsorption or storage material due to their high surface area, low density, and uniform porous structure, the applications of 2D COF films have been mainly focused on utilizing their geometrical advantages. Among various reported applications, we cover three representative applications: semiconducting electronic devices, membranes, and sensors.

3-1. Application to Semiconducting Electronic Devices. Various types of COFs have been studied as potential organic-based electronic materials due to their highly conjugated electronic structure along the in-plane direction and the large π-orbital overlap along the out-of-plane direction. However, bulk COF powders having a rough surface and randomly oriented structure are not suitable for device fabrication to confirm the intrinsic electrical properties of target COFs. On the other hand, highly oriented and uniform 2D COF films not only have suitable geometry for device formations but also allow for structure−property correlation studies. In 2015, Bao and co-workers reported the first field effect transistors (FETs) of 2D COF film, polyTB, synthesized by dehydration reaction of 2,6-dicarbaldehyde-4,8-dioctyloxybenzo[1,2-b:3,4-b′]dithiophene (tapa) and tris(4-aminophenyl)amine (bdta)17 (Figure 5a). To obtain uniform and large-scale thin COF films in intimate contact with the dielectric layer, they reacted tapa and bdta in a covered Petri dish in ambient conditions. After 2 days, highly reflective red films having thickness and roughness of 1.8 and 0.2 nm, respectively, were obtained at the solution/air interface (Figure 5b). The obtained polyTB film was transferred onto a SiO2, and gold was deposited on top of the film for electrical property measurements. The polyTB film transistor shows mobility of 3.0 × 10−6 cm2 V−1 S−1 and an average on/off ratio of 850 (Figure 5c). They revealed that the relatively low mobility of the transistor than calculated values was due to grain boundaries that cause internal defects and loss of crystallinity during the film drying process. Recently, our group reported a highly conjugated crystalline COF (hcc-COF) with an aromatic extended π-conjugated structure18 (Figure 5d). We focused on the synthesis and structural analysis of hcc-COF and studied the effect of electron delocalization on the electrical property along the in-plane direction. We induced an efficient reversible imine condensation reaction that was
critical for reducing structural defects while increasing grain size of the film by adding a small amount of acid catalyst and water. The crystal structure of hcc-COF was confirmed by the Pawley refinement process that shows highly symmetric and extended π-conjugated microporous structure along the lateral direction and has inclined stacking structure due to the interlayer dipole–dipole repulsion force between nitrogen in the pyrazine functional group. To obtain continuous and uniform hcc-COF film, we used a polarity controlled precursor solution that enables uniform floating of precursors on the water substrate. The resulting large-scale and crystalline hcc-COF film shows a clean and homogeneous surface, of which thickness is 3.8 nm that corresponds to nine layers of hcc-COF (Figure 5e). The electrical conductivity along the in-plane direction of hcc-COF film increased depending on the temperature increase, and the measured conductivity in ambient conditions was 0.40 S/m, which is one of the highest conductivity values among not only the reported films but also undoped highly conjugated porous polymer (Figure 5f). The current density–gate voltage curve shows the intrinsic p-type property of the COFTFPY–PPDA and ambipolar charge carrier behavior of the COF/PPDA/graphene as a drain electrode to confirm the vertical electrical property of a COF/PPDA/graphene hybrid structure (Figure 5h). The charge transport along the out-of-plane direction depends on the thickness of BDT-COF due to transport barriers between BDT-COF. The thickness dependence measurements show hole mobilities in the range of $3 \times 10^{-7}$ to $6 \times 10^{-9}$ cm$^2$ V$^{-1}$ S$^{-1}$.

Figure 7. (a) Schematic representation for the synthesis of TpBDH and TfpBDH having different stacking structures. (b) PL quenching toward TNP and (c) degree of fluorescence quenching of TpBDH–CONs with analytes. The quenching constants are in the order TNP ≫ TNT > DNP > DP > DNT. (d) PL spectra of bulk TpBDH and TfpBDH–CONs. CONs exhibited an ~90 times stronger PL intensity compared to that of bulk COFs. (f) PL spectra showing PL enhancement of different analytes with TfpBDH–CONs. The PL spectrum of TN-added CONs was red-shifted and showed enhanced PL intensity due to interaction with the nitrogen atom of TNP and imine bond of CONs. Reproduced with permission from ref 24. Copyright 2015, Royal Society of Chemistry.
Membrane materials have been widely studied as selective barriers for molecules, ions, or small particles for applications in various fields. Compared with other membrane materials, COFs received special attention due to their low density, high surface area, controllable pore size, and crystalline structure. The development of various synthetic strategies for highly oriented and uniform COF films facilitates their applications for separation of organic solvents, salts, and toxic gases. Recently, Lai and co-workers synthesized well-defined porous COF, DFP-DHP COF, through a two-step reaction: the first step is the Schiff-base condensation reaction of 1,3,5-triformylphloroglucinol (TFP) and 9,9-dihexylfluorene-2,7-diamine (DHF), and the next step is an irreversible tautomerism reaction to form a β-ketoenamine structure to maintain the integrity of the structure21 (Figure 6a). The surface of the resulting DFP-DHP COF films obtained at the air–water surface using a Langmuir–Blodget method was uniform and smooth with ca. 0.5 nm of roughness (Figure 6b). To confirm the permeability of organic and inorganic solvents such as water, ethanol, or hexane, DFP-DHP COF films obtained at the air–water surface using a Langmuir–Blodget method was uniform and smooth with ca. 0.5 nm of roughness (Figure 6b). To confirm the permeability of organic and inorganic solvents such as water, ethanol, or hexane, DFP-DHP COF films having 15, 20, and 30 numbers of layers (M15, M20, and M30) were transferred on anodic aluminum oxide (AAO). Regardless of the layer number, the 2D TFP-DHP membrane shows outstanding permeabilities for both polar and nonpolar organic solvents and high rejection rate with a high molecular weight retention onset and molecular weight cutoff value of 600 and 900 Da, respectively (Figure 6c and d). Also, Banerjee and co-workers synthesized four types of COF films (Tp-Bpy, Tp-Azo, Tp-Ttba, Tp-Tta) at the water–chloroform interface for nanofiltration application.8 Among the four types of COFs, Tp-Bpy and Tp-Azo films with large pore sizes (25 and 16 Å, respectively) were used for the separation of dye molecules that are one of the abundant impurities in the wastewater generated by dye-manufacturing processes. Four organic dye molecules, brilliant blue-G (BB), congo red (CR), acid fuchsin (AF), and rhodamine B (RH), were used as target dyes, and their aqueous solutions were passed through the membrane cell at 0.5 bar upstream pressure. The presence of dyes is confirmed by measuring UV–vis spectra. Both Tp-Bpy and Tp-Azo films showed high solute-rejection performance for various dyes, and especially, Tp-Bpy and Tp-Azo films exhibited a high rejection ratio for RH as high as 98% and 99%, respectively. Using a different rejection ratio, selective separation of p-nitrophenol (NP) was successfully achieved from a mixture of NP and AF. In addition, there are several computational studies in the gas separation property of ultrathin COF films.22 Zhong et al. reported the intrinsic features of triazine-based COF, CTF-1, as an ideal membrane for gas separation.23 Through systematic study using a series of few-layered CTF-1 films for CO2 and N2.

Figure 8. (a) TEM image of TPA-COF NSs obtained by the solvent-assisted exfoliation method. Inset: Photograph of the Tyndall effect of the TAP-COF NS suspension. (b) AFM image of TPA-COF NSs with the indicated thickness. (c) Low-dose high-resolution motion-corrected TEM image of a typical TPA-COF NS showing clear hexagonal lattice structure. (d) Schematic illustration of a TPA-COF NS-based fluorescence sensor for detection of DNA. (e) Fluorescence spectra under different experimental conditions: (I) H1 + H2; (II) H1 + H2 + T + TPA-COF NSs; (III) H1 + T + TPA-COF NSs; and (IV) H1 + H2 + TPA-COF NSs. The concentrations of H1, H2, T, and TPA-COF NSs in the final solution are 50 nM, 50 nM, 5 nM, and 12 μg mL−1, respectively. Inset: Kinetic study on the fluorescence change of H1 + H2 and H1 + H2 + T in the presence of TPA-COF NSs. As the concentration of T increases, the fluorescence intensity increases. Reproduced with permission from ref 25. Copyright 2017, American Chemical Society.
separation, they demonstrated that regulation of the membrane size through stacking structure control was important to obtain a highly selective membrane, and also, tuning the stacking modes of CTF-1 film can construct a favorable microenvironment that allows membranes with high flux and high selectivity.

3-3. Application to Sensors. One of the biggest advantages of COFs than other 2D materials is their easy chemical modification that can affect not only their intrinsic electrical and optical properties but also reactivities with other molecules, which allows the modulation of selectivity of COF sensors to various target materials. Not only 2D COF films but also bulk 2D and 3D COFs have outstanding high surface area like other porous materials, which is essential for efficient sensing applications. However, randomly oriented and aggregated powder structures not only reduce reactivity with target molecules but also give geometrical limitation in device fabrication for electrical and optical sensing applications. In addition, the uniform and flat surface of highly oriented 2D structure significantly increases area-to-volume ratios and improves sensitivity toward target materials, while reducing the impact on grain boundaries or chemical defects. Therefore, the 2D COF having highly oriented and uniform film structure is essential for sensing application of COFs.

In 2015, Banerjee and co-workers synthesized two types of COFs, TpBDH and TfpBDH, which were synthesized by the imine condensation reaction of pyromellitic-\(N,N'\)-bisaminoamide (BDH) and formyl-containing precursors (1,3,5-trisformylphloroglucinol (Tp) and 1,3,5-tris(4-formylphenyl)benzene (Tfp), respectively) (Figure 7a). After solvothermal synthesis of bulk TpBDH and TfpBDH powders, they obtained covalent organic nanosheets (CONs) by dispersing and sonicating them in isopropyl alcohol for 45−60 min. The resulting flat and thin TpBDH and TfpBDH CONs have a uniform surface with 0.45 nm and 0.43 periodic lattice fringes, respectively, with a thickness of several nanometers. Different from TpBDH and TfpBDH−CONs that have no photoluminescence (PL) activity due to the disturbance of \(\pi\)-conjugation caused by enol-keto tautomerization, TfpBDH and TfpBDH−CONs with extended \(\pi\)-conjugation structure show intensive PL. Considering higher PL activity, they observed optical sensing behavior of TfpBDH depending on the different nitro-aromatic analytes: 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), 2,6-dinitrophenol (DNP), 2,6-dinitrotoluene (DNT), and 2-nitrophenol (NP) (Figure 7b and c). Interestingly, TNP shows high PL.

Figure 9. (a) Experimental scheme and molecular structure of the \(\pi\)-COF obtained by dehydration between two precursors. (b) Optical microscopy image of the 2D \(\pi\)-COF film transferred on a SiO\(_2\)/Si substrate having uniform surface without notable physical defects. (c) On−off switching behavior upon moisture exposure to the 2D multilayer Lp-\(\pi\)-COF film device. The drain current significantly increases in the presence of water molecules due to hydrogen bonding between water and \(\pi\)-COF. Reproduced with permission from ref 7. Copyright 2018, American Chemical Society.
quenching efficiency of 63% in dispersed TfpBDH–CON solution due to photoinduced charge transfer between the TNP anions and protonated TfpBDH–CONs. On the other hand, bulk TfpBDH–CONs that drop-dried on a solid substrate show highly enhanced PL intensity caused by proton transfer from TNP to basic nitrogen atoms of the imine bond (Figure 7d and f). The simultaneous turn-on/-off sensing properties of 2D COFs provide potential sensing applications of various 2D COFs in bulk and dispersed states. Also, Zhang et al. used the COF as a novel fluorescence sensing material for highly selective and sensitive DNA detection. They synthesized crystalline bulk TPA-COF powder using solvothermal reaction of tris(4-aminophenyl)amine (TAPA) and tris(4-formylphenyl)amine (TFPA). After synthesis, products were exfoliated by the solvent-assisted liquid exfoliation method for obtaining highly uniform and crystalline 2D TPA-COF nanosheets (NSs) with thickness of 3.4–3.8 nm (Figure 8a–c). For DNA sensing, they used two types of hairpin DNA probes, H1 (labeled with a fluorescent dye) and pure H2. When H1 and H2 are adsorbed on the COF NSs, the fluorescence of H1 is rapidly quenched through π–π stacking interactions. However, H1 and H2 make a hybridization chain in the presence of target DNA (T), resulting in the recovery of fluorescence (Figure 8d). The quenching efficiency is 90% in 15 min, and fluorescence is greatly retained even in the presence of TPA-COF NSs, which is comparable with or even better than other 2D material-based DNA sensors (Figure 8e).

Last year, our group synthesized uniform and layer-number controllable polyimine-based COF (π-COF) film at the water surface using polarity-controlled precursor solutions for uniform floating of precursors (Figure 9a and b). For device fabrication to obtain flat and large-scale π-COF films, metal electrodes were deposited on top of the surface using a shadow mask. Although the fabricated π-COF film devices show relatively low electrical conductance ($2 \times 10^{-9}$ S), the drain current drastically increases in the presence of water vapor from 400 nA to 100 μA at $V_{ds}$ of 20 V due to water capture through hydrogen bonding between the imine functional group and water molecules (Figure 9c). Our result is the first report of a COF 2D film as an electrical chemisorption sensor. These interesting sensing properties of various COFs suggest the potential applications as a highly sensitive sensor material.

4. CONCLUSION

In this review, we introduced the efficient synthesis methods and important applications of highly oriented and uniform 2D COFs investigated so far. The development of new synthesis methods of 2D COFs that show outstanding chemical stability, structural regularity, and high crystallinity over a large area extended their potential for various applications. However, there are still many issues that have to be solved. For example, the absence of a critical tool for identifying defect sites and grain boundaries prevents understanding the intrinsic properties and growth mechanism of various 2D COFs. If we identify accurate growth mechanisms and optimize the synthetic conditions of 2D COFs, not only high-quality but also scale-up production will be realized.

Synthesizing COFs is like assembling LEGO at the molecular level. Like atoms gather together to form molecules, many organic molecules become COFs in different structures with different properties through fundamental chemical reactions. In the near future, we believe that 2D COFs could be the leading and representative organic 2D materials with multifunctional properties through the development of specific building blocks having desired properties.

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