Well-defined two dimensional covalent organic polymers: rational design, controlled syntheses, and potential applications
Well-defined two dimensional covalent organic polymers: rational design, controlled syntheses, and potential applications

Zhonghua Xiang, a Dapeng Cao b and Liming Dai *a

Two-dimensional (2D) covalent organic polymers (COPs) and derivatives hold great potential for a large variety of applications, including gas storage, sensing, energy conversion and storage, and electrocatalysis. Moreover, 2D COPs offer excellent opportunities for fundamental study on an exciting class of new polymeric materials with unique 2D structures and novel properties. However, the design and synthesis of well-defined 2D COPs remain a big challenge. In this article, we review recent progress on 2D COPs and their derivatives. Some concepts on the rational design and syntheses of well-defined 2D COPs and their derivatives are discussed, along with their potential applications as well as the perspectives and challenges in this emerging field.

1. Introduction

Synthetic polymers exhibit a wide range of useful properties that can influence most aspects of our modern life. Various polymerization methods have been devised to produce macro-molecules of different topologies (e.g., linear, branched) with well-defined structures and properties.1 However, the synthesis of two-dimensional covalent organic polymers (2D COPs) and derivatives is a recent development in the polymer field.2,3

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The recent discovery of graphene has caused a surge of interest in the research and development of 2D materials and opened up a new era for 2D COPs. The 2D single atomic thick carbon sheet of graphene is a building block for carbon materials of all other dimensionalities, including 0D buckyballs, 1D nanotubes, and 3D graphite. Having a one-atom-thick layer of sp2-bonded 2D honeycomb lattice carbon, graphene possesses a high aspect ratio (the ratio of lateral size to thickness), large surface, excellent charge carrier mobility, and good mechanical properties. The unique structure and properties make graphene and its derivatives very promising for a wide range of potential applications, including electronics, sensors, energy storage and conversion, and electrocatalysis. Similar to graphene and its derivatives, 2D COPs with precisely-controlled molecular structures and holes incorporating metals (i.e., Fe, Co, Mn) or not incorporating them, have recently been demonstrated to show potentials for a wide variety of applications, including energy conversion and storage, gas storage and separation, sensing, and catalysis, to name a few. As a vital class of COPs with predesigned skeletons and nanopores of atomic precision, covalent organic frameworks (COFs) have rapidly developed since the appearance of the first report on COF in 2005. Owing to their high porosity, well-defined molecular structure, and multi-functionalities, COFs show great promise for various applications, ranging from gas storage through catalysis to optoelectronics. Since the research and development of graphene have been extensively reviewed, we mainly focus in this review article on COPs and derivatives by summarizing recent important developments in this emerging field of active research and presenting critical issues, challenges, and perspectives. Some brief discussions on potential applications of COPs and their derivatives are also given in the sections as appropriate. It should be mentioned that 3D crystalline or amorphous COP materials have also been extensively designed and synthesized from some of the rigid monomers mentioned in this review with various polymerization methods. Since the development of 3D COP materials has been recently reviewed, we focus on 2D COPs in this article.

2. Rational design

To make 2D COPs with a well-defined structure, the first important step is to design molecular geometries of the building blocks. Typically, rigid building blocks are used to prevent the networks from collapsing and to construct the networks in free space in an efficient manner. To this end, chemists often employ aromatic monomers and their derivatives, linked either directly together or through other rigid molecular linkages. Fig. 1 schematically shows six typical building blocks (i.e., B2, B3, B4, B4a, B4b, and B6), along with possible COPs resulting from them. The arrows in all of the different types of building blocks refer to the active sites for connecting with other building blocks, while the core in each of the building blocks represents the various backbones to be built into the resulting 2D COPs via self-condensation or cross coupling. As can be seen in Fig. 1, symmetric building blocks B3 and B4 tend to form the honeycomb COP P3 (Fig. 1c) and P6 (Fig. 1f), respectively. The cross building block B4a can form the 2D Kagome network P4a-1 and diamond polymer P4a-2 (Fig. 1d), and the symmetric cross building block B6 forms square 2D polymer P4b (Fig. 1e). Compared with the above building blocks, the T-shaped building block B7 is most complicated, from which four possible 2D COPs can form, depending on the directions for each of the building blocks to point to during the coupling (Fig. 1b). On the other hand, the simplest linear building block B2 (Fig. 1a) alone cannot ensure the formation of 2D COP, but can be incorporated into the COPs formed by other building blocks to extend the 2D topology. The molecular structures for some representative building blocks are summarized in Fig. 2. To date, there are many reported 2D polymers constructed from B2, B3, B4a, B4b, and B6. However, 2D COPs based on the T-shape building block B7 have been rarely reported, presumably because it is difficult to form the three 90°-angled active sites using the rigid aromatic moieties due to their strong steric hindrance. Nevertheless, certain T-shaped macromolecules have been constructed through the coordination of metal ions with organic linkers, though it is still a challenge to design and synthesize T-shaped organic building blocks in general.

3. Controlled syntheses

3.1 Solution condensations

To synthesize the rationally designed 2D COPs, various solvothermal methods, including the boronic acid-based condensation, Schiff-base reaction, cyclotrimerization, phenazine ring fusion reaction, Suzuki cross-coupling
reaction,54,55 Yamamoto reaction,17,56–61 Sonogashira–Hagihara reaction,62,63 oxidative coupling,64,65 and Friedel–Crafts arylation,66,67 have been extensively reported, along with the microwave68–70 and solvent-free mechanical methods.71 The availability of the aforementioned wide-ranging synthetic methods,16 together with the wide diversity of building blocks

Fig. 1 Main building blocks for 2D COPs, and strategies for 2D polymerization. (a) A linear building block $B_2$, which can be combined with other building blocks in (b), (c), (d), (e) and (f) for lengthening the structures of 2D COPs. (b) T-shaped building block $B_T$ and possible structures for the resulting 2D COPs. (c) 1,3,5 Centrosymmetric building block $B_3$ for forming 2D COPs with honeycomb-like structures. (d) Rhombus-shaped building block $B_{ab}$ and the corresponding 2D COP structure. (e) Cross-shaped building block $B_{ab}$ and the corresponding 2D COP structure. (f) 1,2,3,4,5,6 Centrosymmetric building block $B_6$ and the corresponding 2D COP structure. ‘B’ refers to the ‘building block’ and ‘P’ refers to the resulting ‘polymer’.

Fig. 2 The representative molecular structures of the building blocks shown in Fig. 1. R in each of the organic linkers can be one of Br, B(OH)$_2$, NH$_2$, CN, CHO, I, Cl, OH, N$_3$, alkyl, or thienyl group.

reaction,54,55 Yamamoto reaction,17,56–61 Sonogashira–Hagihara reaction,62,63 oxidative coupling,64,65 and Friedel–Crafts arylation,66,67 have been extensively reported, along with the microwave68–70 and solvent-free mechanical methods.71 The availability of the aforementioned wide-ranging synthetic methods,16 together with the wide diversity of building blocks
already reported (Fig. 1 and 2) and more to be developed, provide an invaluable platform for developing a large variety of new 2D COPs.

Three major reversible reactions, mainly including boronic acid-based condensation, Schiff-base reaction, and cyclo-trimerization, are the most common synthetic approaches to crystalline COPs and their derivatives. The mechanistic studies indicate the involvement of both dynamic covalent bond formation and irreversible precipitation in these reversible reactions.\textsuperscript{72} In the synthesis of COF-5, for example, Dichtel's group found the occurrence of COF-5 precipitation by monitoring the optical turbidity under homogeneous growth conditions, and the increase in the crystalline domain size by water addition.\textsuperscript{72} Fig. 3 shows the first two popular coupling schemes (\textit{i.e.}, Boronic acid-based condensation and Schiff-base reaction), along with some representative structures for the resulting crystalline COF materials of large pore size. Using 2,3,6,7,10,11-hexahydroxytriphenylene (HTTP) and $N,N'$-dii-(4-borophenyl)naphthalene-1,4,5,8-tetracarboxylic acid diimide (NDIDA) or $N,N'$-di(4-boronophenyl) pyromellitic-1,2,4,5-tetracarboxylic acid diimide (PyrDIDA) via the boronate ester approach, Jiang’s group prepared, in 2013, two COF materials (\textit{i.e.}, DTP-ANDI-COF and DTP-APyrDI-COF, Fig. 3a) with the largest pore size (5.3 nm) among the COP materials reported to date.\textsuperscript{73} More recently, Fang et al. reported a 2D crystalline polyimide COF with the same pore size of 5.3 nm (\textit{i.e.}, PI-COF-3, Fig. 3b) \textit{via} the Schiff base reaction between pyromellitic dianhydride and the extended triamine 1,3,5-tris[4-amino-(1,1-biphenyl-4-yl)]benzene.\textsuperscript{74} Apart from these 2D COFs with large pore size, many other well-defined COFs have also been synthesized by polycondensation of those various aromatic-based monomers (\textit{cf.} Fig. 2).\textsuperscript{19,30} Along with the development of COFs through boronic acid-based condensation and Schiff-base reaction, triazine-based crystalline COFs (triazine-based frameworks: CTFs) \textit{via} trimerization reaction have also been widely reported. For instance, Thomas and co-workers\textsuperscript{51} synthesized the first triazine-based crystalline COF \textit{via} self-condensation of nitriles in the presence of ZnCl$_2$ as an efficient catalyst for the reversible trimerization reaction. Nitriles show good solubility in the ZnCl$_2$ ionic melt to form a clear solution due to strong Lewis acid–base interactions. Furthermore, most aromatic and heterocyclic nitriles are thermally stable even at temperatures far above 400 °C.\textsuperscript{75} As shown in Fig. 4a, a CTF can be prepared \textit{via} a trimerization reaction of 1,4-dicyanobenzene. By extension, various 2D CTFs with different molecular and geometric structures\textsuperscript{52,76–79} can be constructed with different dicyano- and/or multicyano-building blocks (Fig. 4b). It is worth noting that many reported structures that were computer generated from powder X-ray diffraction (PXRD) data of the above crystalline COFs are still controversial.\textsuperscript{80} In addition to the above-mentioned crystalline COFs and CTFs, a class of quasi-ordered porous COPs with graphene-like
layer textures and ultrahigh hydrothermal stability have also been produced via Ullmann cross-coupling reaction.\textsuperscript{17,18,56,60,61} As shown in Fig. 5a, COP-T, COP-2, COP-3, COP-4 and COP-P were prepared from monomers of 2,4,6-tris-(5-bromothiophen-2-yl)-1,3,5-triazine (TBYT), tris(4-bromophenyl)amine (TBA), 2,4,6-tris-(4-bromo-phenyl)-[1,3,5]triazine (TBB), 2,4,6-tris-(4-bromo-phenyl)-[1,3,5] triazine (TBT), and (4′-bromo-biphenyl-4-yl)-porphyrin (TBBPP), respectively, via the Ni-catalyzed Yamamoto reaction.\textsuperscript{18} Although powered X-ray diffraction patterns revealed no long-range crystallographic order for the resulting COPs, the corresponding SEM, TEM and AFM images indicated the graphene-like layer texture (Fig. 5b–d). Indeed, Ben et al.,\textsuperscript{81} have obtained a relatively well pronounced powder XRD pattern for PAF-5 (also known as COP-2) and simulated a 2D structure, which is consistent with the reported COP-2 structure. All these COP materials were demonstrated to possess highly porous networks, showing a promising potential for CO\textsubscript{2} capture,\textsuperscript{61} in particular, and gas adsorption and separation applications, in general (vide infra).

Since it remains a challenge to synthesize single crystal polymers, it is still hard to solve the structures of most COPs, as is the case with metal organic frameworks (MOFs).\textsuperscript{52} However, significant progress has been made recently. In 2012, Kissel et al., reported the first single crystal 2D polymer by photoinduced polymerization of photoreactive anthracene (Fig. 6a).\textsuperscript{83} More recently, Schluter’s and King’s groups prepared single crystal 2D polymers,\textsuperscript{84–87} even on a gram scale,\textsuperscript{88} from various monomers shown in Fig. 6b. Along with the recent success in developing 2D single-crystal polymers, certain single-crystalline 3D polymers have also been reported.\textsuperscript{37,89}

Since the solvothermal method, involving reversible reactions, including boronic acid-based condensation, Schiff-base reaction, and cyclotrimerization, is the most common synthetic approach to crystalline COPs and their derivatives, the hydrothermal stability and solubility are two important factors for consideration in practical applications of these materials. These reversible reactions often make them prone to hydrolysis even at ambient humidity. In this regard, Lanni et al.,\textsuperscript{90} reported a COF with alkylated pores to improve its hydrolytic stability. By introducing intramolecular hydrogen bonding (Table 1), Kandambeth et al.,\textsuperscript{91} have also prepared a porphyrin-based COF with ultra-chemical stability; its porosity was reserved even after boiling in hot water for 7 days. These authors further produced an acid- and base-stable crystalline COF by combining reversible Schiff base reaction with irreversible tautomerization (Fig. 7).\textsuperscript{92}

3.2 Surface-mediated syntheses
As mentioned above, the efficient condensation of the rigid aromatic-based building blocks (cf. Fig. 2) often leads to 2D polymers of a large molecule weight with strong intermolecu-
lar π–π interactions, and hence poor solubility. This makes solution processing of the 2D polymers for device applications difficult, if not impossible. In order to circumvent the poor processability, surface-mediate synthesis was developed to produce pure single-layer 2D polymers by depositing appropriate monomers onto a crystalline metal surface, followed by heating to activate the covalent-bond formation often via aryl–aryl couplings. The resulting 2D polymers can be characterized by scanning tunneling microscope (STM) in situ to reveal their molecular structures, defects and domain sizes with atomic precision.

Using brominated porphyrin monomers with different numbers of edge-functionalized Br groups, such as single, double, and tetra aryl-bromide monomers (Fig. 8a–c), Grill et al. performed a surface-mediated synthesis to produce multidimensional polymers by depositing appropriate monomers onto a crystalline metal surface, followed by heating to activate the covalent-bond formation often via aryl–aryl couplings. The resulting 2D polymers can be characterized by scanning tunneling microscope (STM) in situ to reveal their molecular structures, defects and domain sizes with atomic precision.

Of the surface-grown macromolecules, Lin et al. used a metal (Cu)-directed template for controlled polymerization of bifunctional monomers with pyridyl and bromine end groups. Due to the efficient topochemical enhancement associated with the conformation flexibility of the Cu–pyridyl bonds, macromolecular porphyrin structures with a narrow size distribution were synthesized. On the other hand, Tanoue et al. have produced several π-conjugated aromatic 2D COPs on Au (111) from amino end-functionalized porphyrin monomers via a co-condensation reaction between aldehydes and amines. Through surface-assisted coupling, Mullen and co-workers have also synthesized a series of well-defined 2D conjugated COPs known as porous graphene.

Molecular structures for some of the surface-grown 2D COPs have been investigated by STM technology. For example, Zwaneveld et al., studied surface-grown COFs (SCOF-1 and SCOF-2) from reactive deposition of 1,4-benzenediboronic acid (BDBA) and BDBA + 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), respectively, on Ag (111). It was found that a porous 2D network was formed on Ag (111) via intermolecular dehydration of BDBA. Through an analogous esterification reaction of BDBA and HHTP, another boron-containing COP network (i.e., SCOF-2) with a pore size of about 29 Å was observed. By manipulating the tip of a STM, Clair et al.
demonstrated the controlled formation of 2D COF on Ag (100). Later, Guan et al.,108 constructed highly ordered surface-grown 2D COFs on HOPG via dehydration of di-borate aromatic molecules. More recently, Liu et al.,109 have demonstrated a self-limiting solid–vapor interface reaction strategy to fabricate highly ordered SCOFs via a Schiff base coupling reaction at the solid–vapor interface by pre-coating the surface with one of the precursor components and introducing the other precursor component in vapor. By so doing, highly ordered honeycomb SCOF-IC1 and SCOF-LZU1 with imine linkage were obtained.

3.3 Few-layer COPs by exfoliation and their hybrids

Apart from the surface-mediated syntheses of monolayer 2D COPs described above, certain few layered or single layered COPs can also be prepared through controlled solution processes.110 For instance, Berlanga et al.,111 first used sonication to produce 10–25 layers of COFs (4–10 nm thick) by exfoliating COF-8 synthesized by condensation HHTP and 1,3,5-benzene-tris(4-phenylboronic acid), followed by collecting them on a carbon grid or as free-standing films. COFs containing boronate-ester linkages exhibited poor hydrolytic and oxidative stabilities90 with appreciable interlayer stacking energies,112 which are drawbacks for practical applications involving few-layered COPs. To produce stable few-layered COFs, Dichtel and co-workers have recently employed a solvothermal method to produce a class of COF@graphene hybrids by in situ growing COFs on the graphene surface.115–117 More recently, Feng and co-workers have also prepared a class of N, S-doped 2D sandwich-type graphene-based conjugated microporous polymers (CMP@graphene hybrids),118 which, after carbonization at 800 °C, showed good electrocatalytic activities for oxygen reduction reaction (ORR) in fuel cells and high performance in supercapacitors. By incorporating Periana’s catalyst with covalent triazine frameworks, Palkovits et al.,78 prepared solid catalysts for...
Table 1  Porphyrin or phthalocyanine-based building blocks and the corresponding covalent organic framework structures: X%N₃-ZnPc-COFs,¹³⁵ 2D-NiPc-BTDA COF,¹³² ZnPc-Py COF,¹⁶ ZnPc-DPB COF,¹⁶ ZnPc-NDI COF,¹⁵¹,¹³¹ ZnPc-PPE COF,¹¹⁶ Pc-PBBA COF,¹²⁹ MP-COF,¹³¹ COF-66,¹³⁰ COF-366,¹³⁰ Cu-P-Ph COF,¹³⁹ CuP-TFPh COF,¹³⁹ [HC≡C=CH-P]-COF,¹³⁶ CuP-SQ COF,¹³⁰ DhaTph.¹¹¹ The relevant linear organic co-linkers were shown on the top of the relevant COF structures.

<table>
<thead>
<tr>
<th>Porphyrin or phthalocyanine-based building blocks</th>
<th>X%N₃-ZnPc-COFs</th>
<th>2D-NiPc-BTDA COF</th>
<th>ZnPc-Py COF</th>
<th>ZnPc-DPB COF</th>
<th>ZnPc-NDI COF</th>
<th>ZnPc-PPE COF</th>
<th>Pc-PBBA COF</th>
<th>MP-COF</th>
<th>COF-66</th>
<th>COF-366</th>
<th>Cu-P-Ph COF</th>
<th>CuP-TFPh COF</th>
<th>[HC≡C=CH-P]-COF</th>
<th>CuP-SQ COF</th>
<th>DhaTph</th>
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low-temperature selective oxidation of methane to methanol. More potential applications of 2D COPs and their hybrids for gas adsorption, catalysis, and energy conversion and storage are discussed in the next section.

4. Potential applications

Among the various condensation reactions towards 2D COPs described above, the boronic acid and HHTP condensation are of particular interest. As shown in Fig. 10, a series of 2D COFs with high porosity (~2000 m² g⁻¹ BET surface area) and tunable pore size could be constructed from HHTP through condensation with different boronic acids. The large surface area and tunable pore size are important advantages for COPs to be used for gas adsorption and purification. Particularly, the ideal absorbed solution theory (IAST) predicted that COP-1 prepared from 1,3,5-tris((4-bromophenyl)ethynyl) benzene (TBEB) possesses a significantly higher gas selectivity compared to COP-2, 3 and 4, due to its smaller pore size. More specifically, the adsorption selectivity of COP-1 for the CO₂:N₂ mixture reached 91 at a CO₂ : N₂ ratio of 15 : 85 and 2.38 for the 21 : 79 O₂–N₂ mixture at 298 K under 1 bar. Furthermore, these COPs also showed a high separation efficiency for the removal of CO₂ from natural gas. The adsorption selectivity of COP-1 for CO₂–CH₄ was in the range of 4.1–5.0 at a CO₂ : CH₄ ratio of 15 : 85 under 0 < P < 40 bar. To enhance the gas storage capacitance, Xiang et al. developed a new lithium
modification approach by converting alkynyl groups to lithium carboxylate groups with the aid of dry ultrapure CO2 in the COP system, and demonstrated high uptakes for hydrogen, methane and carbon dioxide in Li@COP-1 (70.4%, 34.5% and 13.4%, respectively) at 298 K under 18 bar. More recently, Yuan et al. reported that a series of PAFs with halogen anion-templated pore apertures can be used as polymeric sieves for separation of multicomponent gas mixtures.120 As shown in Fig. 11, the connective column could separate a mixture of five-component gases with retention times of 6.05, 10.37, 19.24, 28.26 and 37.54 min for H2, N2, O2, CH4 and CO2, respectively. Interested readers are referred to ref. 20 for more details on the use of porous COFs for hydrogen storage, methane and CO2 capture. Somewhat related to gas separation, Stegbauer et al. reported the first use of hydrazine-based COF material (i.e., TFPT-COF) for photocatalytic hydrogen evolution.121 The amount of hydrogen evolved in the first five hours was determined to be as high as 1970 mmol h−1 g−1 using a 10 vol% aqueous triethanolamine (TEOA) solution as the sacrificial donor, corresponding to a quantum efficiency of 2.2%.

The large surface area and tunable porosity, in conjugation with electrical conductivity, have made certain conjugated 2D COPs and derivatives ideal electrode materials for electrocatalysis.39 By precisely doping/tuning the N distributions in those COP precursors shown in Fig. 5, Xiang et al.18 have successfully developed a class of new well-defined N-doped holey graphitic carbon materials by post-synthesis carbonization. The electrocatalytic activities of these newly developed N-doped holey graphene analogues can be well correlated to the location and content of the nitrogen dopants (Fig. 12a). As shown in Fig. 12b, the first principle calculations suggest O2 molecules prefer to be adsorbed on the top of the phenyl group adjacent to triazine groups via the Yeager model,11 which could effectively weaken the O–O bonding to facilitate ORR at the C-COP-4 electrode. To further enhance electrocatalytic activity, Xiang et al.17 incorporated non-precious transition metals (Fe, Co and Mn) into the porphyrin-based COP precursors, and followed this by carbonization to convert these metal-incorporated COPs into metal-incorporated graphene analogues, which showed efficient ORR electrocatalytic activities via a 4e− path in both alkaline and acid media with excellent long-term stability and free from methanol crossover and CO-poisoning effects, outperforming the benchmarked Pt/C catalysts (Fig. 12c–g). Particularly, C-COP-P-Co electrode exhibited a higher limited current than that of the benchmarked Pt/C (Fig. 12e). A similar trend has also been reported by Wu et al.122 Clearly, therefore, these newly-developed metal-

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Fig. 9 (a) Exfoliation of COF-43 yields a suspension of few-layered 2D polymers. Reproduced from ref. 113 Copyright 2013 American Chemical Society. (b) Schematic representation of the formation of covalent organic nanosheets (CONs) from the as-synthesized COFs via mechanical grinding. Reproduced from ref. 114 Copyright 2013 American Chemical Society.
incorporated COP materials are promising ORR catalysts for fuel cells.

Apart from the gas storage/separation and electrocatalysis, COFs with conjugated backbones are also attractive for optoelectronic applications. In this regard, it is interesting to note that some of the COPs shown in Fig. 5 exhibited strong fluorescence due to the presence of \( \pi \)-conjugated segments. Consequently, COP-2, COP-3 and COP-4 have been demonstrated to be ideal sensing materials for detecting nitroaromatic explosives with fast response and high sensitivity. In particular, both COP-3 and COP-4 exhibited a high selectivity for tracing picric acid (PA) and 2,4,6-trinitrotoluene (TNT) at low concentrations (<1 ppm).

In addition, Wan et al. reported a belt-shaped, blue luminescent, \( p \)-type semiconducting TP-COF in 2008. Soon after, these authors prepared a polypyrene-based COF (PPy-COF) which was found to harvest visible photons, trigger significant photocurrent generation, and allow for repetitive on–off photocurrent switching with an on–off ratio as high as 8.0 × 10^4. Recently, Dogru et al. fabricated a polymer solar cell from a thienothiophene-based COF (TT-COF) donor and PCBM acceptor to show a power conversion efficiency of 0.053%, open circuit potential of 0.622 V, and short circuit current density of 0.213 mA cm\(^{-2}\). In a similar but independent study, Guo et al. synthesized a stable, electronically conjugated organic framework (CS-COF) for photocurrent switching with a high on–off ratio, and polymer solar cells (Al/CS-COF:60/Au) with a relatively high power conversion efficiency of 0.9%, open circuit potential of 0.98 V, and short circuit current density of 1.7 mA cm\(^{-2}\). These studies illustrate the potential of COFs for energy conversion, though the observed cell performances are still very poor with respect to many other more conventional polymer solar cells.

Since porphyrin, phthalocyanine and their derivatives have been widely used in organic solar cells, porphyrin- and phthalocyanine-based COFs are of particular interest for photovoltaic applications. Table 1 shows molecular structures for representative porphyrin- and phthalocyanine-based COFs,
along with the corresponding building blocks, reported to date. In particular, Spitler and Dichtel 129 exploited a new Lewis acid-catalyzed protocol to form boronate esters directly from protected catechols and arylboronic acids, and found that the resulting COF with π–π stacked phthalocyanines for efficient charge transport exhibited broad absorbance over the solar spectrum attractive for applications in organic photovoltaic devices. Using boronic acid-based condensation and Schiff-base reaction, Wan et al.130 have synthesized two porphyrin COFs (COF-366 and COF-66) with charge mobilities as high as 8.1 and 3.0 cm² V⁻¹ s⁻¹, respectively. By comparing with metal incorporated and metal free porphyrin-based COFs, Feng et al.131 found that those focal metals in the porphyrin rings played a dominating role not only in forming channels for electron conduction but also in regulating the charge mobilities. On the other hand, Ding et al.132 reported a panchromatic photoconductive 2D-NiPc-BTDA COF, which exhibited a broad absorbance up to 1000 nm and an excellent electron mobility of 0.6 cm² V⁻¹ s⁻¹. To elucidate the charge transfer dynamics, Jin et al.133 synthesized a donor–acceptor conjugated COF (DZnPc-ANDI-COF) for time-resolved spectroscopic studies. They found that light absorption was directly coupled with exciton generation and charge separation in both solvated and solid states, and that the intramolecular heterojunctions in the COFs enabled an ultrafast charge separation while the aligned bicontinuous π-columns allowed for a long-distance charge delocalization and an exceptional long-term charge retention. These features are all attractive for solar cell applications, and hence this is clearly an area in which future work would be of value.

5. Concluding remarks

After more than one century of extensive research and development, the chemistry of the synthesis of conventional linear polymers has matured and the availability of various synthetic polymers has had profound influence on most aspects of our modern life. However, the synthesis of 2D COPs (i.e., 2D covalent organic polymers) and their derivatives with well-defined structures is just a recent development. In this article, we have reviewed recent important progress in this emerging
field of active research, covering the rational design, controlled syntheses and potential applications of 2D COPs and their derivatives with various well-defined structures and properties. Even this short review has revealed the versatility of condensation chemistries for making 2D COPs and derivatives with various tailor-made molecular architectures and tunable properties for efficient gas adsorption/separation, sensing, and energy conversion and storage.

With so many synthetic methods (e.g., solution condensation, surface-mediated synthesis, and post-synthesis exfoliation) already reported, and more to be developed, there will be vast opportunities for developing many new multifunctional materials and devices from 2D COPs. However, a major challenge remains to be addressed, which is the rational design and syntheses of highly conjugated, but still soluble, 2D COPs. Overcoming this challenge will assist in the development of COP-based optoelectronic devices with enhanced performance for a number of potential applications. Continued research and development efforts in this exciting field could bring 2D COPs and their derivatives to the technological marketplace, which should affect many aspects of our lives, as we have seen with their linear counterparts.

**Abbreviations**

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<th>Abbreviation</th>
<th>Description</th>
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<td>BrTPP</td>
<td>5-(4-Bromophenyl)-10,15,20-tri(phenyl) porphyrin</td>
</tr>
<tr>
<td>Br3TPP</td>
<td>Tetra(4-bromophenyl)porphyrin</td>
</tr>
<tr>
<td>CMPs</td>
<td>Conjugated microporous polymers</td>
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<tr>
<td>COFs</td>
<td>Covalent organic frameworks</td>
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<tr>
<td>COPs</td>
<td>Covalent organic polymers</td>
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<tr>
<td>CTFs</td>
<td>Covalent triazine-based frameworks</td>
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<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>HTTP</td>
<td>2,3,6,7,10,11-Hexahydroxytriphenylene</td>
</tr>
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<td>NDIDA</td>
<td>N,N'-Di(4-boronophenyl)naphthalene-1,4,5,8-tetracarboxylic acid diimide</td>
</tr>
<tr>
<td>PA</td>
<td>Tracing picric acid</td>
</tr>
<tr>
<td>PAFs</td>
<td>Porous aromatic frameworks</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
</tr>
<tr>
<td>PyDIDA</td>
<td>N,N'-di(4-boronophenyl) pyromellitic-1,2,4,5-tetra-carboxylic acid diimide</td>
</tr>
<tr>
<td>SCOF</td>
<td>Surface covalent organic frameworks</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscope</td>
</tr>
<tr>
<td>TBA</td>
<td>Tris(4-bromophenyl)amine</td>
</tr>
<tr>
<td>TBB</td>
<td>2,4,6-Tris(4-bromo-phenyl)-1,3,5-triazine</td>
</tr>
<tr>
<td>TBBPP</td>
<td>(4'-Bromo-biphenyl-4-yl)-porphyrin</td>
</tr>
<tr>
<td>TEB</td>
<td>1,3,5-Tris (4-bromophenyl)ethynyl benzene</td>
</tr>
<tr>
<td>TBT</td>
<td>2,4,6-Tris(4-bromo-phenyl)-1,3,5 triazine</td>
</tr>
<tr>
<td>TBYT</td>
<td>2,4,6-Tris (5-bromothiophen-2-yl)-1,3,5-triazine</td>
</tr>
<tr>
<td>TEOA</td>
<td>Triethanolamine</td>
</tr>
<tr>
<td>TNT</td>
<td>2,4,6-Trinitrotoluene</td>
</tr>
<tr>
<td>trans- BrTPP</td>
<td>bisphenylporphyrin</td>
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**References**