Polymer Chemistry
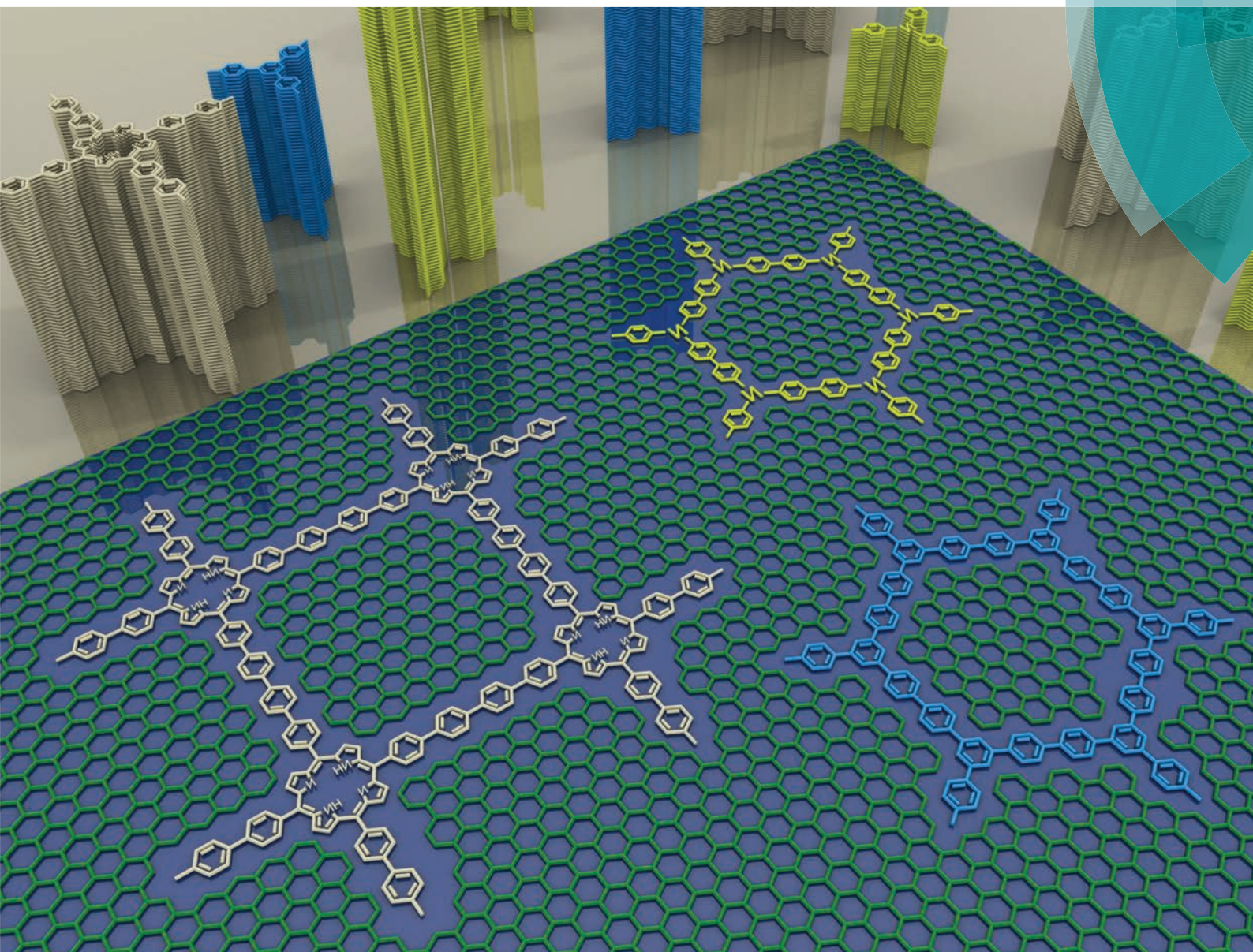
ROYAL SOCIETY
OF CHEMISTRY

REVIEW ARTICLE
Liming Dai *et al.*
Well-defined two dimensional covalent organic polymers: rational design, controlled syntheses, and potential applications

REVIEW

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.

[a]*Center of Advanced Science and Engineering for Carbon (Case4Carbon), Department of Macromolecular Science and Engineering, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, OH 44106, USA. E-mail: liming.dai@case.edu*
[b]*State Key Lab of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, P.R. China*

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 macromolecules 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]

Zhonghua Xiang joined Beijing University of Chemical Technology (BUCT) as a professor in the Department of Chemical Engineering. He is also the director of the Molecular Energy Materials R&D Center in the State Key Lab of Organic–Inorganic Composites at BUCT. Dr Xiang received his Ph.D. degree from BUCT in June 2013 and was a postdoctoral fellow in the Department of Macromolecular Science and Engineering at Case Western Reserve University (2013–2014). His current scientific interests are focused on the design & synthesis of covalent-organic polymers (COPs) for clean energy application.

Zhonghua Xiang
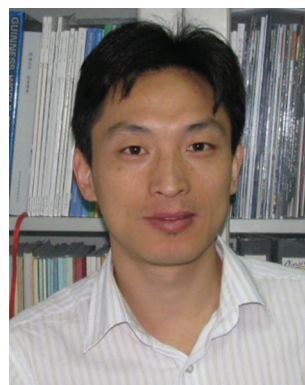
Dapeng Cao is a professor and director of the Division of Molecular and Materials Simulation, State Key Lab for Organic–Inorganic Composites at Beijing University of Chemical Technology (BUCT). He received his Ph.D. from BUCT in 2002, and was a research scientist at Nano-Materials Technology Pte Ltd in Singapore (2002–2003) and a postdoctoral researcher at the University of California, Riverside (2003–2005). His research interests are focused on the targeted synthesis of porous covalent-organic polymers and energy conversion and storage materials related to fuel cells, supercapacitors and solar cells. He has published more than 180 articles in academic journals such as Angew. Chem. Int. Ed., Adv. Mater., Energy Environ. Sci. and ACS Nano.

Dapeng Cao

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.[3–6] 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 sp^2-bonded 2D honeycomb lattice carbon, graphene possesses a high aspect ratio (the ratio of lateral size to thickness), large surface,[4] excellent charge carrier mobility,[5,6] and good mechanical properties.[7–9] The unique structure and properties make graphene and its derivatives very promising for a wide range of potential applications, including electronics,[7,8] sensors,[9,10] energy storage[4,12] and conversion,[4,11,13] biomedical diagnosis,[14] and electrocatalysis.[15] 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.[3,16–18] As a vital class of COPs with predesigned skeletons and nanopores of atomic precision, covalent organic frameworks (COFs) have rapidly developed[19,20–25] since the appearance of the first report on COF in 2005.[26] 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.[16] Since the research and development of graphene have been extensively reviewed,[15,16,27–34] 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.[35–39] Since the development of 3D COP materials has been recently reviewed,[19,39] 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.[37–41] To this end, chemists often employ aromatic monomers and their derivatives, linked either directly together or through other rigid molecular linkages.[16] Fig. 1 schematically shows six typical building blocks (*i.e.*, B_2, B_T, B_3, B_{4a}, B_{4b} and B_6), 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 B_3 and B_6 tend to form the honeycomb COP P_3 (Fig. 1c) and P_6 (Fig. 1f), respectively. The cross building block B_{4a} can form the 2D Kagome network P_{4a-1} and diamond polymer P_{4a-2} (Fig. 1d), and the symmetric cross building block B_{4b} forms square 2D polymer P_{4b} (Fig. 1e). Compared with the above building blocks, the T-shaped building block B_T 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 B_2 (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 B_2, B_3, B_{4a}, B_{4b} and B_6.[16,19,32,40–43] However, 2D COPs based on the T-shape building block B_T 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.[44] Nevertheless, certain T-shaped macromolecules have been constructed through the coordination of metal ions with organic linkers,[45–47] 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,[38,48] Schiff-base reaction,[49,50] cyclotrimerization,[51,52] phenazine ring fusion reaction,[53] Suzuki cross-coupling

Liming Dai is a Kent Hale Smith Professor in the Department of Macromolecular Science and Engineering at Case Western Reserve University. He is also the director of the Center of Advanced Science and Engineering for Carbon. Before joining CWRU, he was an associate professor of polymer engineering at University of Akron and the Wright Brothers Institute Endowed Chair Professor at University of Dayton. He is a Fellow

Liming Dai

of the Royal Society of Chemistry and Fellow of the American Institute for Medical and Biological Engineering. His expertise covers the synthesis, functionalization and fabrication of conjugated polymers and carbon nanomaterials for energy- and bio-device applications.
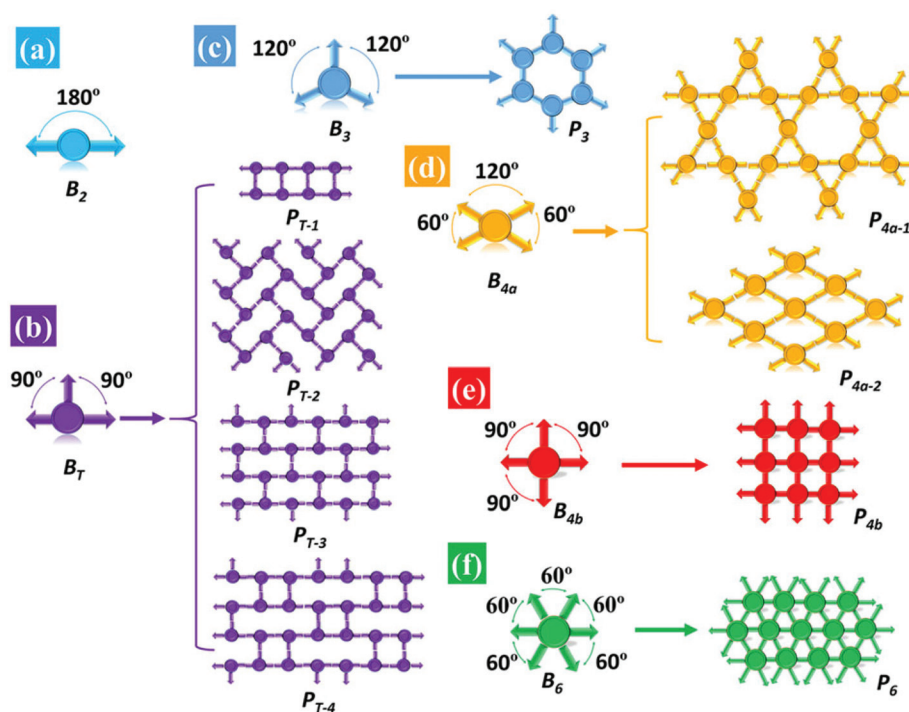
Fig. 1 Main building blocks for 2D COPs, and strategies for 2D polymerization. (a) A linear building block B_2, which can be combined with other building blocks in (b), (c), (d), (e) and (f) for lengthening the structures of 2D COPs. (b) T-shaped building block B_T and possible structures for the resulting 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_{4a} and the corresponding 2D COP structure. (e) Cross-shaped building block B_{4b} 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'.
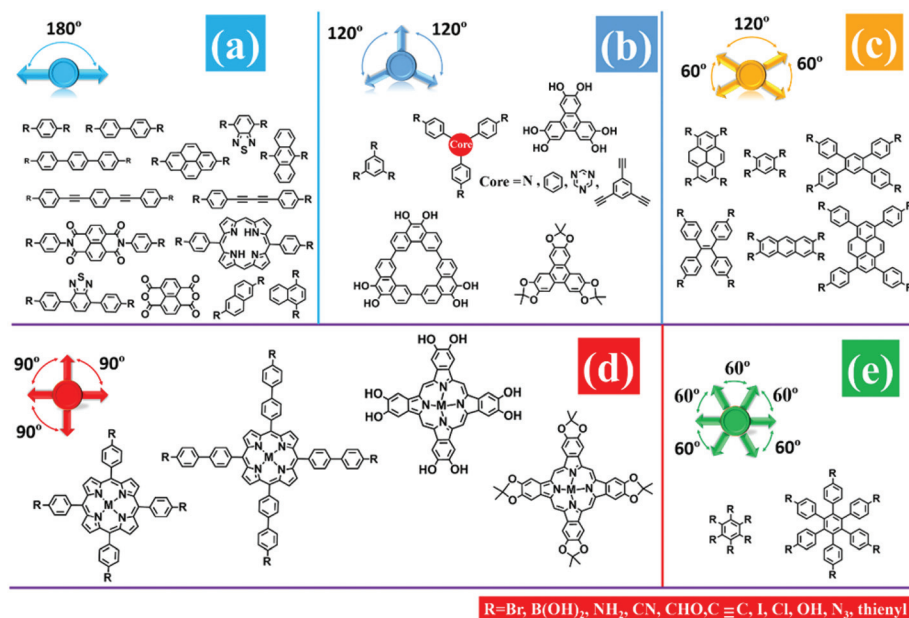

Fig. 2 The representative molecular structures of the building blocks shown in Fig. 1. R in each of the organic linkers can be one of Br, $B(OH)_2$, NH_2, CN, CHO, I, Cl, OH, N_3, alkyl, or thienyl group.

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 microwave[68–70] 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 cyclotrimerization, 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.[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.[72] Fig. 3 shows the first two popular coupling schemes (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'-di-(4-boronophenyl)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 (i.e., D_{TP}-A_{NDI}-COF and D_{TP}-A_{PyrDI}-COF, Fig. 3a) with the largest pore size (5.3 nm) among the COP materials reported to date.[73] More recently, Fang et al. reported a 2D crystalline polyimide COF with the same pore size of 5.3 nm

(i.e., PI-COF-3, Fig. 3b) via the Schiff base reaction between pyromellitic dianhydride and the extended triamine 1,3,5-tris[4-amino-(1,1-biphenyl-4-yl)]benzene.[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 (cf. Fig. 2).[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) via trimerization reaction have also been widely reported. For instance, Thomas and co-workers[51] synthesized the first triazine-based crystalline COF 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.[75] As shown in Fig. 4a, a CTF can be prepared via a trimerization reaction of 1,4-dicyanobenzene. By extension, various 2D CTFs with different molecular and geometric structures[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.[80]

In addition to the above-mentioned crystalline COFs and CTFs, a class of quasi-ordered porous COPs with graphene-like
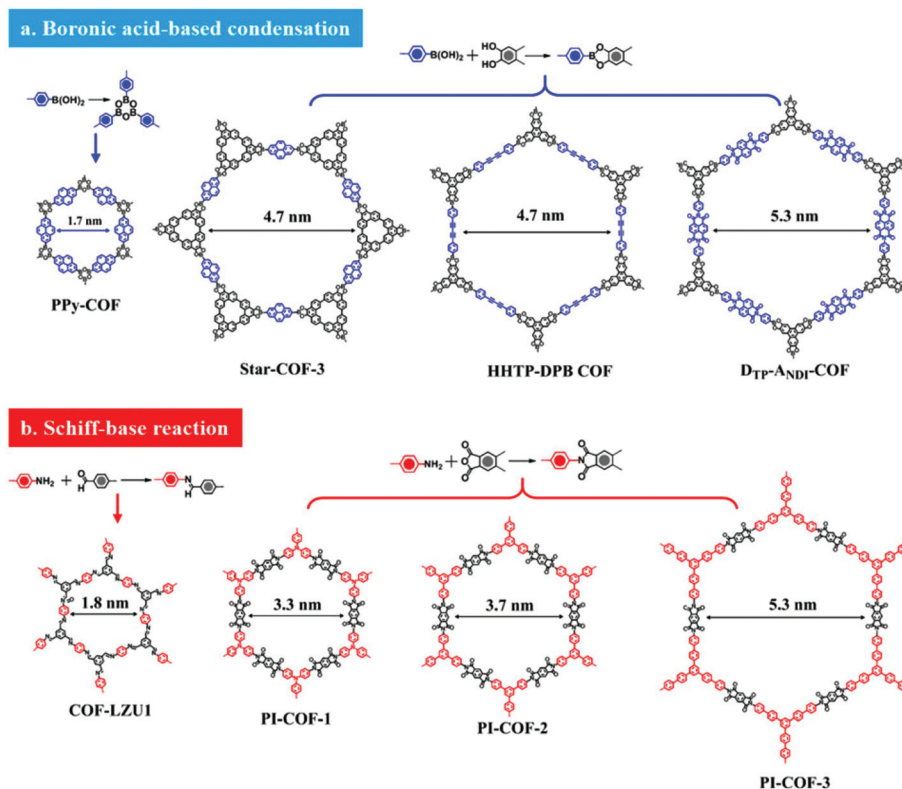

Fig. 3 The structures of the representative crystalline COF materials (PPy-COF,[123] Star-COP-3,[134] HHTP-DPB COF,[112] D_{TP}-A_{NDI}-COF,[73] COF-LZU1,[30] PI-COF-1,[74] PI-COF-2 and PI-COF-3) with large pore using two major reversible reaction methods: (a) Boronic acid-based condensation and (b) Schiff-base reaction. In each method, two popular coupling schemes were incorporated.
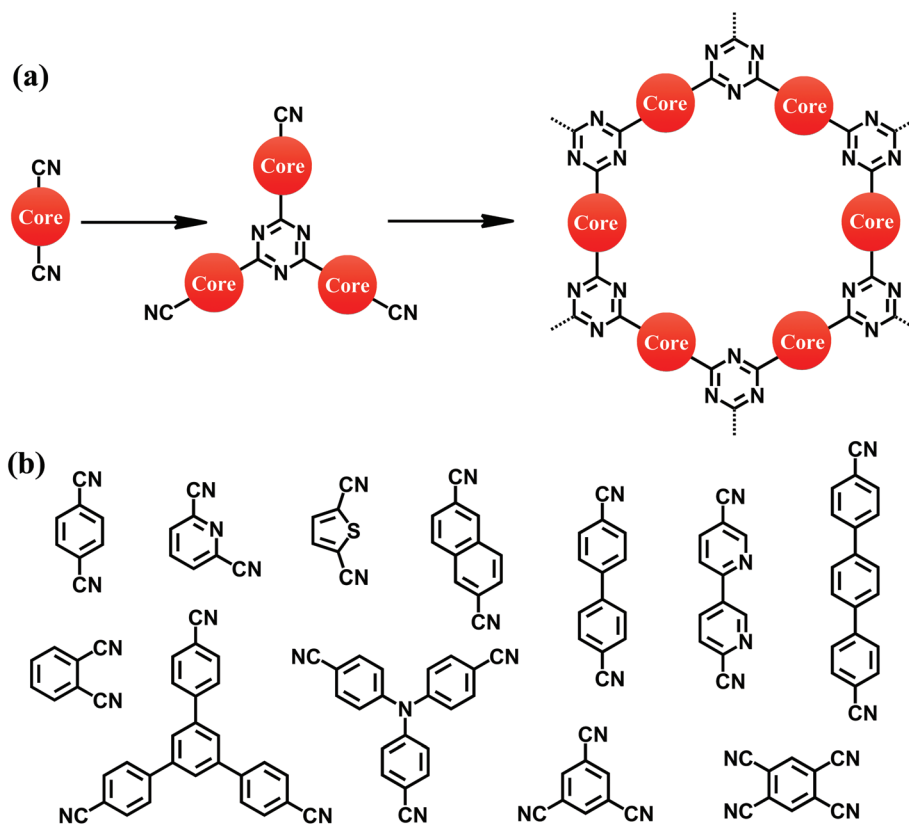
Fig. 4 (a) Schematic representation of the synthetic route to 2D triazine-based polymer networks (CTF-1). (b) The representative organic linkers for the core shown in (a) to form different CTF structures.

layer textures and ultrahigh hydrothermal stability have also been produced *via* Ullmann cross-coupling reaction.[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.[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.*,[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_2 capture,[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).[82] 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).[83] More recently, Schluter's and King's groups

prepared single crystal 2D polymers,[84–87] even on a gram scale,[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.[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.*,[90] reported a COF with alkylated pores to improve its hydrolytic stability. By introducing intramolecular hydrogen bonding (Table 1), Kandambeth *et al.*,[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).[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-
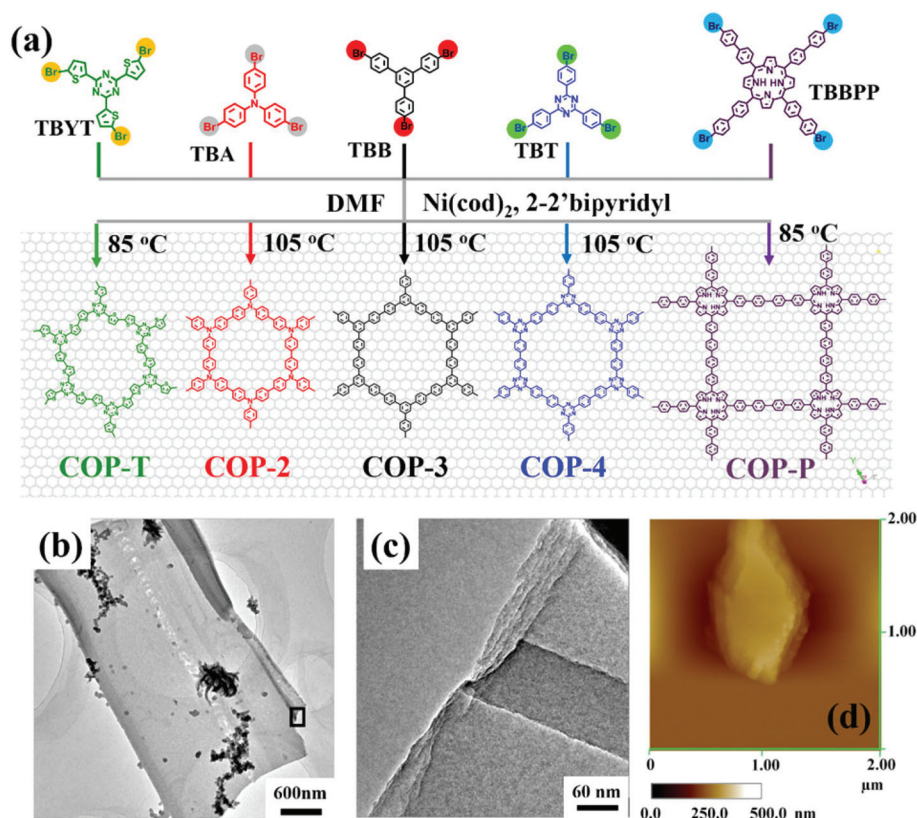
Fig. 5 (a) Schematic representation of the synthetic routes to COP-T, COP-2, COP-3, COP-4, COP-P from the respective monomers *via* the nickel-catalyzed Yamamoto-type Ullmann cross-coupling reaction. Adapted from ref. 18 Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Transmission electron microscopic (TEM) image of COP-4. (c) Enlarged view of the boxed area in (b).[56] (d) Tapping-mode atomic force microscopic (AFM) image of COP-4. The AFM image of COP-4 suggests the layer texture for the as-synthesized material, further supporting the TEM image in (c). Reproduced from ref. 56 Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

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[3] 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.[93–99]

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.*,[77] performed a surface-mediated synthesis to produce multidimensional polymers with different shapes. As can be seen in Fig. 8, the 5-(4-bromophenyl)-10,15,20-tri(phenyl) porphyrin (BrTPP) monomer with a single Br functional group gave a single aryl-bromide dimer (Fig. 8a). As expected, the 5,15-bis(4-bromophenyl)-10,20-bisphenylporphyrin (*trans*-Br₂TPP) monomer with two Br functional groups yielded 1D molecular wires (Fig. 8b) while the tetra(4-bromophenyl)-porphyrin (Br₄TPP) monomer with four Br functional groups led to 2D polymers on the surface. To minimize the disorder

of the surface-grown macromolecules, Lin *et al.*,[100] 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.*,[101] 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.[102–104]

Molecular structures for some of the surface-grown 2D COPs have been investigated by STM technology.[105] For example, Zwaneveld *et al.*, studied surface-grown COFs (SCOF-1 and SCOF-2) from reactive deposition of 1,4-benzene-diboronic acid (BDBA) and BDBA + 2,3,6,7,10,11-hexahydroxy-triphenylene (HHTP), respectively, on Ag (111).[106] It was found that a porous 2D network was formed on Ag (111) *via* inter-molecular dehydration of BDBA. Through an analogous esterification reaction of BDBA and HHTP, another boron-containing COF 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.*,[107]
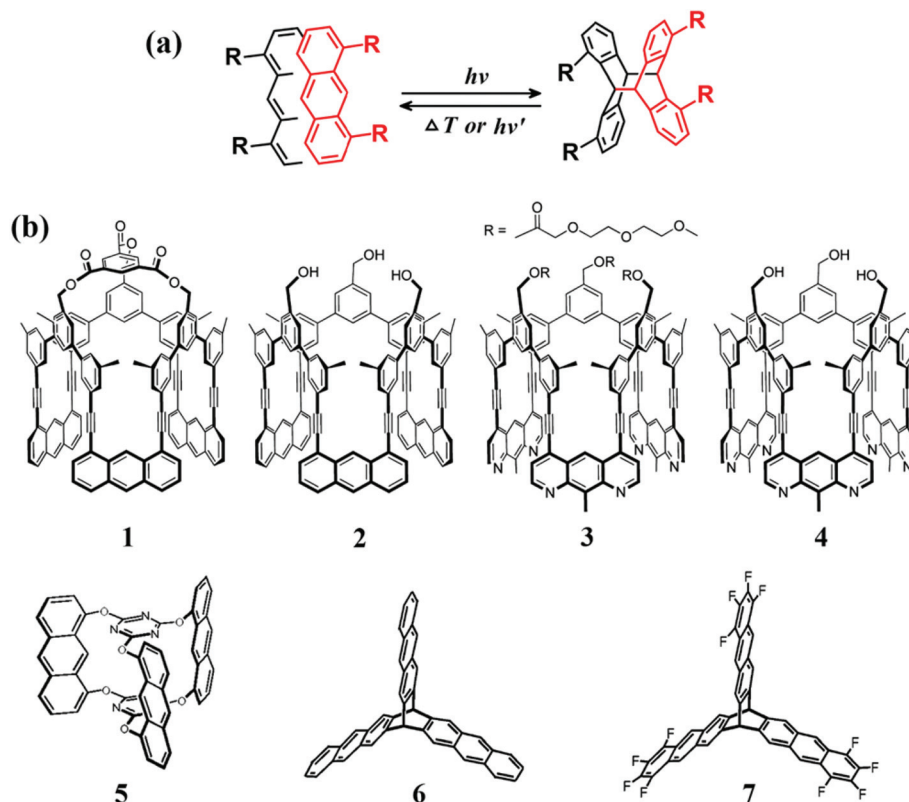
Fig. 6 (a) The photochemical dimerization of 1,8-disubstituted anthracenes and their thermally or photochemically triggered back reaction. (b) The chemical structures of the representative monomers for photochemical dimerization.
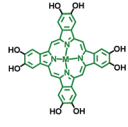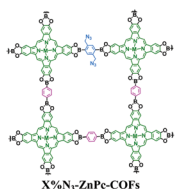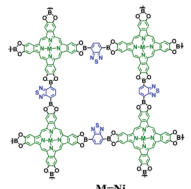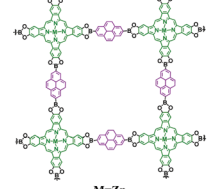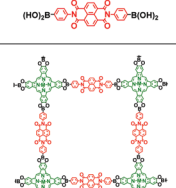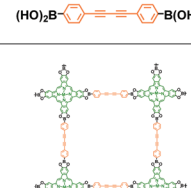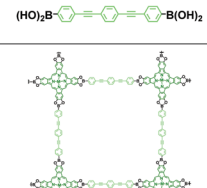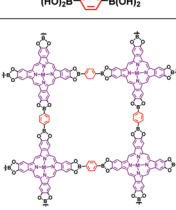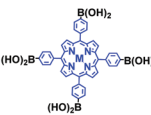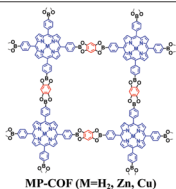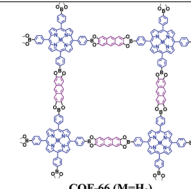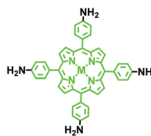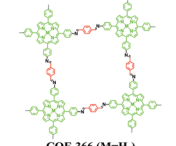
demonstrated the controlled formation of 2D COF on Ag (100). Later, Guan et al.,[108] constructed highly ordered surface-grown 2D COFs on HOPG via dehydration of di-borate aromatic molecules. More recently, Liu et al.,[109] have demonstrated a self-limiting solid–vapor interface reaction strategy to 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 gird or as free-standing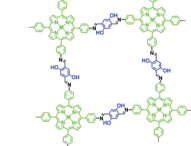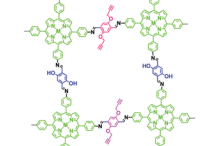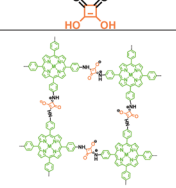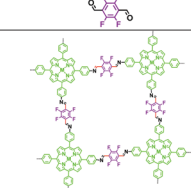 films. COFs containing boronate-ester linkages exhibited poor hydrolytic and oxidative stabilities[90] with appreciable interlayer stacking energies,[112] which are drawbacks for practical applications involving few-layered COPs. To produce stable few-layered COFs, Dichtel and co-workers have successfully exfoliated 2D stable hydrazone-linked COF-43 in common solvent using a sonication technique (Fig. 9a).[113] In this case, the presence of acyl hydrazones

could improve hydrolytic and oxidative stabilities while the absence of the interlayer B–O Lewis acid–base interactions (as presented in boronate ester-linked COFs) facilitated the exfoliation process. Using mechanical delamination, Chandra et al.,[114] developed a new exfoliated method to prepare a series of thin layered hydrazone-linked covalent organic nanosheets (Fig. 9b), which retained their structural integrity throughout the delamination process. They also remained stable in aqueous acidic (3–9 M HCl) and basic (3 M NaOH) media.

Although layered 2D COPs with conjugated frameworks prepared by the above-mentioned solution condensation, surface-mediated syntheses and/or post-synthesis exfoliation could show optoelectronic properties of practical significance, many other reported COPs are often poor electrical conductors because of the insulating nature associated with their non-conjugated constituent organic ligands. To enhance the electrical conductivity of non-conducting COPs, 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-worker 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%N$_3$-ZnPc-COFs,[135] 2D-NiPc-BTDA COF,[132] ZnPc-Py COF,[116] ZnPc-DPB COF,[116] ZnPc-NDI COF,[116,133] ZnPc-PPE COF,[116] Pc-PBBA COF,[129] MP-COF,[131] COF-66,[130] COF-366,[130] Cu-P-Ph COF,[129] CuP-TFPh COF,[129] [HC≡C]X-H$_2$P-COF,[136] CuP-SQ COF,[130] DhaTph.[91] The relevant linear organic co-linkers were shown on the top of the relevant COF structures
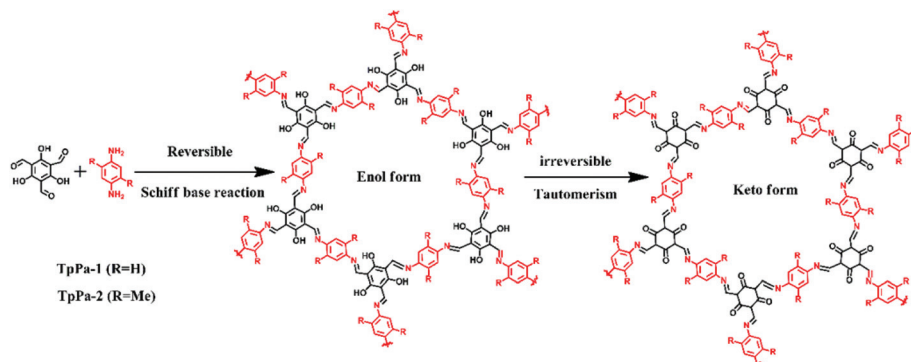
Fig. 7 Schematic representation of the synthesis of TpPa-1 and TpPa-2 by the combined reversible and irreversible reaction of 1,3,5-triformylphlor-oglucinol with *p*-phenylenediamine and 2,5-dimethyl-*p*-phenylenediamine, respectively. The total reaction proceeds in two steps: (1) reversible Schiff-base reaction and (2) irreversible enol-to-keto tautomerism. Reproduced from ref. 92 Copyright 2012 American Chemical Society.
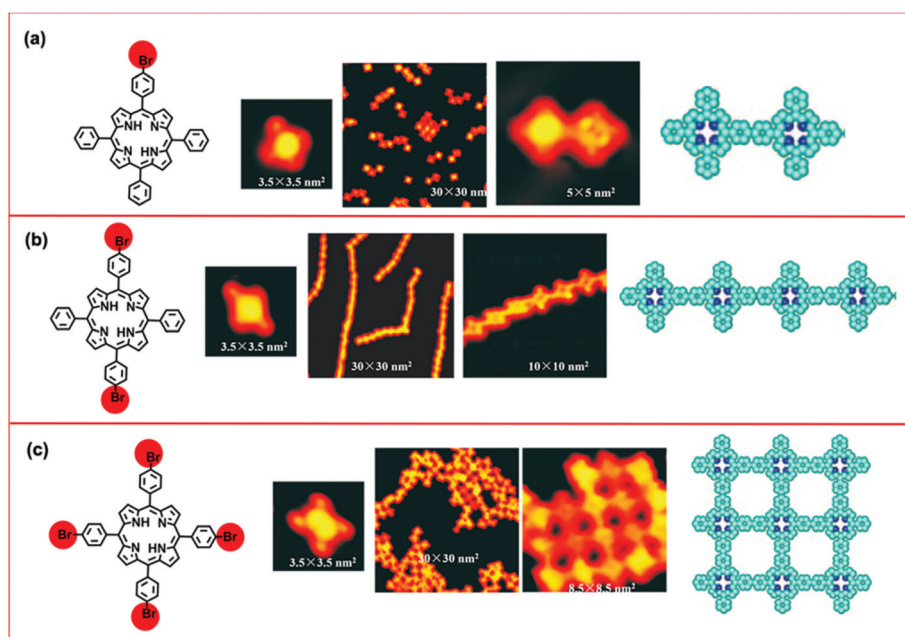
Fig. 8 Structures of monomers and the AFM images for the corresponding polymers (a) 5-(4-bromophenyl)-10,15,20-tri(phenyl) porphyrin (BrTPP). (b) 5,15-Bis(4-bromophenyl)-10,20-bisphenylporphyrin (*trans*-Br$_2$TPP). (c) Tetra(4-bromophenyl)porphyrin (Br$_4$TPP). Reproduced from ref. 77 Copyright 2007 NPG.

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 m^2 g^{-1} BET surface area) and tunable pore size could be constructed from HHTP through condensation with different boronic acids.[119] 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.[61] More specifically, the adsorption selectivity of COP-1 for the CO$_2$–N$_2$ mixture reached 91 at a CO$_2$: N$_2$ ratio of 15 : 85 and 2.38 for the 21 : 79 O$_2$–N$_2$ mixture at 298 K under 1 bar. Furthermore, these COPs also showed a high separation efficiency for the removal of CO$_2$ from natural gas. The adsorption selectivity of COP-1 for CO$_2$–CH$_4$ was in the range of 4.1–5.0 at a CO$_2$: CH$_4$ ratio of 15 : 85 under 0 < *P* < 40 bar. To enhance the gas storage capacitance, Xiang *et al.*[60] developed a new lithium

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 th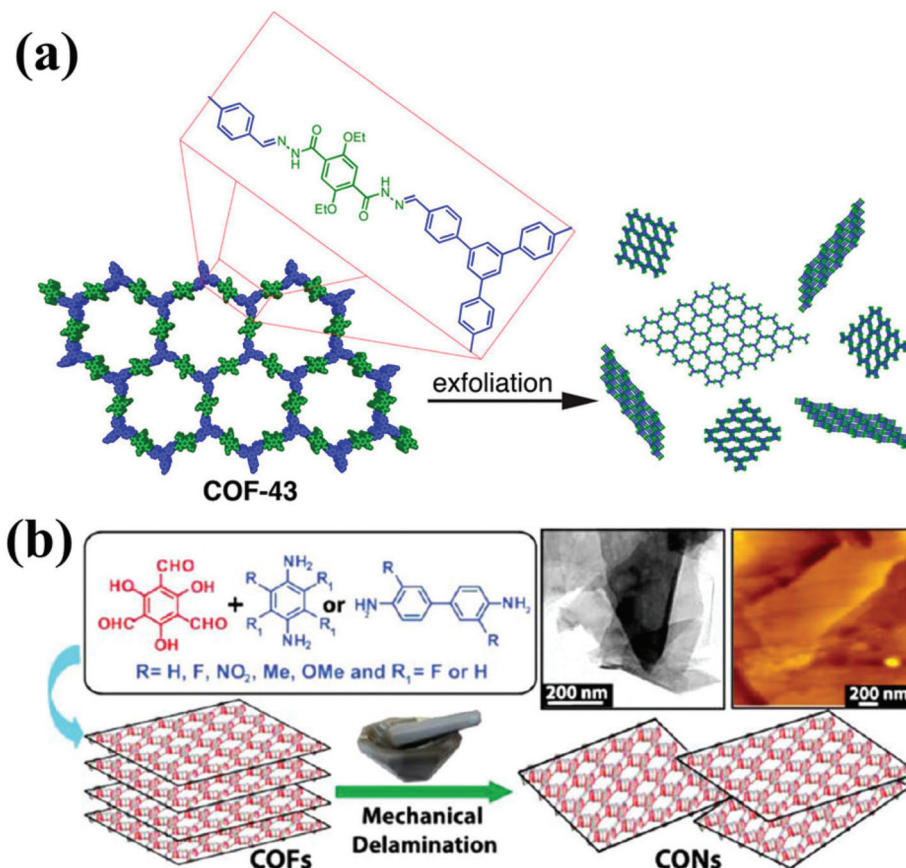e formation of covalent organic nanosheets (CONs) from the as-synthesized COFs *via* mechanical grinding. Reproduced from ref. 114 Copyright 2013 American Chemical Society.

modification approach by converting alkynyl groups to lithium carboxylate groups with the aid of dry ultrapure CO_2 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 H_2, N_2, O_2, CH_4 and CO_2, respectively. Interested readers are referred to ref. 20 for more details on the use of porous COFs for hydrogen storage, methane and CO_2 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 electrocata-

lysis.[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 O_2 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-
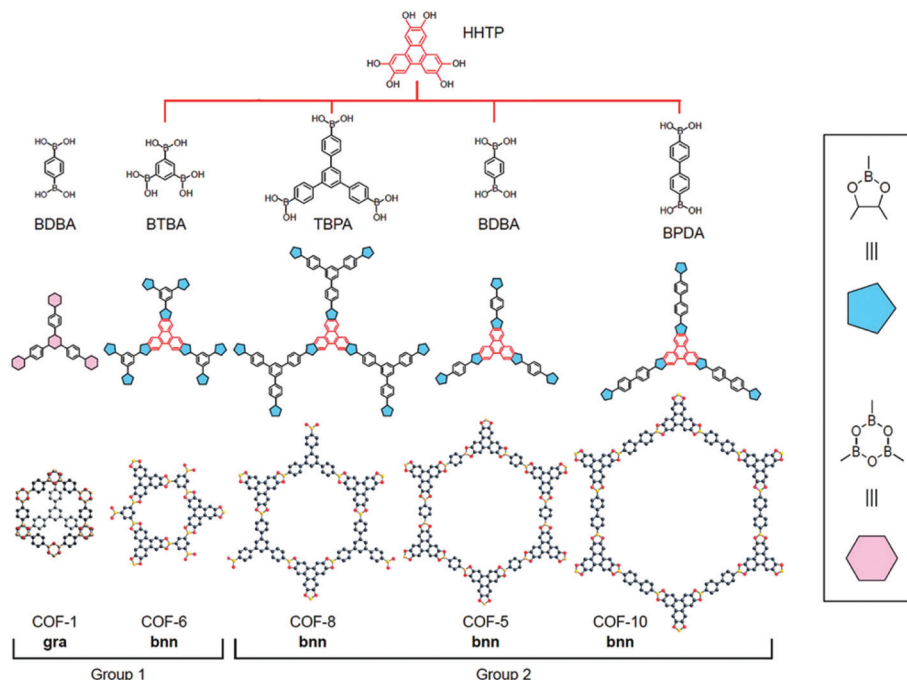
Fig. 10 Condensation reactions between boronic acids and 2,3,6,7,10,11-hexahydroxy triphenylene (HHTP) to produce COFs (top), and resulting fragments of the COFs (middle). Atomic connectivity and structure of crystalline products of 2D (COF-1, -5, -6, -8, and -10) COFs (bottom). B, orange; O, red; C, black; blue tetrahedron; all hydrogen atoms are omitted for clarity. Inset: the C_2O_2B (blue) and the B_3O_3 (pink) rings formed by condensation reactions. The topology and the group classification number are indicated for each COF. BDBA = 1,4-benzenediboronic acid; BTBA = 1,3,5-benzenetriboronic acid; TBPA = 1,3,5-benzenetris(4-phenylboronic acid); BPDA = 4,40-biphenyldiboronic acid. Reproduced from ref. 119 Copyright 2009 American Chemical Society.
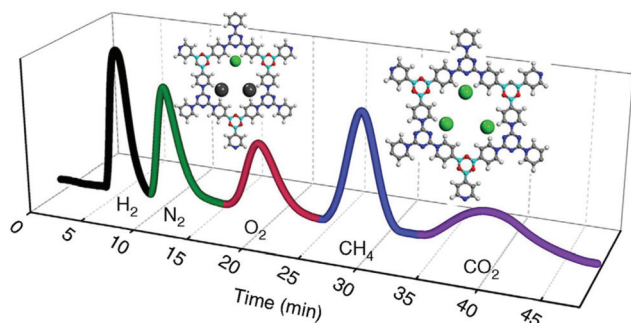

Fig. 11 Total separation for H_2, N_2, O_2, CH_4 and CO_2 mixture using Cl-PAF-50 and 2I-PAF-50 connective GC chromatograms column. Reproduced from ref. 120 Copyright 2014 NPG.

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 opto-electronic applications.[16] 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 π conjugated segments. Consequently, COP-2, COP-3 and COP-4 have been demonstrated to be ideal sensing materials for detecting nitro-aromatic explosives with fast response and high sensitivity.[16] In particular, both COP-3 and COP-4 exhibited a high selecti-

vity for tracing picric acid (PA) and 2,4,6-trinitrotoluene (TNT) at low concentrations (<1 ppm).

In addition, Wan et al.,[123] reported a belt-shaped, blue luminescent, p-type semiconducting TP-COF in 2008. Soon after, these authors prepared a polypyrene-based COF (PPy-COF),[124] 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.,[125] 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.,[126] 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 ⊃ C60/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.[4]

Since porphyrin, phthalocyanine and their derivatives have been widely used in organic solar cells,[127,128] porphyrin- and phthalocyanine-based COFs are of particular interest for photovoltaic applications. Table 1 shows molecular structures for representative porphyrin- and phthalocyanine-based COFs,
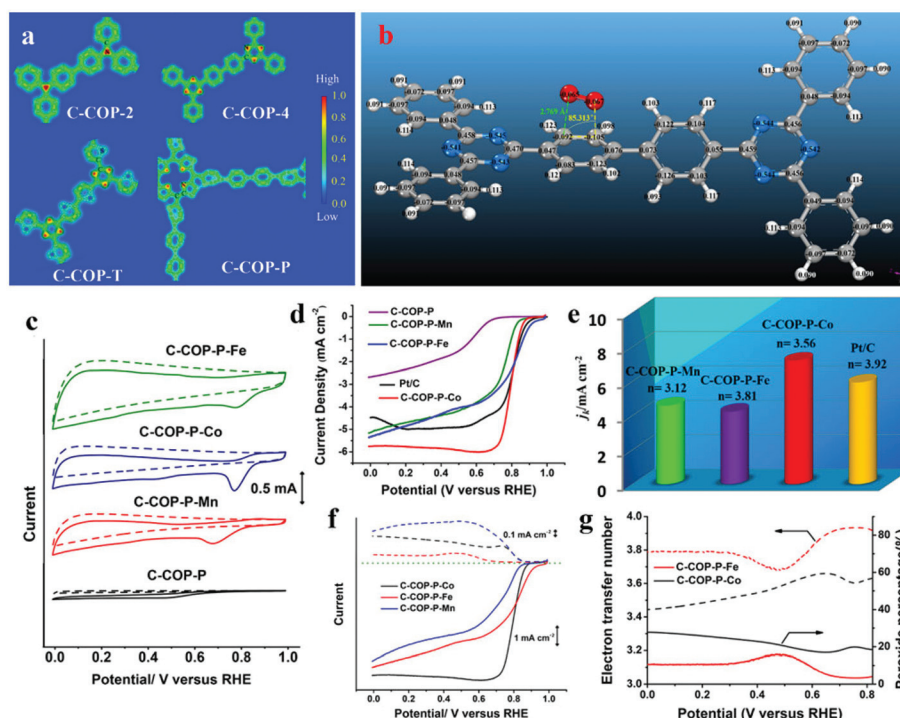
Fig. 12 (a) Partial charge density of N-doped COP graphene: C-COP-2, C-COP-4, C-COP-T, C-COP-P. The values of contours in the plots are form 0.001 e Bohr^{-3} to 1.000 e Bohr^{-3} with an increment of 0.903 e Bohr^{-3}. (b) Calculated charge distributions for the cluster for optimal O_2 adsorbed on the COP-4 graphitic carbon. The measured distance is presented in angstroms, and the measured angle is presented in degrees. (c) CV curves of the metal-incorporated and metal-free C-COP-P on glassy carbon electrodes in O_2-saturated (solid line) or N_2-saturated (dash line) in 0.1 M KOH at a sweep rate of 10 mV s^{-1}. (d) LSV curves of metal-incorporated C-COP-P-M in O_2-saturated 0.1 M KOH at 1600 rpm at a sweep rate of 5 mV s^{-1}. (e) The comparison of electrochemical activity given as the kinetic-limiting current density (j_k) at 0.75 V (*versus* RHE) for the metal-incorporated C-COP-P-M. Also included are the calculated electron transfer numbers. (f) Rotating ring-disk electrode (RRDE) voltammograms recorded with the metal-incorporated C-COP-P-M graphene in O_2-saturated 0.1 MKOH at 1600 rpm. Disk current (I_d) (solid line) is shown on the lower half and the ring current (I_r) (dotted line) is shown on the upper half of the graph. The disk potential was scanned at 5 mV s^{-1} and the ring potential was constant at 1.5 V *versus* RHE. (g) The calculated percentage of peroxide (solid line) and the electron transfer number (n) (dotted line) for the metal-incorporated C-COP-P-M (M = Fe, Co) samples at various potentials, derived from the corresponding RRDE data in (f). Reproduced from ref. 17, 18 Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

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 cm^2 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 cm^2 V^{-1} s^{-1}. To elucidate the charge transfer dynamics, Jin *et al.*,[133] synthesized a donor–acceptor conjugated COF (D$_{ZnPc}$-A$_{NDI}$-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

BrTPP	5-(4-Bromophenyl)-10,15,20-tri(phenyl) porphyrin
Br_4TPP	Tetra(4-bromophenyl)porphyrin
CMPs	Conjugated microporous polymers
COFs	Covalent organic frameworks
COPs	Covalent organic polymers
CTFs	Covalent triazine-based frameworks
HOPG	Highly oriented pyrolytic graphite
HTTP	2,3,6,7,10,11-Hexahydroxytriphenylene
IAST	Ideal absorbed solution theory
MOFs	Metal–organic frameworks
NDIDA	*N,N'*-Di-(4-boronophenyl)naphthalene-1,4,5,8-tetracarboxylic acid diimide
PA	Tracing picric acid
PAFs	Porous aromatic frameworks
PXRD	Powder X-ray diffraction
PyrDIDA	*N,N'*-di(4-boronophenyl) pyromellitic-1,2,4,5-tetra-carboxylic acid diimide
SCOF	Surface covalent organic frameworks
STM	Scanning tunneling microscope
TBA	Tris(4-bromophenyl)amine
TBB	2,4,6-Tris-(4-bromo-phenyl)-[1,3,5]triazine
TBBPP	(4'-Bromo-biphenyl-4-yl)-porphyrin
TBEB	1,3,5-Tris((4-bromophenyl)ethynyl) benzene
TBT	2,4,6-Tris-(4-bromo-phenyl)-[1,3,5] triazine
TBYT	2,4,6-Tris (5-bromothiophen-2-yl)-1,3,5-triazine
TEOA	Triethanolamine
TNT	2,4,6-Trinitrotoluene
trans-Br_2TPP	5,15-Bis(4-bromophenyl)-10,20-bisphenylporphyrin.

Acknowledgements

References

1. L. M. Dai, *Intelligent Macromolecules for Smart Devices*, Springer-Verlag, Berlin, 2004.
2. J. W. Colson and W. R. Dichtel, *Nat. Chem.*, 2013, **5**, 453–465.
3. J. Sakamoto, J. van Heijst, O. Lukin and A. D. Schlüter, *Angew. Chem., Int. Ed.*, 2009, **48**, 1030–1069.
4. L. Dai, D. W. Chang, J.-B. Baek and W. Lu, *Small*, 2012, **8**, 1130–1166.
5. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
6. X. Du, I. Skachko, A. Barker and E. Y. Andrei, *Nat. Nanotechnol.*, 2008, **3**, 491–495.
7. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigoriev, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197–200.
8. R. M. Westervelt, *Science*, 2008, **320**, 324–325.
9. F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 652–655.
10. V. Dua, S. P. Surwade, S. Ammu, S. R. Agnihotra, S. Jain, K. E. Roberts, S. Park, R. S. Ruoff and S. K. Manohar, *Angew. Chem., Int. Ed.*, 2010, **49**, 2154–2157.
11. K. Gong, F. Du, Z. Xia, M. Dustock and L. Dai, *Science*, 2009, **323**, 760–764.
12. T. Chen and L. Dai, *Mater. Today*, 2013, **16**, 272–280.
13. L. Qu, Y. Liu, J.-B. Baek and L. Dai, *ACS Nano*, 2010, **4**, 1321–1326.
14. W. Yang, K. R. Ratinac, S. P. Ringer, P. Thordarson, J. J. Gooding and F. Braet, *Angew. Chem., Int. Ed.*, 2010, **49**, 2114–2138.
15. L. M. Dai, D. W. Chang, J. B. Baek and W. Lu, *Small*, 2012, **8**, 1130–1166.
16. Z. H. Xiang and D. P. Cao, *J. Mater. Chem. A*, 2013, **1**, 2691–2718.
17. Z. H. Xiang, Y. H. Xue, D. P. Cao, L. Huang, J. F. Chen and L. M. Dai, *Angew. Chem., Int. Ed.*, 2014, **53**, 2433–2437.
18. Z. H. Xiang, D. P. Cao, L. Huang, J. L. Shui, M. Wang and L. M. Dai, *Adv. Mater.*, 2014, **26**, 3315–3320.
19. X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.*, 2012, **41**, 6010–6022.
20. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469–472.
21. S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.

22 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714.

23 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673–674.

24 Z. H. Xiang, D. P. Cao, J. H. Lan, W. C. Wang and D. P. Broom, *Energy Environ. Sci.*, 2010, **3**, 1469–1487.

25 Z. H. Xiang, W. C. Wang and D. P. Cao, *Sci. China: Chem.*, 2012, **42**, 235–244.

26 A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170.

27 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.

28 L. M. Dai, *Acc. Chem. Res.*, 2013, **46**, 31–42.

29 J. Zhang, F. Zhao, Z. Zhang, N. Chen and L. Qu, *Nanoscale*, 2013, **5**, 3112–3126.

30 S. Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548–568.

31 Y. H. Xu, S. B. Jin, H. Xu, A. Nagai and D. L. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012–8031.

32 R. Dawson, A. I. Cooper and D. J. Adams, *Prog. Polym. Sci.*, 2012, **37**, 530–563.

33 Z. Chang, D. S. Zhang, Q. Chen and X. H. Bu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5430–5442.

34 A. Filer, H. J. Choi, J. M. Seo and J. B. Baek, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11150–11161.

35 A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291–1295.

36 L. Chen, P. S. Reiss, S. Y. Chong, D. Holden, K. E. Jelfs, T. Hasell, M. A. Little, A. Kewley, M. E. Briggs, A. Stephenson, K. M. Thomas, J. A. Armstrong, J. Bell, J. Busto, R. Noel, J. Liu, D. M. Strachan, P. K. Thallapally and A. I. Cooper, *Nat. Mater.*, 2014, **13**, 954–960.

37 Y. B. Zhang, J. Su, H. Furukawa, Y. F. Yun, F. Gandara, A. Duong, X. D. Zou and O. M. Yaghi, *J. Am. Chem. Soc.*, 2013, **135**, 16336–16339.

38 H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, *Science*, 2007, **316**, 268–272.

39 D. Wu, F. Xu, B. Sun, R. Fu, H. He and K. Matyjaszewski, *Chem. Rev.*, 2012, **112**, 3959–4015.

40 S.-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548–568.

41 Q. R. Fang, S. Gu, J. Zheng, Z. B. Zhuang, S. L. Qiu and Y. S. Yan, *Angew. Chem., Int. Ed.*, 2014, **53**, 2878–2882.

42 F. Vilela, K. Zhang and M. Antonietti, *Energy Environ. Sci.*, 2012, **5**, 7819–7832.

43 Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012–8031.

44 J. Kaleta, J. Michl and C. Mazal, *J. Org. Chem.*, 2010, **75**, 2350–2356.

45 R. Kieffer, M. Prehm, K. Pelz, U. Baumeister, F. Liu, H. Hahn, H. Lang, G. Ungar and C. Tschierske, *Soft Matter*, 2009, **5**, 1214–1227.

46 M. Felloni, A. J. Blake, P. Hubberstey, S. J. Teat, C. Wilson and M. Schroder, *CrystEngComm*, 2010, **12**, 1576–1589.

47 Y.-B. Dong, M. D. Smith, R. C. Layland and H.-C. zur Loye, *Chem. Mater.*, 2000, **12**, 1156–1161.

48 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170.

49 F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 4570–4571.

50 F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki and O. M. Yaghi, *J. Am. Chem. Soc.*, 2011, **133**, 11478–11481.

51 P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem., Int. Ed.*, 2008, **47**, 3450–3453.

52 P. Kuhn, A. Forget, J. Hartmann, A. Thomas and M. Antonietti, *Adv. Mater.*, 2009, **21**, 897–901.

53 Y. Kou, Y. Xu, Z. Guo and D. Jiang, *Angew. Chem., Int. Ed.*, 2011, **50**, 8753–8757.

54 A. Suzuki, *Angew. Chem., Int. Ed.*, 2011, **50**, 6722–6737.

55 A. Suzuki, *Chem. Commun.*, 2005, 4759–4763, DOI: 10.1039/B507375H.

56 Z. H. Xiang and D. P. Cao, *Macromol. Rapid Commun.*, 2012, **33**, 1184–1190.

57 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457–9460.

58 T. Ben and S. Qiu, *CrystEngComm*, 2013, **15**, 17–26.

59 D. Yuan, W. Lu, D. Zhao and H.-C. Zhou, *Adv. Mater.*, 2011, **23**, 3723–3725.

60 Z. H. Xiang, D. P. Cao, W. C. Wang, W. T. Yang, B. Y. Han and J. M. Lu, *J. Phys. Chem. C*, 2012, **116**, 5974–5980.

61 Z. H. Xiang, X. Zhou, C. H. Zhou, S. Zhong, X. He, C. P. Qin and D. P. Cao, *J. Mater. Chem.*, 2012, **22**, 22663–22669.

62 J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper, *J. Am. Chem. Soc.*, 2008, **130**, 7710–7720.

63 J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, *Angew. Chem., Int. Ed.*, 2007, **46**, 8574–8578.

64 C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.*, 2011, **111**, 1780–1824.

65 W. Shi, C. Liu and A. Lei, *Chem. Soc. Rev.*, 2011, **40**, 2761–2776.

66 J.-Y. Lee, C. D. Wood, D. Bradshaw, M. J. Rosseinsky and A. I. Cooper, *Chem. Commun.*, 2006, 2670–2672, DOI: 10.1039/B604625H.

67 J. Germain, J. Hradil, J. M. J. Fréchet and F. Svec, *Chem. Mater.*, 2006, **18**, 4430–4435.

68 N. L. Campbell, R. Clowes, L. K. Ritchie and A. I. Cooper, *Chem. Mater.*, 2009, **21**, 204–206.

69 L. K. Ritchie, A. Trewin, A. Reguera-Galan, T. Hasell and A. I. Cooper, *Microporous Mesoporous Mater.*, 2010, **132**, 132–136.

70 S. Ren, M. J. Bojdys, R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Adv. Mater.*, 2012, **24**, 2357–2361.

71 B. P. Biswal, S. Chandra, S. Kandambeth, B. Lukose, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2013, **135**, 5328–5331.

72 B. J. Smith and W. R. Dichtel, *J. Am. Chem. Soc.*, 2014, **136**, 8783–8789.

73 S. B. Jin, K. Furukawa, M. Addicoat, L. Chen, S. Takahashi, S. Irle, T. Nakamura and D. L. Jiang, *Chem. Sci.*, 2013, **4**, 4505–4511.

74 Q. R. Fang, Z. B. Zhuang, S. Gu, R. B. Kaspar, J. Zheng, J. H. Wang, S. L. Qiu and Y. S. Yan, *Nat. Commun.*, 2014, **5**, 4530.

75 I. B. Johns, E. A. McElhill and J. O. Smith, *I&EC Prod. Res. Dev.*, 1962, **1**, 2–6.

76 P. Kuhn, A. l. Forget, D. Su, A. Thomas and M. Antonietti, *J. Am. Chem. Soc.*, 2008, **130**, 13333–13337.

77 L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters and S. Hecht, *Nat. Nanotechnol.*, 2007, **2**, 687–691.

78 R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas and F. Schüth, *Angew. Chem., Int. Ed.*, 2009, **48**, 6909–6912.

79 M. J. Bojdys, J. Jeromenok, A. Thomas and M. Antonietti, *Adv. Mater.*, 2010, **22**, 2202–2205.

80 B. Lukose, A. Kuc and T. Heine, *Chem. – Eur. J.*, 2011, **17**, 2388–2392.

81 T. Ben, K. Shi, Y. Cui, C. Pei, Y. Zuo, H. Guo, D. Zhang, J. Xu, F. Deng, Z. Tian and S. Qiu, *J. Mater. Chem.*, 2011, **21**, 18208–18214.

82 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 974–986.

83 P. Kissel, R. Erni, W. B. Schweizer, M. D. Rossell, B. T. King, T. Bauer, S. Gotzinger, A. D. Schluter and J. Sakamoto, *Nat. Chem.*, 2012, **4**, 287–291.

84 Y. G. Chen, M. Li, P. Payamyar, Z. K. Zheng, J. Sakamoto and A. D. Schluter, *ACS Macro Lett.*, 2014, **3**, 153–158.

85 P. Payamyar, K. Kaja, C. Ruiz-Vargas, A. Stemmer, D. J. Murray, C. J. Johnson, B. T. King, F. Schiffmann, J. VandeVondele, A. Renn, S. Gotzinger, P. Ceroni, A. Schutz, L. T. Lee, Z. K. Zheng, J. Sakamoto and A. D. Schluter, *Adv. Mater.*, 2014, **26**, 2052–2058.

86 R. Bhola, P. Payamyar, D. J. Murray, B. Kumar, A. J. Teator, M. U. Schmidt, S. M. Hammer, A. Saha, J. Sakamoto, A. D. Schluter and B. T. King, *J. Am. Chem. Soc.*, 2013, **135**, 14134–14141.

87 P. Kissel, D. J. Murray, W. J. Wulftange, V. J. Catalano and B. T. King, *Nat. Chem.*, 2014, **6**, 774–778.

88 M. J. Kory, M. Worle, T. Weber, P. Payamyar, S. W. van de Poll, J. Dshemuchadse, N. Trapp and A. D. Schluter, *Nat. Chem.*, 2014, **6**, 779–784.

89 D. Beaudoin, T. Maris and J. D. Wuest, *Nat. Chem.*, 2013, **5**, 830–834.

90 L. M. Lanni, R. W. Tilford, M. Bharathy and J. J. Lavigne, *J. Am. Chem. Soc.*, 2011, **133**, 13975–13983.

91 S. Kandambeth, D. B. Shinde, M. K. Panda, B. Lukose, T. Heine and R. Banerjee, *Angew. Chem., Int. Ed.*, 2013, **52**, 13052–13056.

92 S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, **134**, 19524–19527.

93 J. Coraux, A. T. N'Diaye, C. Busse and T. Michely, *Nano Lett.*, 2008, **8**, 565–570.

94 A. Hashimoto, K. Suenaga, A. Gloter, K. Urita and S. Iijima, *Nature*, 2004, **430**, 870–873.

95 S. Marchini, S. Gunther and J. Wintterlin, *Phys Rev B: Condens. Matter*, 2007, **76**, 075429.

96 Y. Niimi, T. Matsui, H. Kambara, K. Tagami, M. Tsukada and H. Fukuyama, *Phys Rev B: Condens. Matter*, 2006, **73**, 085421.

97 G. M. Rutter, J. N. Crain, N. P. Guisinger, T. Li, P. N. First and J. A. Stroscio, *Science*, 2007, **317**, 219–222.

98 L. Zhao, R. He, K. T. Rim, T. Schiros, K. S. Kim, H. Zhou, C. Gutiérrez, S. P. Chockalingam, C. J. Arguello, L. Pálová, D. Nordlund, M. S. Hybertsen, D. R. Reichman, T. F. Heinz, P. Kim, A. Pinczuk, G. W. Flynn and A. N. Pasupathy, *Science*, 2011, **333**, 999–1003.

99 P. Mallet, F. Varchon, C. Naud, L. Magaud, C. Berger and J. Y. Veuillen, *Phys Rev B: Condens. Matter*, 2007, **76**, 041403(R).

100 T. Lin, X. S. Shang, J. Adisoejoso, P. N. Liu and N. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 3576–3582.

101 R. Tanoue, R. Higuchi, N. Enoki, Y. Miyasato, S. Uemura, N. Kimizuka, A. Z. Stieg, J. K. Gimzewski and M. Kunitake, *ACS Nano*, 2011, **5**, 3923–3929.

102 M. Bieri, M. Treier, J. Cai, K. Ait-Mansour, P. Ruffieux, O. Groning, P. Groning, M. Kastler, R. Rieger, X. Feng, K. Mullen and R. Fasel, *Chem. Commun.*, 2009, 6919–6921, DOI: 10.1039/B915190G.

103 M. Treier, C. A. Pignedoli, T. Laino, R. Rieger, K. Mullen, D. Passerone and R. Fasel, *Nat. Chem.*, 2011, **3**, 61–67.

104 M. Bieri, S. Blankenburg, M. Kivala, C. A. Pignedoli, P. Ruffieux, K. Mullen and R. Fasel, *Chem. Commun.*, 2011, **47**, 10239–10241.

105 X. Zhang, Q. Zeng and C. Wang, *Nanoscale*, 2013, **5**, 8269–8287.

106 N. A. A. Zwaneveld, R. Pawlak, M. Abel, D. Catalin, D. Gigmes, D. Bertin and L. Porte, *J. Am. Chem. Soc.*, 2008, **130**, 6678–6679.

107 S. Clair, O. Ourdjini, M. Abel and L. Porte, *Chem. Commun.*, 2011, **47**, 8028–8030.

108 C.-Z. Guan, D. Wang and L.-J. Wan, *Chem. Commun.*, 2012, **48**, 2943–2945.

109 X.-H. Liu, C.-Z. Guan, S.-Y. Ding, W. Wang, H.-J. Yan, D. Wang and L.-J. Wan, *J. Am. Chem. Soc.*, 2013, **135**, 10470–10474.

110 S. F. Abd Rahman, S. Kasai and A. M. Hashim, *Sains Malays.*, 2013, **42**, 187–192.

111 I. Berlanga, M. L. Ruiz-González, J. M. González-Calbet, J. L. G. Fierro, R. Mas-Ballesté and F. Zamora, *Small*, 2011, **7**, 1207–1211.

112 E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy and W. R. Dichtel, *J. Am. Chem. Soc.*, 2011, **133**, 19416–19421.

113 D. N. Bunck and W. R. Dichtel, *J. Am. Chem. Soc.*, 2013, **135**, 14952–14955.

114 S. Chandra, S. Kandambeth, B. P. Biswal, B. Lukose, S. M. Kunjir, M. Chaudhary, R. Babarao, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2013, **135**, 17853–17861.

115 J. W. Colson, A. R. Woll, A. Mukherjee, M. P. Levendorf, E. L. Spitler, V. B. Shields, M. G. Spencer, J. Park and W. R. Dichtel, *Science*, 2011, **332**, 228–231.

116 E. L. Spitler, J. W. Colson, F. J. Uribe-Romo, A. R. Woll, M. R. Giovino, A. Saldivar and W. R. Dichtel, *Angew. Chem., Int. Ed.*, 2012, **51**, 2623–2627.

117 J. W. Colson, J. A. Mann, C. R. DeBlase and W. R. Dichtel, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **53**, 378–384.

118 X. Zhuang, F. Zhang, D. Wu, N. Forler, H. Liang, M. Wagner, D. Gehrig, M. R. Hansen, F. Laquai and X. Feng, *Angew. Chem., Int. Ed.*, 2013, **52**, 9668–9672.

119 H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 8875–8883.

120 Y. Yuan, F. X. Sun, L. N. Li, P. Cui and G. S. Zhu, *Nat. Commun.*, 2014, **5**, 4260.

121 L. Stegbauer, K. Schwinghammer and B. V. Lotsch, *Chem. Sci.*, 2014, **5**, 2789–2793.

122 Z. S. Wu, L. Chen, J. Z. Liu, K. Parvez, H. W. Liang, J. Shu, H. Sachdev, R. Graf, X. L. Feng and K. Mullen, *Adv. Mater.*, 2014, **26**, 1450–1455.

123 S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.*, 2008, **47**, 8826–8830.

124 S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5439–5442.

125 M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel and T. Bein, *Angew. Chem., Int. Ed.*, 2013, **52**, 2920–2924.

126 J. Guo, Y. H. Xu, S. B. Jin, L. Chen, T. Kaji, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. L. Jiang, *Nat. Commun.*, 2013, **4**, 2736.

127 S. S. Sun and N. S. Sariciftci, *Organic Photovoltaics: Mechanisms, Materials, and Devices*, CRC Press, Boca Raton, 2005.

128 Q. Sun, L. Dai, X. Zhou, L. Li and Q. Li, *Appl. Phys. Lett.*, 2007, **91**, 253505.

129 E. L. Spitler and W. R. Dichtel, *Nat. Chem.*, 2010, **2**, 672–677.

130 S. Wan, F. Gándara, A. Asano, H. Furukawa, A. Saeki, S. K. Dey, L. Liao, M. W. Ambrogio, Y. Y. Botros, X. Duan, S. Seki, J. F. Stoddart and O. M. Yaghi, *Chem. Mater.*, 2011, **23**, 4094–4097.

131 X. Feng, L. Liu, Y. Honsho, A. Saeki, S. Seki, S. Irle, Y. Dong, A. Nagai and D. Jiang, *Angew. Chem., Int. Ed.*, 2012, **51**, 2618–2622.

132 X. Ding, L. Chen, Y. Honsho, X. Feng, O. Saengsawang, J. Guo, A. Saeki, S. Seki, S. Irle, S. Nagase, V. Parasuk and D. Jiang, *J. Am. Chem. Soc.*, 2011, **133**, 14510–14513.

133 S. Jin, X. Ding, X. Feng, M. Supur, K. Furukawa, S. Takahashi, M. Addicoat, M. E. El-Khouly, T. Nakamura, S. Irle, S. Fukuzumi, A. Nagai and D. Jiang, *Angew. Chem., Int. Ed.*, 2013, **52**, 2017–2021.

134 X. Feng, Y. P. Dong and D. L. Jiang, *CrystEngComm*, 2013, **15**, 1508–1511.

135 L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. P. Dong and D. L. Jiang, *J. Am. Chem. Soc.*, 2014, **136**, 9806–9809.

136 H. Xu, X. Chen, J. Gao, J. B. Lin, M. Addicoat, S. Irle and D. L. Jiang, *Chem. Commun.*, 2014, **50**, 1292–1294.