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Perspective

# Have Covalent Organic Framework Films Revealed Their Full Potential?

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**Abstract:** Porous organic polymers provide high accessible surface areas, which make them attractive for gas storage, separation, and catalysis. In addition to those classical usage areas, such compounds are particularly interesting for electronic applications since their high dimensional, electron-rich backbone provides advanced electronic and photophysical properties. However, their non-soluble nature is a challenge for their processability, especially in the case of film formation, hence their limited utilization in organic electronic devices so far. Nevertheless, there are several techniques presented in the literature to overcome that issue, most of which were on the crystalline porous organic polymers, namely covalent organic frameworks (COFs). In this perspective, the developments on COF film formation and prospects for the improvements are discussed with suggestions to further their performances in organic electronics.

**Keywords:** porous materials; porous organic polymers; covalent organic frameworks; COFs; porous films; thin films; organic electronics



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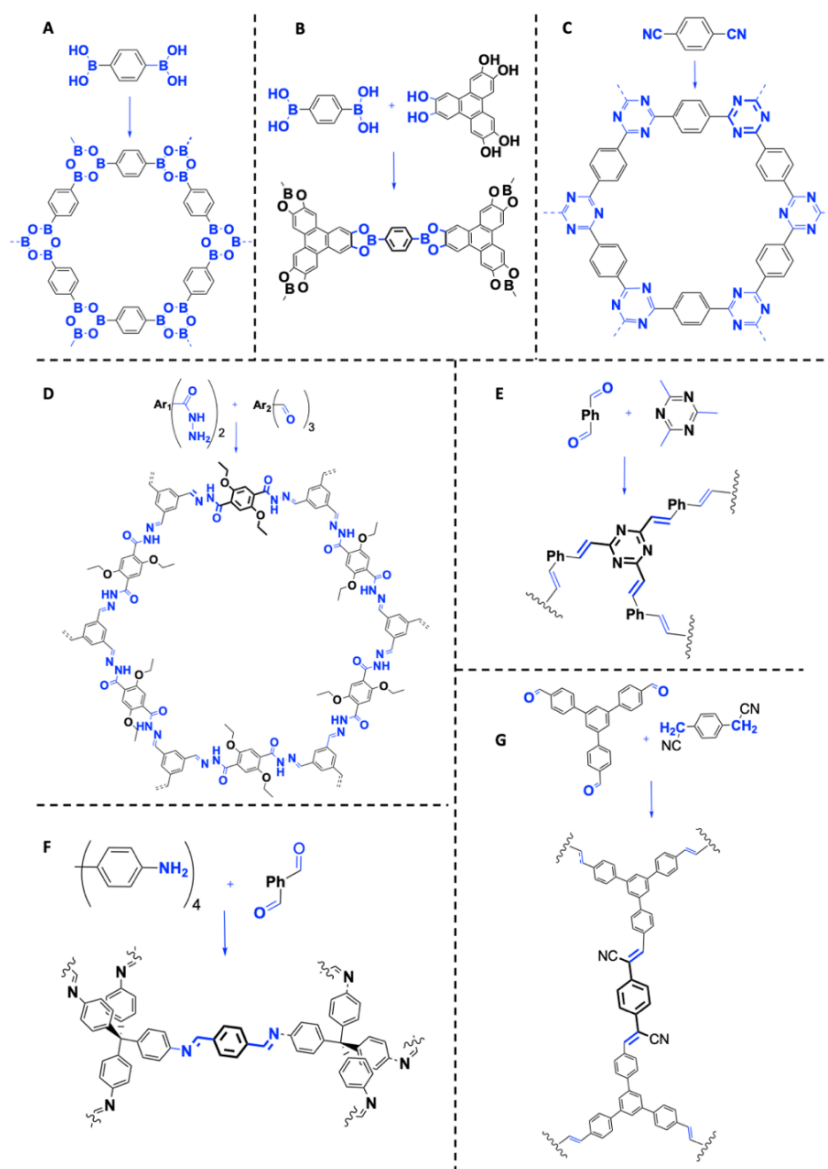
## 1. Introduction

Porous materials have been used in a great range of applications from gas storage, separation to catalysis, and have shown excellent performances thanks to their accessible high surface areas and structural diversity [1,2]. Such materials can be molecular or polymeric, in solid or liquid forms (recently porous glasses have been promoted as a sub-form), and are categorized into three groups depending on their building-blocks; inorganic (e.g., zeolites, porous carbon), organic-inorganic hybrid (e.g., metal-organic frameworks (MOFs), organosilicas), and fully organic porous materials (e.g., conjugated microporous polymers (CMPs), covalent organic frameworks (COFs)) [3].

Each of the above classes has its advantages or disadvantages for the corresponding usage areas, which make them unique for various applications [4]. For example, fully inorganic porous materials provide very good hydro-thermal stability; thus, they are preferred for high-temperature catalytic reactions [5,6]. On the other hand, MOFs have been the most attractive sub-class amongst porous materials [7–10], from which the highest surface areas were reported until now [11]. The last group, fully organic porous materials, are particularly promising for photocatalysis and electronics due to the easier tunability of their backbone via combining different electron-donating/accepting moieties bearing task-specific functionalities [12,13]. Since this perspective will focus on the developments and further challenges of (crystalline) porous organic polymer film formation and their utilization in organic electronics, discussions on other classes henceforth will be omitted.

The suitable building blocks to produce porous organic polymers should be rigid and should not possess bulky side groups. The former is important to prevent the collapse of the structure through the empty voids (pores) and the latter is necessary to avoid pore blockage. Moreover, the polymerization direction should not be linear, therefore, at least one of the (co)monomers should be angled. These struts are named as structure directing motives or tectons [14], which are generally crosslinkers.

Common methods for COF syntheses involve hydrothermal and ionothermal techniques by using either thermal or microwave heating [15,16]. Additionally, other routes such as light irradiation and using catalysts to produce COFs under ambient conditions were also reported [17–19]. COF formation reactions mostly take place in a closed cup (i.e., in an autoclave equipped with a Teflon inlet) for extended periods (up to 5 days) in order to yield the most thermodynamically stable, non-soluble, and crystalline product through dynamic covalent chemistry (DCC) [20]. It is worth noting that DCC requires specific end groups and reaction mechanisms (some popular examples can be seen in Figure 1) allowing the reversible reactions for structural error-check and fixing [21,22]. On the other hand, standard *put and stir* techniques lead to the most kinetically favorable products which generally yield an amorphous backbone, among which the most famous ones are CMPs, polymers with intrinsic microporosity (PIMs), and porous aromatic frameworks (PAFs) [23].

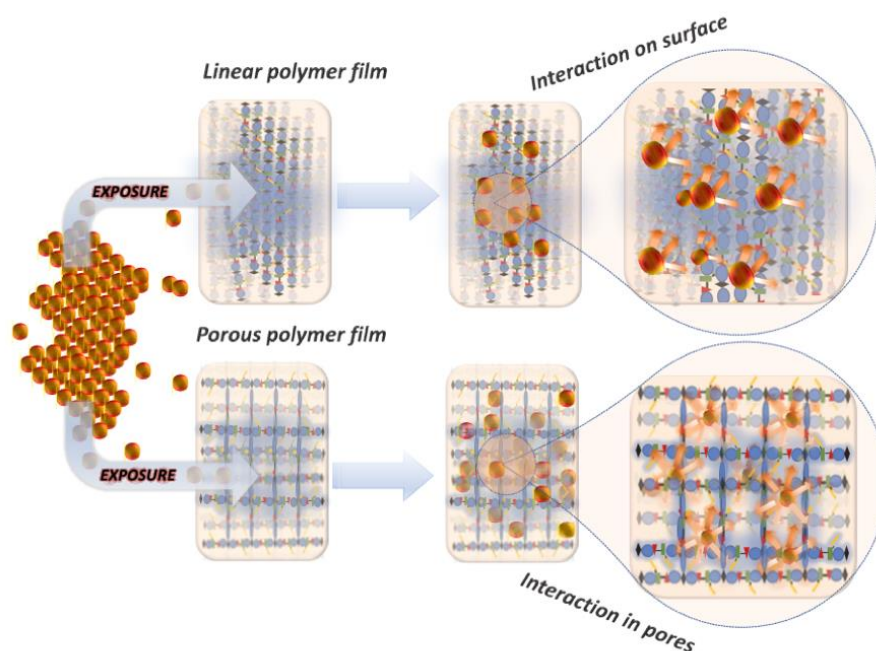


**Figure 1.** Examples of different reactive groups which allow DCC for COF formation and corresponding connecting moieties; (A) boroxine [24], (B) boronate ester [24], (C) triazine [25], (D) hydrazone [26], (E) vinylene with triazine [27,28], (F) imine [29], (G) full vinylene C-C bonded [30,31] (see the following references for full structures).

## 2. Techniques for Covalent Organic Framework Film Formation

The moderate–high surface areas and (hydro)thermal stability of porous polymers allow them to exhibit comparable performances with their fully inorganic and organic–inorganic hybrid cousins for the common application areas listed above. That being said, the porous and high dimensional backbone of such organic compounds make them more attractive for light-driven and electronic applications such as sensing, photocatalysis, and organic electronics [13,32–39]. This is because the empty voids inside the pores are perfectly separated phases allowing enhanced charge-transfer with the prospective guests (i.e., analytes for sensors or fullerenes for bulk-heterojunction photovoltaic devices) while high dimensionality provide direction-independent electronic conductivity (i.e., no face-on/edge-on limitations which occur in the devices built by using 1D polymers) through the devices [33,35,40–43].

As is illustrated in Figure 2, the guests expected to be placed in the pores rather than populating on the surfaces of porous polymeric compounds. Similar conclusions were drawn through computational techniques [44,45]. Moreover, those studies indicated the interferences along  $\pi$ -electrons are the main driving forces for the host-guest interactions in case of such electron-rich, conjugated host-guests [44,45]. The quench of photoluminescence after nitrobenzene (electron acceptor) exposure during the optical sensing applications can be a good experimental proof for this behavior [33,46–49].

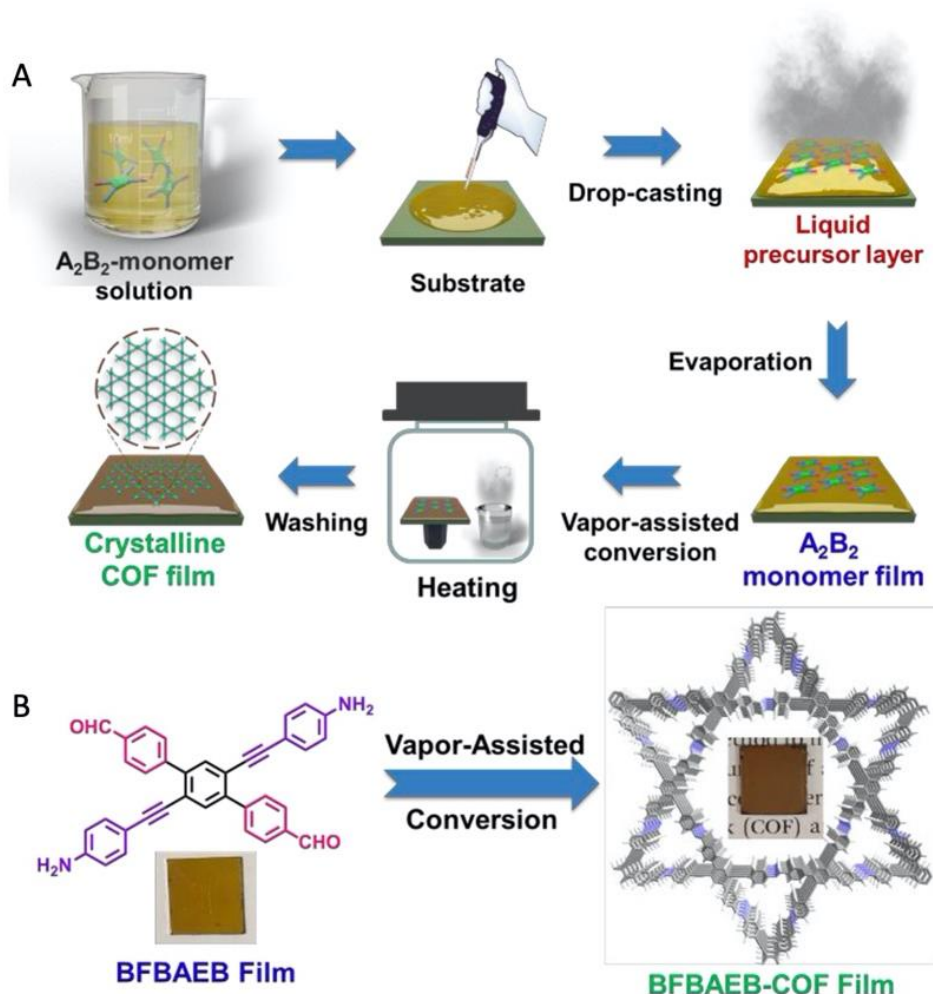


**Figure 2.** Illustration of the films formed from linear and porous polymers, and the comparison of their interaction with the guests or analytes after exposure.

Since porous organic polymers have a non-soluble nature (except some PIMs) due to their highly rigid, branched, long-alkyl-free backbone, forming uniform films from those compounds has been a challenge for their integration to devices, hence their limited utilization for electronic applications [50]. Indeed, there have been several attempts to overcome this issue [41,51]. The frequently used method to produce COF films is their in-situ formation over the substrates placed in the reaction media [52,53]. The tricky part of this method is to place the active side of the substrate face-down (to the bottom of the reaction vessel) to prevent agglomeration of the big particles on the film surface.

Another similar approach is the vapor-assisted film formation, which is basically drop-casting of the co-monomers and allowing them to react in a closed cup with the help of solvent vapor (Figure 3) [54,55]. The film properties can be adjusted by changing the vapor exposure time, concentration of the co-monomers, and the coating style

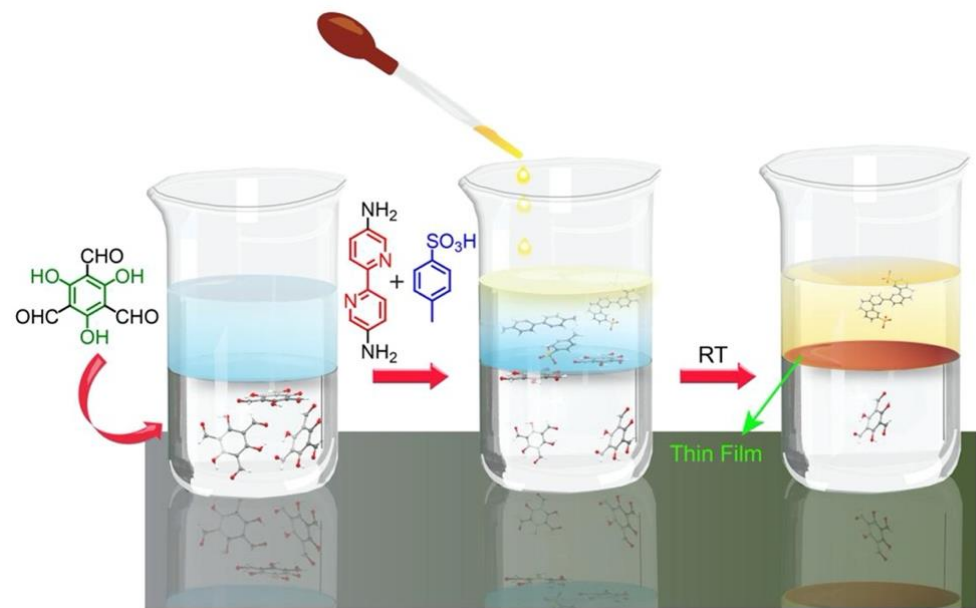
(e.g., spin coating, drop-casting, dip coating), which gives more control on the output when compared to the previous “in-situ” method.



**Figure 3.** (A) Schematic description of vapor-assisted conversion of monomer film to COF film and (B) the pictures of monomer film and COF film (reproduced from Ref. [55] with permission CCS Chemistry).

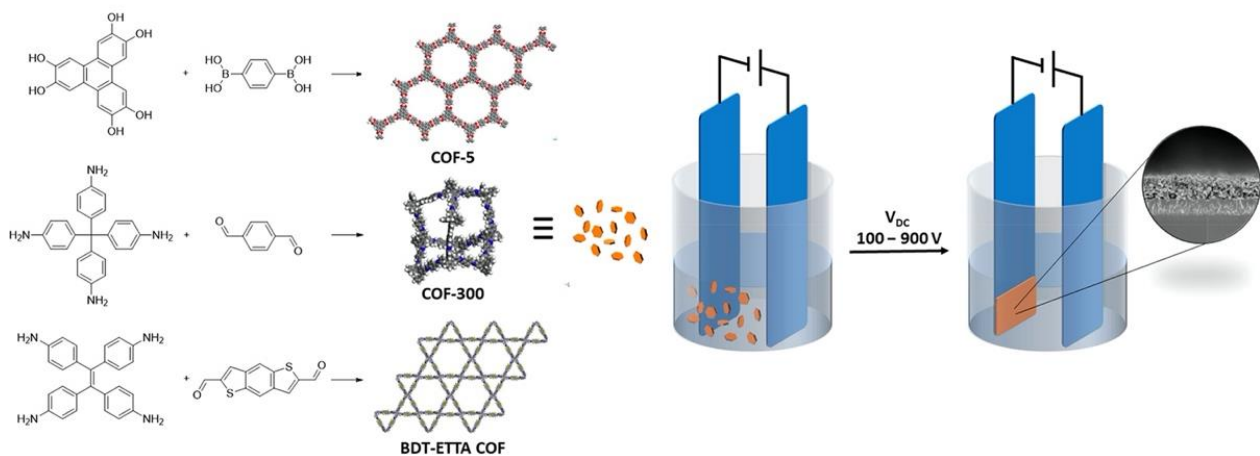
The use of flow chemistry to produce uniform COF films was also presented [56]. Since the flow technique allows large-scale and continuous production, the method is rather intriguing for the industry. Moreover, the study shows the flow technique enables more control over the film formation kinetics when compared to the above mentioned in-situ method (statical film formation in bulk) [56]. Aside from adjusting the (co)monomer concentrations poured over the substrate, reaction temperature and residence time in the reactor can be key factors to control film properties. Notwithstanding the amorphous nature of the final material, a similar method was applied to form PAF films over pre-functionalized substrates [57], and the findings showed that flow chemistry helped to improve film quality with respect to the previously published bulk method [58].

In-situ forming free-standing COF films on the surface of the reaction media (i.e., liquid + air interface) [59,60] or between the heterogeneous liquid-liquid mixtures (i.e., water phase + organic phase) [61,62] have been attractive methods as well. The latter technique has been applied more frequently probably due to easier handling and the possibility of controlled large-area free-standing film production, which has expanded the application areas of COF films to gas separation products (Figure 4) [63–66].



**Figure 4.** COF film formation via liquid-liquid interface method (Reproduced from Ref. [64] with the permission from American Chemical Society).

Aside from growing COFs on the substrates from precursors, depositing the formed COF particles on surfaces has also been studied. There are examples of forming COF films from their dispersed powders via spin-coating, and the films obtained were able to be utilized in solar cells [67,68]. Additionally, suspending COF powders in a highly viscous polymer matrix and the subsequent film formation was also reported, and the films were applied in organic light-emitting diodes (OLEDs) [69]. Synthesis of colloidal COF particles and the subsequent casting of their films from those solutions were also presented [70]. Spray coating of COF powders dispersed in inks to yield large area COF films was another interesting method [71]. Moreover, electrophoretic deposition of COFs onto substrates was also successfully presented in the literature (Figure 5) [72]. Aside from reporting a novel method for COF film formation, another interesting piece of information in this article was the deposition of all of the three structurally different COFs (see Figure 5) took place on the positive electrode due to their negative surface potential [72].



**Figure 5.** Electrophoretic deposition of COF particles on substrates (reproduced from Ref. [72] with permission from American Chemical Society).

In addition to the above methods focusing on the crystalline porous organic polymers, it is worth mentioning that electrochemical polymerization was also applied to yield

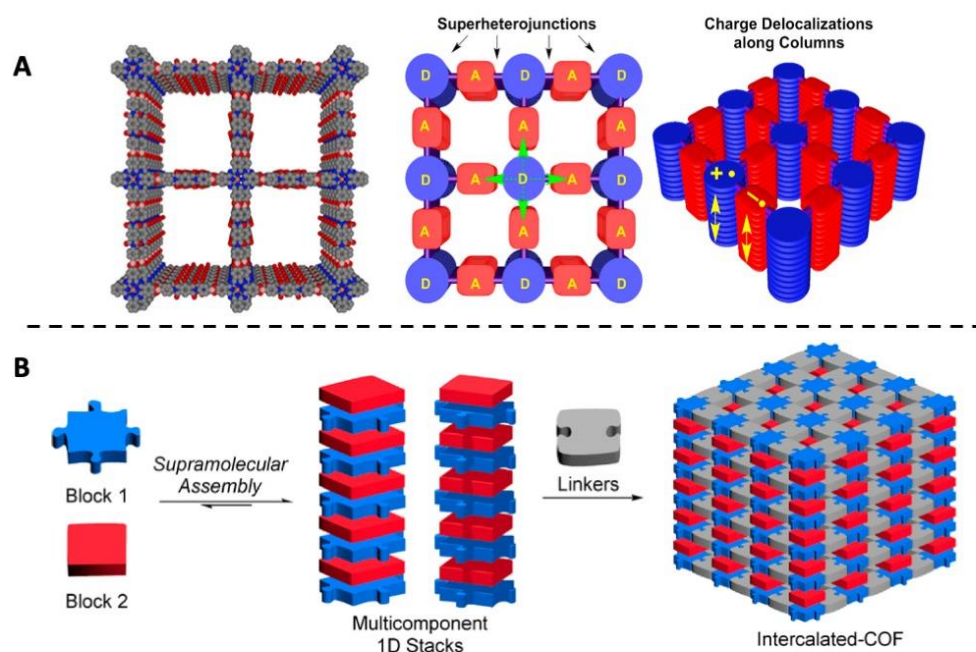
amorphous porous organic polymer films [73]. Crosslinking of electrochemically active monomers under suitable potentials yielded highly porous films, which were applied in sensors and organic electronic devices [74–80]. Moreover, thin films of long alkyl chain bearing CMP-like structures (conjugated and hyper-branched, yet non-porous due to the pore blockage of the bulky alkyl groups) were formed via classical techniques (e.g., spin coating from the homogenous solutions), and successfully applied in photovoltaics [81–83].

### 3. Outlook and Conclusion

Although there have been many approaches to form uniform films from (crystalline) porous organic polymers, their full potential in organic electronics has not been revealed. Several reasons can be speculated for this issue; for example, the structural torsion, defects, and grain boundaries over the formed films affecting uniformity and pore accessibility [84–86]. Especially the last one should not be underestimated since it can happen due to various issues such as hindered catalysts/monomers in the voids or partially blocked pores due to poor solvent removal (pore activation). Moreover, even though the COF films look smooth and uniform just after casting, accessibility of pores may change during processing or device operation. For example, some devices operate under elevated temperatures which may lead to evaporation of solvents stuck in the pores, which can result in altered porous structure or shrinking of the films [87].

Aside from developing strategies for film formation, thinking over the structural properties of COFs planned to be filmed should also be considered for improvement [88,89]. For example, limited conjugation through the common connection moieties (e.g., boronic acid esters, hydrazones) or traditional cross-linkers (e.g., triazine, triphenylamine, triphenylene) lead to short conjugation lengths through the branched polymer chains [90]. For the former, investigations concentrated on the COFs connected by vinylene ( $-C=C-$ ) bonds can be a solution [91] while introducing crosslinkers allowing extended conjugation such as spirobifluorenes [92,93] can help to overcome the latter. Furthermore, given most of the COFs are 2D, the formed films can still suffer from orientation issues despite the high-dimensionality since 2D COFs have a tendency to form “face-on” films [94]. In that case, the crosslinkers like spirobifluorenes can also help to increase the dimensionality of the sheets from 2D to 3D and may lead to better hole/electron conductivity through devices [40].

On the other hand, it is better to keep in mind that mixing the conventional and unconventional can yield unique behaviors, which may lead to revolutionary outputs. Therefore, rational design strategies to combine those variables should be an option to enrich the portfolio of such materials. For example, the cross-conjugation [95] in common COFs can also be an asset for electronics [49,96] as well as some irregularities along the structure [97,98]. Furthermore, donor-acceptor COFs have a tendency to form nearly perfect donor-donor and acceptor-acceptor eclipsed stackings leading to excellent charge separation and extended bicontinuous electron/hole conducting columns (Figure 6A), which is unlike slipped/tilted alternating intermolecular donor-acceptor overlaps of the ordinary (linear and soluble) conjugated polymers [99–102]. Yet, this strict order in COFs might also result in a poor charge delocalization through the COF interlayers [103]. Recently, Li et al. showed it is possible to react a donor-acceptor charge-transfer complex via DCC to form COFs [104]. In that work, an aldehyde functionalized acceptor unit previously interacted with a non-functionalized donor compound to produce the charge-transfer complex, which was further reacted with an imine crosslinker to yield a COF having donor-acceptor stackings (Figure 6B) [104]. Additionally, performing band-gap engineering via post-synthetic linker exchange on already formed COFs or in-situ *linker doping* may result in alternation on the structure, and lead to interesting electronic properties [105–109].



**Figure 6.** Donor-Acceptor COF structures: (A) Eclipsed donor-acceptor stackings of common COFs and their perfectly separated bicontinuous electron-hole columns (reproduced from Ref. [100] with permission from American Chemical Society) (B) Electron poor COF sheets intercalated with electron-donating moieties (acceptor = blue, crosslinker = gray, donor = red, reproduced from Ref. [104] with permission from American Chemical Society).

In conclusion, intensive investigations in COF films started a decade ago and topped last year. Thus, the recent developments on the characterization methods with adaptation of advanced techniques will indeed improve the understanding on the fundamental properties of COFs, which will surely lead to their better utilization [84,85,110–112]. Furthermore, increasing numbers of consortiums on solar fuel production will pave the way for further collaborations with expert researchers in organo-electronics and porous materials, which will probably result in better integration of COFs to organic electronic devices, and help them to demonstrate their full potential.

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